UNIVERSITY OF CALIFORNIA, SAN DIEGO

DESIGN AND SYNTHESIS OF MESOIONIC CARBENES

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy

in

Chemistry

by

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Professor Clifford Kubiak

2013

The Dissertation of Gaël Ung is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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University of California, San Diego
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LIST OF ABBREVIATIONS

Ac: Acetyl.

Ad: 1-adamantyl.

Ar: Aryl.

COD: Cycloocta-1,5-diene.

Dipp: 2,6-diisopropylphenyl.

Et: Ethyl.

FLP: Frustrated Lewis pairs.

KHMDS: Potassium bis(trimethylsilyl)amide.

***i*Pr**: Isopropyl.

LDA: Lithium diisopropylamide.

LiHMDS: Lithium bis(trimethylsilyl)amide.

Me: Methyl.

Mes: Mesityl, 2,4,6-trimethylphenyl.

Ms: Mesylate.

***n*Bu**: Butyl.

NHC: N-heterocyclic carbene.

NMR: Nuclear Magnetic Resonance.

***p*-cym**: *Para*-cymene.

Ph: Phenyl.

RT: Room temperature.

***t*Bu**: Tertbutyl.

TEP: Tolman Electronic Parameter.

Tipp: 2,4,6-triisopropylphenyl.

Tf: Trifluoromethanesulfonyl.

thf: tetrahydrofurane.

tht: tetrahydrothiophene.

Ts: Tosylate.

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ACKNOWLEDGEMENTS

I would like to first thank Prof. Adah Almutairi, Prof. Joshua Figueroa, Prof. Carlos Guerrero and Prof. Clifford Kubiak for taking the time to evaluate this work.

Thanking my advisor, Prof. Guy Bertrand, in a few lines is something very difficult to do. I will do a short list of a few everyday things he does, which taught me a lot, and that I will miss the most. First of all, I have to mention Guy's ability to write manuscripts. He can turn simple chemistry results into wonderful stories, always with the patented "I-type-with-two-fingers-looking-at-the-keyboard" technique. His ability to analyze NMR spectra in a few minutes always impresses me, although some spectra would require special techniques such as "the thinking position": feet on the desk, massaging his forehead, or the "sophisticated coupling constant calculator": a post-it. Guy is most of all very close to his students. The traditional (sometimes feared) "something new??" at the end of the day has always been a good moment to discuss the latest results, or the latest crazy idea. The "guided freedom" I received to conduct research was the best mentoring I could get, and I will be forever thankful for that.

I also would like to thank Prof. Gernot Frenking for welcoming me in Marburg and giving me the chance to discover computational chemistry in one of the leading groups in the field. Mali also deserves a lot of credits for making this stay a very good learning experience!

Many thanks to Prof. Arnold Rheingold and Curtis Moore for their perpetual help with X-ray crystallography. I also thank Anthony Mrse for his help with NMR spectroscopy, as well as for the list of things to do in New Orleans!

The four years I spent in this lab would not have been the same without all the people that I had the chance to meet. Thoughts go to all of those whom I unfortunately did not get the chance to know a lot: Aholibama, Alan, Amos, Andy, Emrah, Eugenia, Fred, Johanna, Nicolas, Shigeru, Xiao-Yu and Xingbang. For the rest, you really all deserve a little paragraph. Brace yourselves, it is going to be long!

David W. was the guardian of solvents when I arrived. Always keeping them safe and running, despite the numerous mistakes that are done around them! Thank you for teaching me about the American culture and also for helping me improve my understanding of very fast spoken English!

Big thoughts for Martin, with whom I had the chance to share this experience with since the beginning. Thank you for your presence and help during the first times, adapting to the US life and good luck for the last bit!

Olivier really brought the craziness in the lab. From (too?) creative nicknames to weird noises, we always knew when he was around.

The furthest lab in Riverside was the refuge for Gregorio and Jean at first, before they were joined by Daniela.

I remember Jean as a very meticulous chemist. Very sharp with his analyses and extremely knowledgeable, he truly impressed me. Thank you for letting me deprotonate

the dithiolium salt! Grego had a totally different style from Jean, and it was really amazing to see the synergy between the both of them. Thank you for all the "gut-chemistry" tips, the driving lessons, all the delicious recipes, and all the good times!

Daniela joined their team a little later, bringing a touch of cute South-African accent to the lab. Despite the capricious nature of her carbazole compounds, her enthusiasm was never broken.

Maria was never far from Grego and Daniela, forming the "smoking"-postdoc group. Her help was much appreciated during the move from UCR, labeling and sorting everything!

The far lab at UCR was completed by David M., a brilliant chemist who manages to combine both theoretical and experimental chemistry with success. His adoration for sweets caused the lab to rush for any goodies left on the coffee table. He would however eliminate the excess glucose by joining our championship winning volleyball team, in which his little duel with David R. was always entertaining!

Whaaaaaat?!?!?! Was I going to forget Fabian? Of course not! Fabian started the German invasion of the lab in the middle of my Ph.D. He brought his attachment (paranoia?) to clean solvents and gloveboxes, which was absolutely great! Thank you for all that I have learned watching you manipulate and discussing chemistry with you. But more importantly, thank you for all the good times outside the lab, playing soccer, volleyball or barbecuing. Take good care of your wonderful family!

The German invasion continued with Robert, who brought his skills of recycling (and sometimes shopping) to improve the lab, followed by Flo(Flu)(Fli)rian, a very kind person who is as competitive as he is tall!

Mo also deserves a lot of thanks! From the initial days helping me find a place to any other random errands, Mo was always available to give a hand. Thank you for all the help and advice, and also for all of the random sport fun facts! This guy is a true Sport-pedia!!

Liqun arrived at the end of my Ph.D. and deserves a lot of credit for bringing her enthusiasm in the lab. She managed to motivate everyone for weekly soccer games. Too bad I am not staying a little longer to enjoy your company! Miaha!!

Little word for our newest recruits Cory and Janell, who are already doing so great! Good luck with everything and keep the volleyball trophy!!

I would like to specially thank someone, whom I believe is not thanked enough in this lab. I connected very quickly with Michèle, a little by choice (our mutual interest in classical music) and also a little by good misfortune (burned down fume hood). We shared a lab for almost 4 years and even a fume hood for 8 months. Thank you for all the tips about chemistry, cooking, baking, visiting,… Thank you also for making the lab run so smoothly and efficiently!

Apart from Michèle, I had the great chance to share the lab with two other mousquetaires: Prof. Rei Kinjo and Prof. Daniel Mendoza-Espinosa.

Rei helped me my very first day to clean up mercury from a vacuum gauge I just broke, and he never stopped helping. He is the most talented and gifted experimentalist I had the chance to know. From discussions around a piece of scratch paper in between our adjacent desks to discussions around a few liters of alcoholic beverages, or soccer, or sushi cooking, everything with Kinjo was a good time.

Daniel arrived in the lab at the same time and we had the chance to connect quickly. I could write so much about Daniel, but I believe the short following statement does him justice: Daniel is true kindness on feet. Thank you for all of our (crazy) moments: visits, movies, soccer, banana throws, and of course the world famous Futlab!

When both mousquetaires were gone, I was left with David R. After enduring a boring move, we had to fight the San Diego curse together. Good thing that we both found our tricks, because David is now on the path to success! Keep at it! Thank you also for teaching me the American way to work my tiny muscles out, and all of the great times spent in the lab and outside! See you around in Pasadena!

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My last year of Ph.D. was enlightened by the sun of San Diego, but also by someone who stood by me, putting up with my hyperactivity despite her love to sleep. Thank you Amber for everything!

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Chapter 4 has been adapted from materials published in G. Ung, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 758–761. The dissertation author was the primary investigator of the paper.

VITA

Education

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Mar-Aug 2008:	**Sanofi-Aventis (Centre de Recherche de Vitry-Alfortville, France)**, Dr. Christian Viskov Total synthesis of a pentasaccharide

Publications

9) Ruiz, D. A.; **Ung, G.**; Melaimi, M.; Bertrand, G. "Deprotonation of a Borohydride: Synthesis of a Carbene-Stabilized Boryl Anion", *Angew. Chem.* **2013**, *125*, 7739 – 7742; *Angew. Chem. Int. Ed.* **2013**, *52*, 7590 – 7592. Selected as "Very Important Paper".

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Academic presentations

2) **Ung, G.**; Bertrand, G. "Simple Alkynes as Mesoionic carbene (MIC) ligand equivalents.", 2013, 245rd American Chemical Society National Meeting, New Orleans, LA, USA.

1) **Ung, G.**; Bertrand, G. "Apparently benign ethynylcarbamodithioate [Ar-C≡C-S-C(S)NR_2] as a masked carbene", 2012, 243rd American Chemical Society National Meeting, San Diego, CA, USA.

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2007-2009:	**Lycée Janson de Sailly**, Paris, France Chemistry oral examiner in a preparation class for the nationwide competitive entrance exams.

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2009:	**École Nationale Supérieure de Chimie de Paris (Chimie ParisTech)**, Paris, France **"Prix du Centenaire"** awarded to the student who managed to combine academic achievement necessary for graduation in engineering ENSCP (being in the first third of the ranking of three years) and activity in associations of students (who demonstrated initiative, team leadership, and obtained results for a project in activities outside school)

Languages and Skills

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English:	Fluent
German:	Intermediate level
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Laboratory skills:	Organic, inorganic and organometallic synthesis, Inert atmosphere techniques (Schlenk, dry-box techniques)
Analysis:	1D and 2D NMR spectroscopy of common nuclei (^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P), Infrared spectroscopy, Gas chromatography, X-ray diffraction studies (crystal mounting, data acquisition and structure solving with simple cases of disorders)

ABSTRACT OF THE DISSERTATION

DESIGN AND SYNTHESIS OF MESOIONIC CARBENES

by

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Doctor of Philosophy in Chemistry

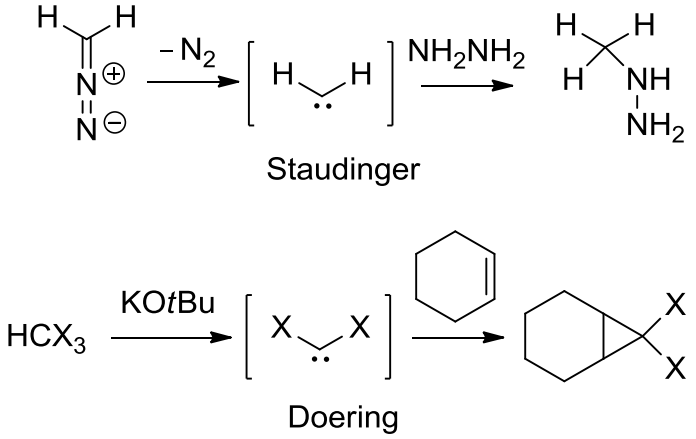
University of California, San Diego, 2013

Professor Guy Bertrand, Chair

Carbenes play a prominent role as ligands for transition metal catalysts. This is mainly due to their strong σ-donor properties and the robustness of the corresponding complexes. These two features result from the presence of the electropositive carbon center and the strength of the carbon-metal bond. Therefore, other types of carbon-based L ligands are highly desirable. This manuscript describes the design and synthesis of a variety of new carbenes belonging to the family of mesoionic carbenes. It will be shown that the stability of mesoionic carbenes depends on the nature of the heteroatoms of their aromatic system. We will also demonstrate that simple alkynes can be used as mesoionic carbene ligand equivalents of various ring sizes towards various transition metals. Moreover, the use of one simple unsaturated compound for the activation of small molecules and the cleavage of enthalpically strong bonds will be discussed.

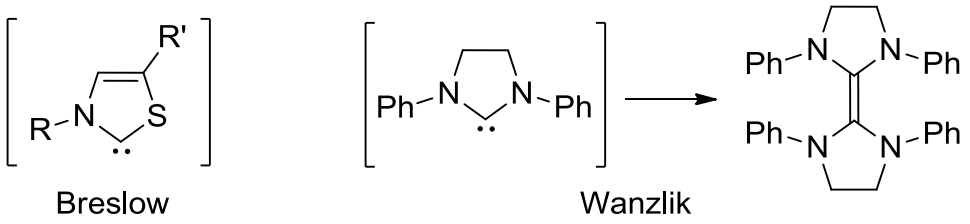
GENERAL INTRODUCTION

Carbenes are neutral molecules featuring a divalent carbon atom which possesses an electron sextet. Although they started as chemical curiosity over a century ago, carbenes now play a prominent role as powerful tools in both transition metal catalysis and organocatalysis. Pioneering work by Curtius[1] and Staudinger[2] showed the high reactivity of carbenes which were generated from diazo compounds. Their potential was further exploited by Doering in cyclopropanation reactions with the transient dichlorocarbene.[3] Additional work by Moss using nanosecond kinetic methods provided very good insights on the reactivity of these highly reactive species.[4]



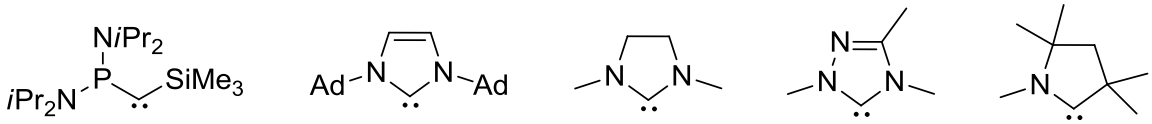
Scheme I. 1: Reactivity of transient carbenes; X = Cl, Br.

A few years later, a milestone was reached with the discovery by Breslow[5] and Wanzlick[6] of persistent singlet carbenes. The enhanced stability of these carbenes is due to the presence of nitrogen atoms around the carbene center. Although they could not be characterized, these carbenes were exploited as organocatalysts in benzoin condensation reactions.



Scheme I. 2: Persistent singlet carbenes postulated.

The most significant breakthrough came in 1988, with the isolation of the first stable carbene by Bertrand and co-workers. The phosphino-silyl-carbene **I.A** was obtained by the photolysis of the corresponding diazo precursor.[7] A few years later, Arduengo and co-workers synthesized the first stable imidazol-2-ylidene **I.B** by deprotonating the corresponding imidazolium salt.[8] Since then, a very broad range of stable carbenes emerged and the field has greatly flourished.[9] In addition to the widely used imidazol-2-ylidenes and imidazolin-2-ylidenes **I.C**, 1,3,4-triazol-2-ylidenes **I.D** developed by Enders[10] and the cyclic (alkyl)(amino)carbenes **I.E** of Bertrand[11] also played a major role in the development of organocatalysis, transition metal catalysis and stabilization of highly reactive species.

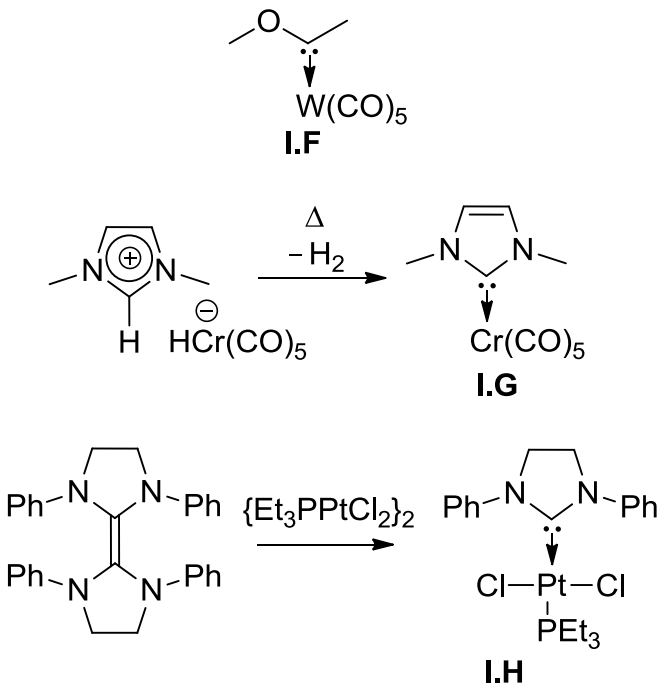


I.A **I.B** **I.C** **I.D** **I.E**

Figure I. 1: Selected examples of stable carbenes; Ad = 1-adamantyl.

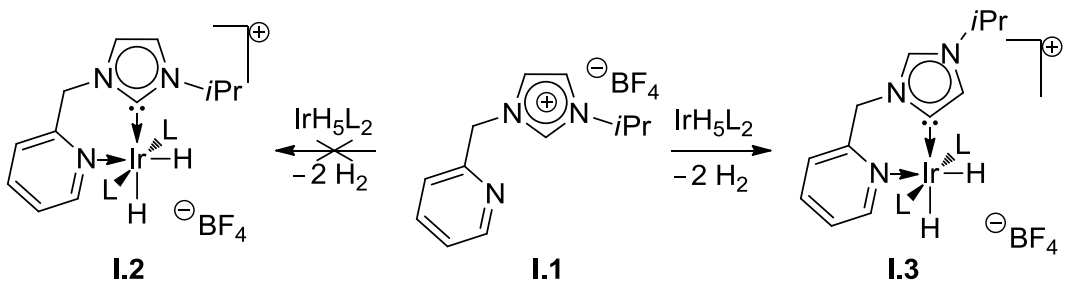
In addition to free carbenes, transition metal complexes of carbenes have also attracted a lot of interest. The first carbene transition metal complex was a tungsten complex **I.F** synthesized by Fischer.[12] Later on, the first imidazol-2-ylidene chromium

complex **I.G** was obtained by Öfele by using $HCr(CO)_5^-$ to deprotonate the imidazolium precursor.[13] Another notable contribution was made by Lappert when he reacted the dimer discovered by Wanzlik with platinum yielding the corresponding carbene complex **I.H**.[14]



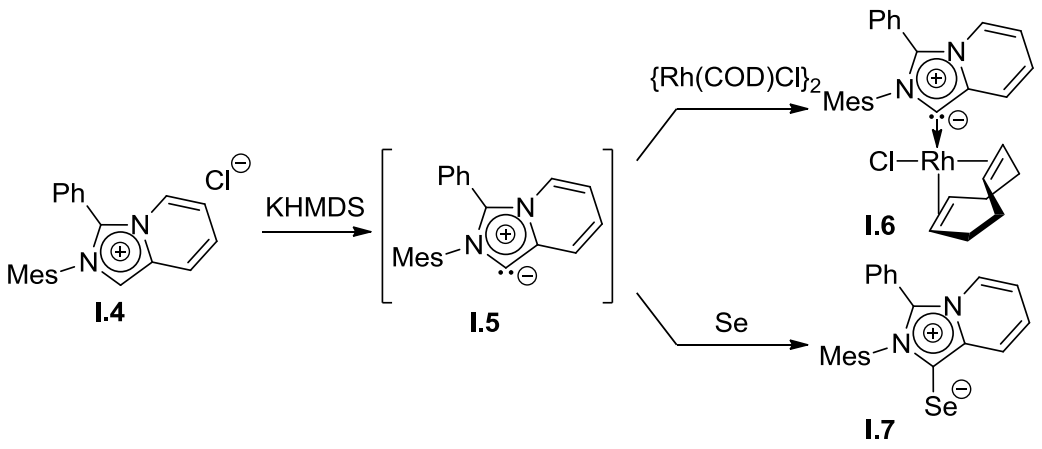
Scheme I. 3: Synthesis of the first carbene transition metal complexes.

In 2001, a new mode of complexation for imidazolylidenes was discovered. Crabtree and co-workers observed that the complexation of imidazolium **I.1** did not yield the expected imidazol-2-ylidene complex **I.2** but the unusual "abnormally bound" imidazol-5-ylidene **I.3**.[15]



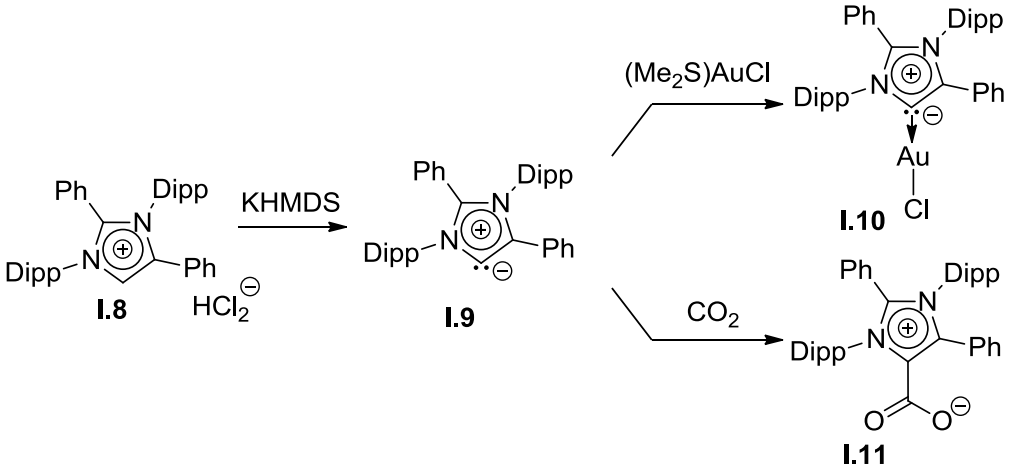
Scheme I. 4: Abnormal complexation of an imidazolium salt; L = PPh_3.

Syntheses of these so-called abnormal carbenes-transition metal complexes were rapidly developed after this finding,[16] and it was quickly shown that abnormal carbenes were much stronger electron donors than their classical isomers. This feature was key for the development of electron rich metal complexes capable of activating very unreactive C–H bonds.[17] However, the isolation of a free imidazol-5-ylidene eluded the community for several years. In 2005, Lassaletta and co-workers reported the deprotonation and trapping of a C-2 protected imidazolium salt **I.4** yielding the rhodium complex **I.6** and selenium adduct **I.7**. The free carbene **I.5** was unfortunately not stable enough to be isolated or observed.[18]



Scheme I. 5: Deprotonation and trapping of an imidazol-5-ylidene; Mes = 2,4,6-trimethylphenyl.

Four years later, the isolation of the first crystalline free imidazol-5-ylidene was finally achieved. Bertrand and co-workers, using a similar deprotonation route, managed to isolate carbene **I.9** from the corresponding imidazolium salt **I.8**. Carbene **I.9** displayed typical reactivity with transition metal complexes and carbon dioxide, yielding complex **I.10** and betaine **I.11**, respectively.[19]



Scheme I. 6: Synthesis and reactivity of the first stable imidazol-5-ylidene; Dipp = 2,6-diisopropylphenyl.

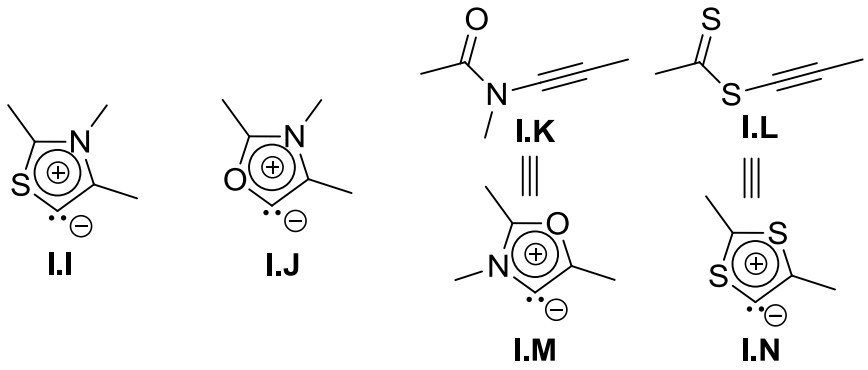


Figure I. 2: Carbenes discussed in this manuscript.

The isolation of a stable, free "abnormal" imidazol-5-ylidene represented a major step forward in the design of a new family of carbon-based ligands. In this manuscript, we will describe the design of a variety of carbenes belonging to that family. Chapter 1 will be dedicated to other imidazol-5-ylidenes, as well as thiazol-5-ylidenes **I.I** and oxazol-5-ylidenes **I.J**. In Chapter 2, we will demonstrate a new concept for the synthesis of carbene-transition metal complexes using simple alkynes **I.K** and **I.L** as synthetic equivalents of the corresponding oxazol-4-ylidenes **I.M** and dithiol-5-ylidenes **I.N**, respectively. Surprisingly, one of these alkynes was able to activate a large variety of small molecules and enthalpically strong bonds, which will be shown in Chapter 3. Finally, in Chapter 4, we will generalize the concept of using alkynes as carbene ligand equivalents to the synthesis of larger ring sized carbenes.

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CHAPTER 1:

Extending the concept of mesoionic carbenes

Adapted from:

G. Ung, G. Bertrand, *Chem. Eur. J.* **2011**, *17*, 8269–8272

and D. Mendoza-Espinosa, G. Ung, B. Donnadieu, G. Bertrand, *Chem. Commun.* **2011**, *47*, 10614–10616

Introduction

As previously mentioned, the first example of a stable abnormal carbene, namely an imidazol-5-ylidene **1.A**, was reported in our group in 2009.[1] Because of the unusual position of the carbene, no resonance structure of this new type of ligands can be drawn without charge separation. Thus, the best representation for these carbenes is to draw them with a positive charge delocalized over the aromatic system, and a negatively charged lone pair, as depicted for **1.A**. The synthesis of carbene **1.A** opened new gates in the design of carbon based ligands; indeed, any cationic aromatic system can be utilized as base skeleton for these mesoionic compounds.[2] In addition, because the p orbital of the so-called "mesoionic carbene" is completely filled, no obvious dimerization pathway can be foreseen. This observation allows us to design numerous mesoionic carbenes, even with relaxed steric environments.

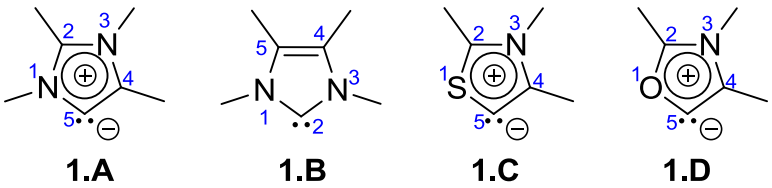
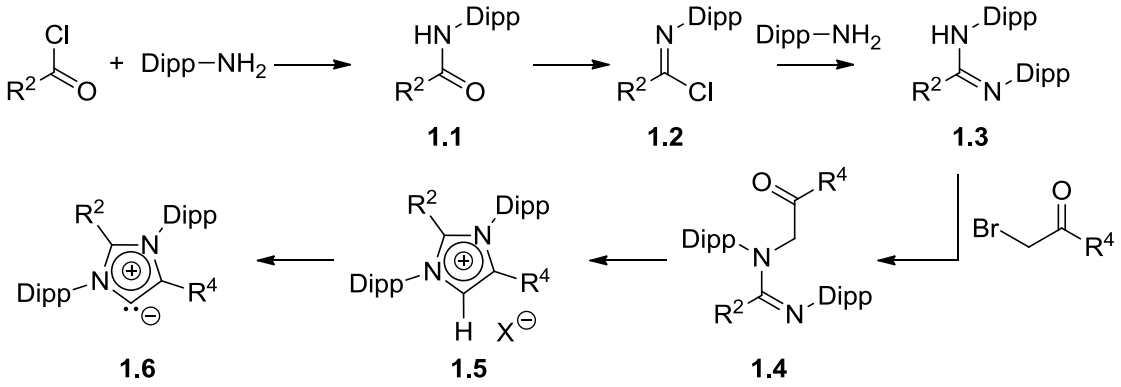


Figure F1. 1: Carbenes discussed in Chapter 1.

In this chapter, we describe the improved synthesis of a variety of imidazol-5-ylidenes. Their stability and electronic properties were investigated and compared to the classical imidazol-2-ylidenes **1.B**. The study on mesoionic carbenes was also expanded to carbenes with less steric protection, namely thiazol-5-ylidenes **1.C** and oxazol-5-ylidenes **1.D** (Figure **F1. 1**).

A) Imidazol-5-ylidenes.

The synthesis of imidazol-5-ylidenes proceeds in 6 steps: reaction of an acyl chloride with a primary amine yields amide **1.1**. The amide is converted to the corresponding chloroimine **1.2**, and then transformed into amidine **1.3** by reaction with a primary amine. Coupling with an α-bromoketone provides the open form **1.4**. Dehydrative cyclization of **1.4** yields imidazolium salt **1.5** which is deprotonated into the desired imidazol-5-ylidene **1.6** (Scheme **S1. 1**).

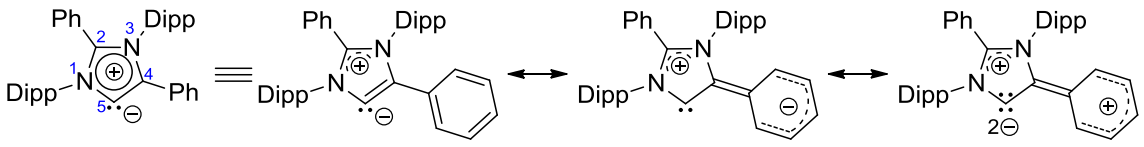


Scheme S1. 1: General synthesis of imidazol-5-ylidenes.

This synthesis is versatile and allows for the introduction of the substituents at position 2 and 4 of the heterocycle independently.

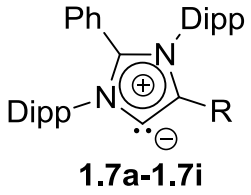
1) Tuning at position 4.

The first imidazol-5-ylidene was reported with $R^2 = R^4 = Ph$. Interestingly, the phenyl substituent at the position 4 is conjugated to the carbene position (Scheme **S1. 2**). This prompted us to investigate the effect of electroactive substituents at this position.



Scheme S1. 2: Resonance structures of 2,4-diphenyl-3,5-di(diisopropylphenyl)imidazol-5-ylidene.

We focused our studies on *meta*- or *para*-substituted phenyl groups, which preserve a comparable steric environment around the carbene center. Carbenes **1.7a-i** (Figure **F1. 2**) were targeted.



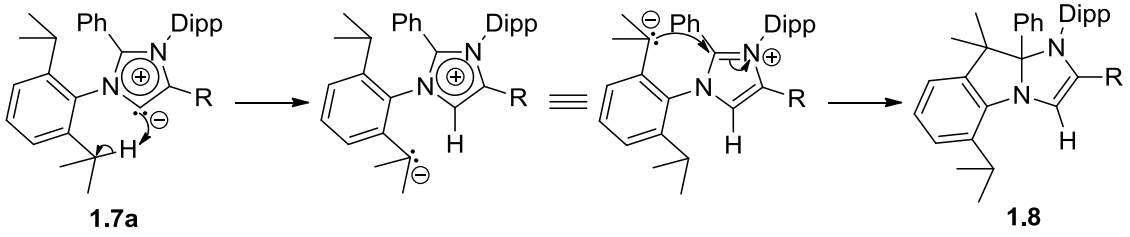
1.7a-1.7i

a: R = 4-(*N*-pyrrolidine)-C_6H_4
b: R = 4-MeO-C_6H_4
c: R = 4-CH_3-C_6H_4
d: R = C_6H_5
e: R = 4-Cl-C_6H_4
f: R = 4-Br-C_6H_4
g: R = 4-F-C_6H_4
h: R = 4-CF_3-C_6H_4
i: R = 3,5-$(CF_3)_2$-C_6H_3

Figure F1. 2: Imidazol-5-ylidenes synthesized.

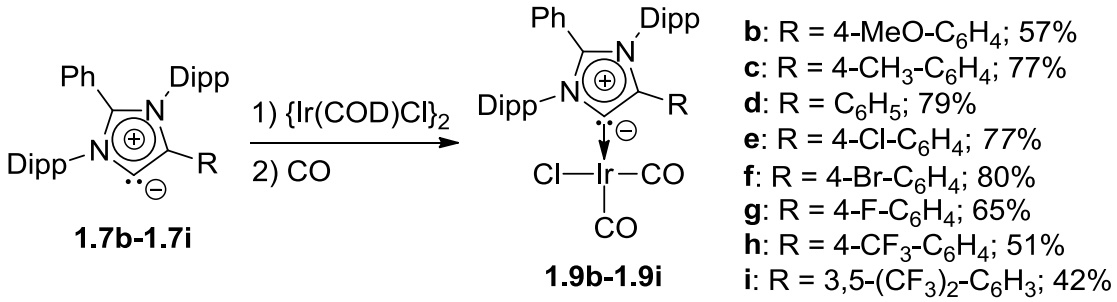
We first studied the stability of the free imidazol-5-ylidene. Carbene **1.7a** cannot be isolated since it rearranges to compound **1.8** in a few minutes (Scheme **S1. 3**). This product formally results from the deprotonation of an isopropyl substituent of the 2,6-diisopropylphenyl group by the carbene center followed by nucleophilic addition of the resulting benzyl anion to the carbon at position 2 (Scheme **S1. 3**). This rearrangement process has previously been reported when the position 4 substituent was an unsubstituted phenyl group (**1.7d**), but only under heating at 50 °C for 2 days.[1] The significant rate enhancement observed for **1.7a** can readily be rationalized by the enhanced basicity of the carbene bearing the strong electron donating pyrrolidine in *para*-position of the aryl group. Imidazol-5-ylidenes **1.7b** and **1.7c**, also bearing electron

donating substituents, can be isolated and fully characterized by NMR spectroscopy, but decompose in a few hours in solution, as well as in the solid state, giving complex mixtures. Carbenes **1.7e-1.7i** bearing an electron-withdrawing group, are stable both in solution and in the solid state. For example, no decomposition was observed for **1.7i** after a week in solution at room temperature.



Scheme S1. 3: Rearrangement of imidazol-5-ylidene **1.7a**; R = 4-(*N*-pyrrolidine)C_6H_4.

The $^{13}C\{^1H\}$ NMR spectra of imidazol-5-ylidenes **1.7b-i** exhibit carbene carbon signals at approximately 200 ppm, with a rather consistent trend; electron withdrawing substituents induce a small downfield shift (Table **T1. 1**). To better quantify the electronic effects of the substituents, the corresponding iridium chloride *cis*-dicarbonyl complexes **1.9b-i** were prepared by reacting the carbene with half an equivalent of $\{Ir(COD)Cl\}_2$ followed by a treatment with excess of carbon monoxide (Scheme **S1. 4**). Because of the lack of stability of carbene **1.7a**, complex **1.9a** was synthesized by performing the deprotonation of the imidazolium salt in the presence of the metal fragment.



Scheme S1. 4: Synthesis of iridium complexes **1.9b-i**.

Table T1. 1: Selected ^{13}C NMR data for carbenes **1.7a-i** and Tolman Eletronic Parameter (TEP)[3] for complexes **1.9a-i**.

	R (C4 substituent)	δ $C_{carbene}$ **1.7** (ppm)	δ $C_{C–Ir}$ **1.9** (ppm)	TEP (cm^{-1})[a]
a	4-(*N*-pyrrolidine)-C_6H_4	N/A[b]	157.8	2036.5
b	4-MeO-C_6H_4	200.2	159.7	2039.3
c	4-CH_3-C_6H_4	200.0	159.1	2038.3
d	C_6H_5	201.9	159.6	2038.5
e	4-Cl-C_6H_4	201.3	160.0	2039.8
f	4-Br-C_6H_4	202.9	160.3	2039.8
g	4-F-C_6H_4	200.1	159.7	2040.5
h	4-CF_3-C_6H_4	204.1	161.3	2040.9
i	3,5-$(CF_3)_2$-C_6H_3	205.8	162.9	2043.0

[a] TEP (cm^{-1}) = 0.847 ν_{CO}^{av} + 336.[4] [b] Carbene could not be spectroscopically characterized.

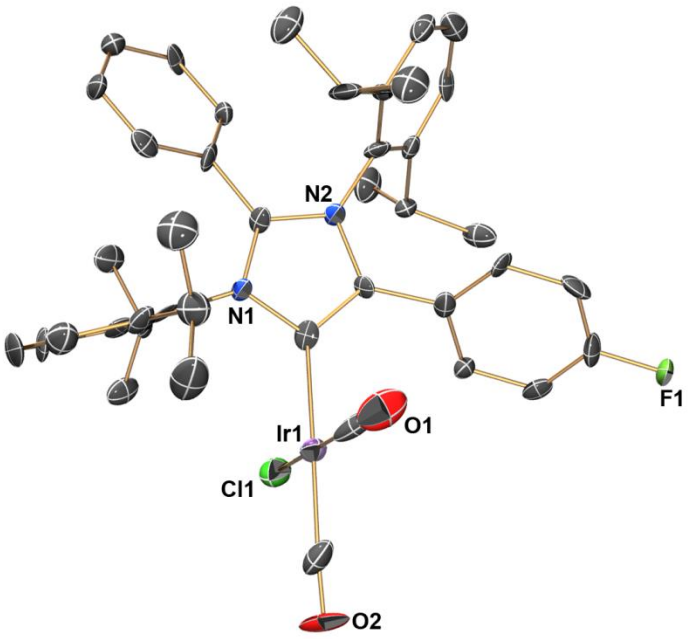
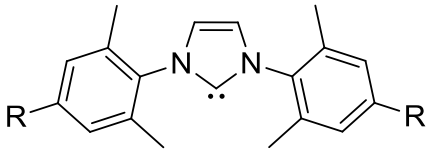


Figure F1. 3: Structure of **1.9g** in the solid state, hydrogen atoms are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

The Tolman Electronic Parameters (TEPs) of complexes **1.9a-i** are given in Table **T1. 1**. The observed values, ranging from 2036.5 cm^{-1} (**1.9a**) to 2043.0 cm^{-1} (**1.9i**), clearly indicate that all imidazol-5-ylidenes **1.9a-i**, even those bearing electron-withdrawing groups, are significantly stronger electron-donors than the imidazol-2-ylidene isomers **1.10a-c** (Figure **F1. 4**). The TEP of complexes **1.9a-i** follows the expected trend, and the differences in the values are comparable to those observed by varying the substituent at the two nitrogen atoms of imidazol-2-ylidenes, as exemplified by **1.10a-c** (range of 4 cm^{-1}).[5]



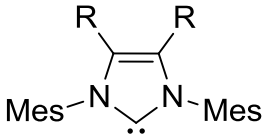
1.10a-1.10c

a: R = NEt_2; TEP = 2049.0 cm^{-1}
b: R = H; TEP = 2051.5 cm^{-1}
c: R = Br;TEP = 2052.8 cm^{-1}

Figure F1. 4: Comparative imidazol-2-ylidenes possessing electroactive substituents.

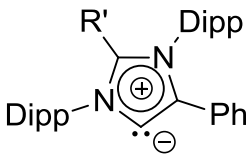
2) *Tuning at position 2.*

In the chemistry of imidazol-2-ylidenes, the substituents on the backbone have a significant impact on the electronic properties of the carbene as evidenced by **1.11a**[5] and **1.11b** (Figure **F1. 5**).[6] We therefore extended our study at the position 2 of the imidazol-5-ylidenes.



1.11a-1.11b

1.11a: R = H; TEP = 2050.8 cm^{-1}
1.11b: R = Cl; TEP = 2054.2 cm^{-1}



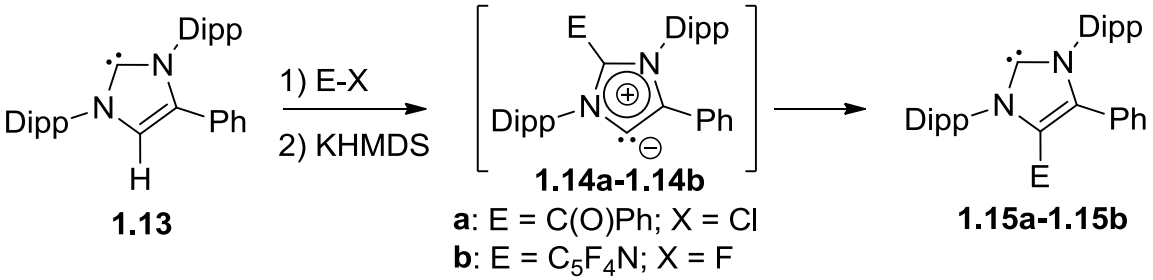
1.12a-1.12b

1.12a: R' = 4-(*N*-pyrrolidine)-C_6H_4
1.12b: R' = 3,5-$(CF_3)_2$-C_6H_3

Figure F1. 5: Comparative imidazol-2-ylidenes **1.11a,b** and targeted imidazol-5-ylidenes **1.12a,b** with substitution on the backbone.

From the study done on the substituents at position 4, we realized that only strong electroactive substituents had a notable effect on the electronic properties of the carbene. We therefore targeted pyrrolidine substituted- as well as *bis*-trifluoromethyl substituted-aryls at position 2 (Figure **F1. 5**). Unfortunately, we were unable to synthesize the pyrrolidine substituted acyl chloride; however, carbene **1.12b** bearing a *bis*-

trifluoromethylphenyl was successfully synthesized. The introduction of an electron withdrawing group at an early stage of the synthesis diminished the yields and reaction rates of each step, which encouraged us to seek alternative routes to access those types of carbenes. We employed a method developed in our group to synthesize imidazol-5-ylidene precursors using imidazol-2-ylidene **1.13** (Scheme **S1. 5**) and targeted **1.14a** and **1.14b** bearing a benzoyl and a 4-tetrafluoropyridine substituent, respectively.[7]



Scheme S1. 5: Synthesis of imidazol-5-ylidenes from imidazol-2-ylidenes and subsequent rearrangement.

Free carbenes **1.14a** and **1.14b** could not be isolated because of the migration of the electrophilic substituent from position 2 to position 5 yielding imidazol-2-ylidenes **1.15a** and **1.15b** (Scheme **S1. 5**). Nevertheless, their iridium chloride *cis*-dicarbonyl complexes could be obtained by trapping the carbene with the metal fragment at low temperature.

Table T1. 2: Selected ^{13}C NMR data for carbenes **1.7d**, **1.12b**, **1.14a** and **1.14b**, and Tolman Eletronic Parameter (TEP) for their corresponding iridium chloride *cis*-dicarbonyl complexes.

	R' (C2 substituent)	δ $C_{carbene}$ (ppm)	δ $C_{C–Ir}$ (ppm)	TEP (cm^{-1})[a]
1.7d	C_6H_5	201.9	159.6	2038.5
1.12b	3,5-$(CF_3)_2$-C_6H_3	202.9	161.5	2041.1
1.14a	$C(O)C_6H_5$	N/A[b]	164.8	2041.3
1.14b	C_5F_4N	N/A[b]	165.7	2041.4

[a] TEP (cm^{-1}) = 0.847 ν_{CO}^{av} + 336. [b] Carbene could not be spectroscopically characterized.

The electronic influence of substituents in position 2 of imidazol-5-ylidenes is only moderate, even with strong electron withdrawing groups (Table **T1. 2**). This result contrasts with the backbone substitution of imidazol-2-ylidenes.

In summary, we have successfully designed a versatile synthesis of imidazol-5-ylidenes, which allowed the placement of a series of electroactive substituents in close proximity to the carbene center. Electron withdrawing groups stabilize the carbenes, while electron donating substituents do not allow the isolation of the free carbenes. Their corresponding metal complexes can be prepared by coordinating the free carbene, or performing the deprotonation of imidazolium salts in the presence of the metal fragment. According to the Tolman Electronic Parameters, the electronic properties of imidazol-5-ylidenes can be reasonably tuned, and the carbenes remain stronger electron donors than imidazol-2-ylidenes, even when they bear electron withdrawing substituents.

B) Thiazol-5-ylidenes.

The first stable thiazol-2-ylidenes of type **1.16** were isolated in 1997. However, the dimerization of thiazol-2-ylidenes is fast and can only be prevented by very large substituents on the nitrogen atom (Figure **F1. 6**).[8] Compared to imidazol-2-ylidenes, thiazol-2-ylidenes are overall weaker electron donors (TEP ~ 2081 cm^{-1}). This is due to the replacement of one of the nitrogen atoms by a poorer π-donor sulfur atom, allowing the carbene to accept more electron density from the metal center.

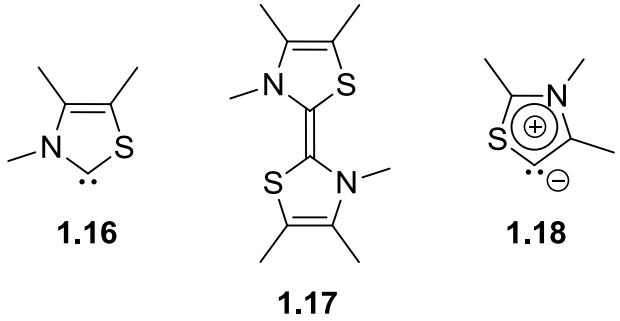
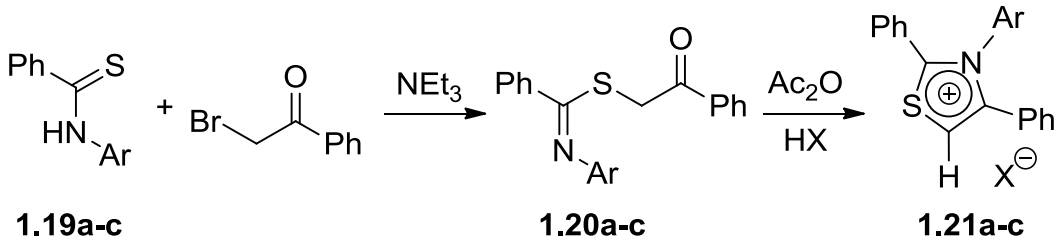


Figure F1. 6: Thiazol-2-ylidenes **1.16**, their dimers **1.17** and the targeted thiazol-5-ylidenes **1.18**.

As mentioned in the introduction, no obvious dimerization path can be foreseen for the mesoionic carbenes. It is therefore reasonable to design carbenes with relaxed steric encumbrance. As a proof of concept, we designed thiazol-5-ylidene **1.18** (Figure **F1. 6**).

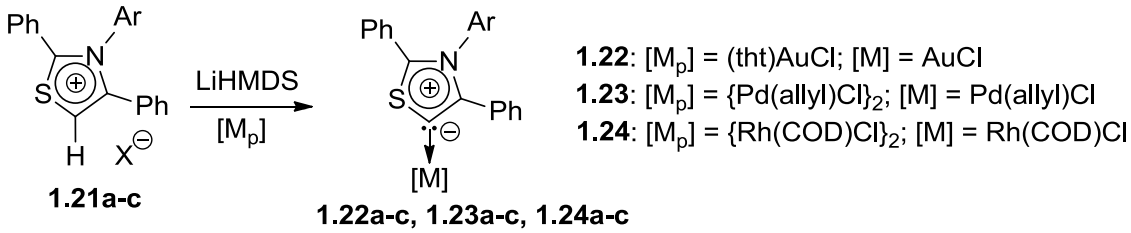
The synthesis of thiazol-5-ylidenes was inspired from the synthesis of imidazol-5-ylidenes. Reaction of a thioamide **1.19** with an α-bromoketone provided **1.20** with

selective alkylation on the sulfur atom. Dehydrative cyclization of **1.20** provided the desired thiazolium salts **1.21** (Scheme **S1. 6**).



Scheme S1. 6: Synthesis of thiazolium salts **1.21a-c**; **a**: Ar = C_6H_5; **b**: Ar = Mes; **c**: Ar = Dipp.

All attempts to deprotonate salts **1.21a-c** with a variety of bases [MHMDS (M = Li, Na, K), *n*BuLi, KO*t*Bu and LDA] resulted in complex mixtures. Even monitoring the deprotonation reaction by NMR spectroscopy at −50 °C, did not allow for the observation of the desired thiazol-5-ylidenes. However, when salts **1.21a-c** were treated at −78 °C with an equimolar amount of LiHMDS, in the presence of (tht)AuCl, $\{Pd(allyl)Cl\}_2$ or $\{Rh(COD)Cl\}_2$ the corresponding thiazol-5-ylidene transition metal complexes **1.22a-c**, **1.23a-c** and **1.24a-c** were obtained and isolated in moderate to good yields (51 to 90%) (Scheme **S1. 7**). To unambiguously confirm the existence of the new thiazol-5-ylidene ligands, single crystals of complex **1.22b**, obtained by slow diffusion of hexane into a concentrated chloroform solution, were subjected to an X-ray diffraction analysis (Figure **F1. 7**).



Scheme S1. 7: Synthesis of thiazol-5-ylidene metal complexes; **a**: Ar = C_6H_5; **b**: Ar = Mes; **c**: Ar = Dipp.

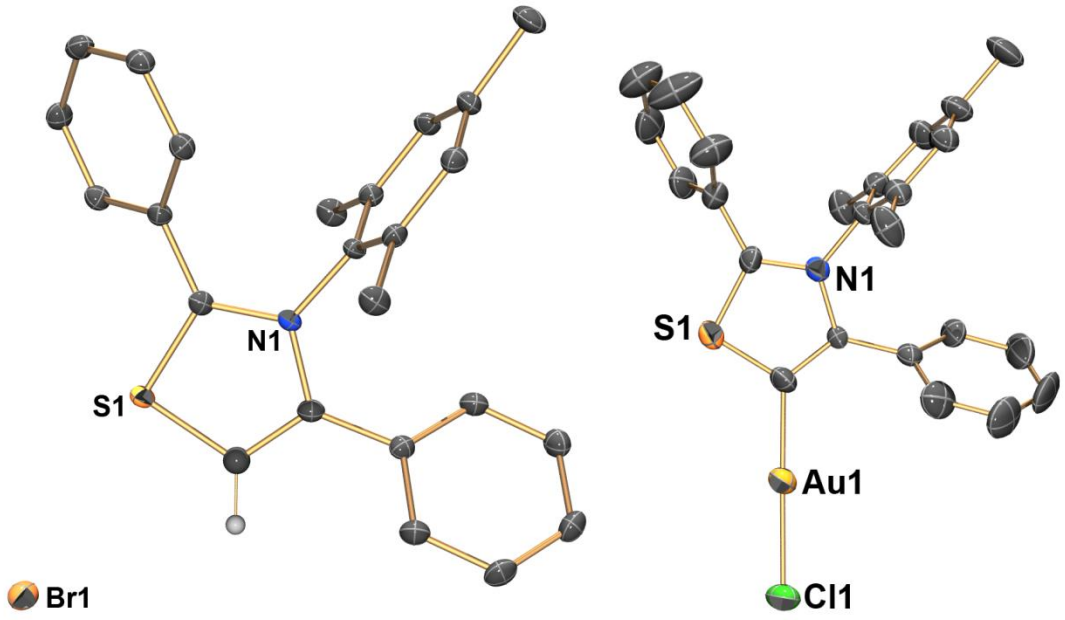


Figure F1. 7: Structure of **1.21b·($CH_3C(O)CH_3$)·(H_2O)** (left) and **1.22b** (right) in the solid state, hydrogen atoms except the thiazolium C–H for **1.21b**, and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

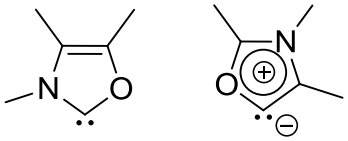
To evaluate the donor properties of thiazol-5-ylidene ligands, the corresponding rhodium chloride *cis*-dicarbonyl complexes **1.25a-c** were prepared by treating **1.24a-c** with excess carbon monoxide. The TEP for **1.25a-c** (2047.4 cm^{-1}) indicate that thiazol-5-ylidenes are much stronger electron donor than their thiazol-2-ylidene isomers (TEP ~ 2081 cm^{-1}). The thiazol-5-ylidenes are less electron donor than imidazol-5-ylidenes, even

those bearing electron withdrawing substituents, but are still stronger donor than the classical imidazol-2-ylidenes.

In summary, although thiazol-5-ylidenes cannot be observed, the readily available 2,3,4-triaryl-substituted thiazolium salts are modular precursors for the synthesis of a variety of thiazol-5-ylidenes transition metal complexes.

C) Oxazol-5-ylidenes

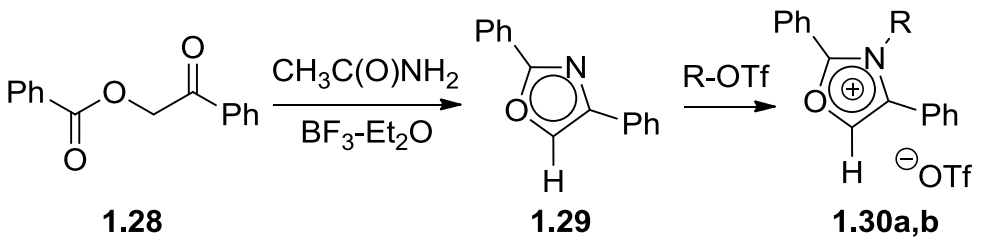
In contrast to thiazol-2-ylidenes, no examples of stable oxazol-2-ylidenes **1.26** are known, although metal complexes exist.[9] The presence of the oxygen atom seems to significantly impact the stability of the carbene. We targeted the synthesis of oxazol-5-ylidenes like **1.27** as free species, as it would represent the first example of a mesoionic carbene which is stable while its normal isomer is not known.



1.26 **1.27**

Figure F1. 8: Unknown oxazol-2-ylidenes **1.26** and the targeted oxazol-5-ylidenes **1.27**.

The synthesis of 2,3,4-triarylated oxazolium salts proved to be not as straightforward as for 2,3,4-triarylated thiazolium salts. However, the synthesis of oxazoles is well developed and we chose to simply alkylate 2,4-diarylated oxazole **1.29** to the corresponding oxazolium salts **1.30**.



1.28 **1.29** **1.30a,b**

Scheme S1. 8: Synthesis of oxazolium salts; **a**: R = CH_3; **b**: R = *i*Pr.

Similarly to the thiazolium salts, all attempts to deprotonate oxazolium salts **1.30a,b** with various bases only yielded complex mixtures. Even the deprotonation at low temperature in the presence of a metal fragment was unsuccessful, indicating that the carbene is not generated, or is too short-lived to be able to be trapped.

Conclusion

In this chapter, we demonstrated that the variety of available mesoionic carbenes can be expanded. A large number of stable imidazol-5-ylidenes bearing various electroactive substituents can be isolated. Thiazol-5-ylidenes, possessing less steric protection, are not stable, but the carbene can be trapped at low temperature with a metal fragment. However, oxazol-5-ylidenes are too fragile to be isolated or trapped.

For imidazol-5-ylidenes, the electronic effect of electroactive substituents is moderate, but they remain strong electron donors. Thiazol-5-ylidenes are weaker donors than imidazol-5-ylidenes, but offer a less congested environment around the metal center. Both carbenes complexes are readily obtained via modular syntheses. These advantages are the key for potential applications of mesoionic carbenes in transition metal catalysis.

Chapter 1 has been adapted from materials published in G. Ung, G. Bertrand, *Chem. Eur. J.* **2011**, *17*, 8269–8272 and D. Mendoza-Espinosa, G. Ung, B. Donnadieu, G. Bertrand, *Chem. Commun.* **2011**, *47*, 10614–10616. The dissertation author was the primary investigator of the first paper and initiated and participated in the project for the second paper.

Appendix: Experimental section

A) Imidazol-5-ylidenes

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Varian Inova 500 and Bruker 300 spectrometers at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

2) General Procedures

Synthesis of N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-arylethyl)benzimidamides ***1.4a-i****.*

A 93:7 *iso*propanol/acetonitrile solution (3.5/0.25 mL) of *N,N'*-bis-(2,6-di*iso*propylphenyl)benzimidamide (1.1 g, 2.5 mmol), 2-bromo-1-arylethanone (2.75 mmol) and potassium bicarbonate (600 mg, 6 mmol) was heated under reflux for 5 hours. Filtration followed by gentle evaporation of the solvent induces the precipitation of **1.4a-i**.

Synthesis of N,N'-bis-(2,6-diisopropylphenyl)-4-aryl-2-phenylimidazolium salts (HCl_2^-) ***1.5a-i****.*

HCl (0.65 mL, 12.1 M in water) was added dropwise to a cold suspension (0°C) of *N,N'*-bis-(2,6-di*iso*propylphenyl)-*N*-(2-oxo-2-arylethyl)benzimidamide (0.9 mmol) in acetic anhydride (2.2 mL) under vigorous stirring. The mixture was warmed to room temperature and stirred overnight. Water was added until a white precipitate persists (~10 mL). The resulting suspension was extracted with methylene chloride (2 x 10 mL). The combined organic layer was washed with water (5 x 10 mL), dried on anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was stirred with 15 mL of diethyl ether for 45 min, and then filtered. The resulting solid was washed with 3 x 5 mL of diethyl ether and dried, affording salts **1.5a-i**.

Synthesis of N,N'-bis-(2,6-diisopropylphenyl)-4-aryl-2-phenylimidazol-5-ylidenes ***1.7b-i****.*

THF (2 mL) was added to a mixture of solid *N,N'*-bis-(2,6-di*iso*propylphenyl)-4-aryl-2-phenylimidazolium salts (HCl_2^-) **1.5b-i** (200 mg) and potassium hexamethyldisilazide (2 equivalents) at −78°C. The mixture was stirred 30 min at −78°C, warmed to room temperature and stirred 30 min. Evaporation of the solvent gave a solid residue which

was extracted with hexanes and filtered (2 x 5 mL). Evaporation of the solvent afforded the free carbenes **1.7b-i**.

*Synthesis of chloro-MIC-Iridium(I)-cis-dicarbonyl complex **1.9b-i**.*

THF (1.5 mL) was added at room temperature to a mixture of solid *N,N'*-bis-(2,6-di*iso*propylphenyl)-4-aryl-2-phenylimidazol-5-ylidene **1.7b-i** (100 mg) and chloro-(1,5-cyclooctadiene)-Iridium(I)-dimer (0.5 equivalent). The mixture was stirred overnight at room temperature. Evaporation of the solvent gave a solid residue which was extracted with diethyl ether and filtered. Evaporation of diethyl ether afforded a brown solid which was dissolved in deuterated benzene. Carbon monoxide was bubbled during 45 min. The solvent was evaporated and the resulting solid was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate). Crystallization in chloroform/hexanes afforded the desired complexes **1.9b-i** as pale yellow solids.

*Synthesis of chloro-MIC-Iridium(I)-cis-dicarbonyl complex with carbenes **1.9a**, **1.14a,b**.*

THF (3 mL) was added to a solid mixture of the corresponding imidazolium salts potassium hexamethyldisilazide (2 equivalents) and chloro-(1,5-cyclooctadiene)-Iridium(I)-dimer (0.5 equivalent) at −78°C. The mixture was stirred 30 min at −78°C, then warmed to room temperature and stirred overnight. Evaporation of the solvent gave a solid residue which was extracted with diethyl ether and filtered. Evaporation of diethyl ether afforded a brown solid which was dissolved in deuterated benzene. Carbon monoxide was bubbled during 45 min. Solvent was evaporated and the resulting solid was purified by column chromatography on silica gel (eluant hexanes/ethyl acetate). Crystallization in chloroform/hexanes afforded the desired complexes **3a,k,l** as yellow solids.

3) Synthesis and Characterization

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-pyrrolidinophenyl)ethyl)benzimidamide **1.4a**.*

From 2-bromo-1-(4-pyrrolidinophenyl)ethanone (737 mg), **1.4a** was obtained as pale yellow solid (906 mg, 58 % yield); **m.p.** 208°C; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.9 Hz, 2H), 6.94-7.15 (m, 8H), 6.77-6.88 (m, 3H), 6.50 (d, *J* = 8.9 Hz, 2H), 5.00 (s, 2H), 4.12 (sept, *J* = 6.7 Hz, 2H), 3.29-3.37 (m, 4H), 3.20 (sept, *J* = 6.7 Hz, 2H), 1.99-2.06 (m, 4H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.24 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.7 Hz, 6H), 0.97 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 191.2 (*C*O), 156.3 (*C*^{q}), 150.9 (*C*^{q}), 148.1 (*C*^{q}), 145.3 (*C*^{q}), 141.1 (*C*^{q}), 138.6 (*C*^{q}), 133.0 (*C*^{q}), 130.2 (*C*H$_{ar}$), 128.9 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 128.2 (*C*H$_{ar}$), 127.1 (*C*H$_{ar}$), 124.3 (*C*H$_{ar}$), 124.0 (*C*^{q}), 122.4 (*C*H$_{ar}$), 121.7 (*C*H$_{ar}$), 110.9 (*C*H$_{ar}$), 57.5 (*C*H$_2$), 47.7 (N*C*H$_2$), 28.3 (*C*H(CH$_3$)$_2$), 27.9 (*C*H(CH$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 25.6 (*C*H$_2$), 25.0 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.2 (CH(*C*H$_3$)$_2$); **HRMS**: m/z calculated for $C_{43}H_{54}N_3O$ $(M+H)^+$ 628.4261, found 628.4273.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-methoxyphenyl)ethyl)benzimidamide **1.4b**.*

From 2-bromo-1-(4-methoxyphenyl)ethanone (630 mg), **1.4b** was obtained as a white solid **(**594 mg, 40 % yield). **m.p.** 214°C; **^{1}H (300 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.6 Hz, 2H), 6.76-7.18 (m, 13H), 4.98 (s, 2H), 4.05 (sept, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 3.15 (sept, *J* = 6.7 Hz, 2H), 1.23 (d, *J* = 6.7 Hz, 12H), 1.04 (d, *J* = 6.7 Hz, 6H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 192.0 (*C*O), 163.3 (C^q), 156.4 (C^q), 147.9 (C^q), 144.9 (C^q), 140.8 (C^q), 138.7 (C^q), 132.6 (C^q), 130.2 (CH_{ar}), 129.7 (C^q), 128.9 (CH_{ar}), 128.7 (CH_{ar}), 128.4 (CH_{ar}), 127.1 (CH_{ar}), 124.3 (CH_{ar}), 122.5 (CH_{ar}), 122.0 (CH_{ar}), 113.9 (CH_{ar}), 57.8 (CH_2), 55.6 (OCH_3), 28.3 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.2 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{40}H_{49}N_2O_2$ $(M+H)^+$ 589.3776, found 589.3873.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-methylphenyl)ethyl)benzimidamide **1.4c***.

From 2-bromo-1-(4-methylphenyl)ethanone (585 mg), **1.4c** was obtained as a white solid **(**604 mg, 42 % yield). **m.p.** 187°C; **^{1}H (300 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.0 Hz, 2H), 6.92-7.24 (m, 3H), 6.76-6.90 (m, 10H), 5.00 (s, 2H), 4.04 (sept, *J* = 6.8 Hz, 2H), 3.5 (sept, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 1.21-1.25 (m, 12H), 1.04 (d, *J* = 6.7 Hz, 6H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 193.1 (*C*O), 156.4 (C^q), 147.9 (C^q), 144.9 (C^q), 143.6 (C^q), 140.7 (C^q), 138.7 (C^q), 134.2 (C^q), 132.6 (C^q), 129.4 (CH_{ar}), 128.9 (CH_{ar}), 128.7 (CH_{ar}), 128.4 (CH_{ar}), 128.1 (CH_{ar}), 127.1 (CH_{ar}), 124.4 (CH_{ar}), 122.5 (CH_{ar}), 122.0 (CH_{ar}), 58.1 (CH_2), 28.3 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$) 25.1 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), 21.8 (CH_3); **HRMS**: m/z calculated for $C_{40}H_{49}N_2O$ $(M+H)^+$ 573.3839, found 573.3839.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-chlorophenyl)ethyl)benzimidamide **1.4e***.

From 2-bromo-1-(4-chlorophenyl)ethanone (640 mg), **1.4e** was obtained as a white solid (980 mg, 66 % yield). **m.p.** 212°C; **^{1}H (300 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.13-7.19 (m, 1H), 6.91-7.06 (m, 7H), 6.78-6.89 (m, 3H), 4.95 (s, 2H), 4.01 (sept, *J* = 6.7 Hz, 2H), 3.11 (sept, *J* = 6.7 Hz, 2H), 1.24 (d, *J* = 6.7 Hz, 6H), 1.23 (d, *J* = 6.7 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 192.4 (*C*O), 156.4 (C^q), 147.8 (C^q), 144.5 (C^q), 140.4 (C^q), 139.2 (C^q), 138.7 (C^q), 135.1 (C^q), 132.2 (C^q), 129.4 (CH_{ar}), 129.0 (CH_{ar}), 128.9 (CH_{ar}), 128.8 (CH_{ar}), 128.6 (CH_{ar}), 127.2 (CH_{ar}), 124.4 (CH_{ar}), 122.6 (CH_{ar}), 122.2 (CH_{ar}), 57.9 (CH_2), 28.3 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{39}H_{46}ClN_2O$ $(M+H)^+$ 593.3293, found 593.3297.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-bromophenyl)ethyl)benzimidamide **1.4f***.

From 2-bromo-1-(4-bromophenyl)ethanone (765 mg), **1.4f** was obtained as a white solid (400 mg, 25 % yield). **m.p.** 218°C; **^{1}H (300 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.77-7.19 (m, 11H), 4.94 (s, 2H), 4.01 (sept, *J* = 6.8 Hz, 2H), 3.10 (sept, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.02 (d, *J* = 6.8 Hz, 6H), 0.95 (d, *J* = 6.8 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 192.6 (*C*O), 156.4 (C^q), 147.8 (C^q), 144.5 (C^q), 140.4 (C^q), 138.7 (C^q), 135.6 (C^q), 132.1 (C^q), 132.0 (CH_{ar}), 129.6 (CH_{ar}), 128.9 (CH_{ar}), 128.8 (CH_{ar}), 128.6 (CH_{ar}), 127.9 (C^q), 127.2 (CH_{ar}), 124.4 (CH_{ar}),

122.6 (*C*H_{ar}), 122.2 (*C*H_{ar}), 57.9 (*C*H_2), 28.3 (*C*H(CH_3)$_2$), 28.0 (*C*H(CH_3)$_2$), 26.5 (CH(*C*H_3)$_2$) 25.2 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$); **HRMS**: m/z calculated for $C_{39}H_{46}BrN_2O$ $(M+H)^+$ 637.2788/639.2775, found 637.2786/639.2774.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-fluorophenyl)ethyl)benzimidamide **1.4g**.*

From 2-bromo-1-(4-fluorophenyl)ethanone (505 mg), **1.4g** was obtained as a white solid (600 mg, 35 % yield). **m.p.** 171°C; **^{1}H (300 MHz, $CDCl_3$)** δ 8.03-8.10 (m, 2H), 6.82-7.19 (m, 10H), 6.77-6.81 (m, 3H), 4.97 (s, 2H), 4.02 (sept, *J* = 6.7 Hz, 2H), 3.12 (sept, *J* = 6.9 Hz, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 192.0 (*C*O), 165.6 (d, $^1J_{(C-F)}$ = 252 Hz, C^q), 156.4 (C^q), 147.8 (C^q), 144.6 (C^q), 140.5 (C^q), 138.7 (C^q), 133.2 (C^q), 132.3 (C^q), 130.6 (d, $^3J_{(C-F)}$ = 9 Hz, *C*H_{ar}), 128.9 (*C*H_{ar}), 128.8 (*C*H_{ar}), 128.5 (*C*H_{ar}), 127.2 (*C*H_{ar}), 124.4 (*C*H_{ar}), 122.5 (*C*H_{ar}), 122.2 (*C*H_{ar}), 115.8 (d, $^2J_{(C-F)}$ = 22 Hz, *C*H_{ar}), 58.0 (*C*H_2), 28.3 (*C*H(CH_3)$_2$), 28.0 (*C*H(CH_3)$_2$), 26.5 (CH(*C*H_3)$_2$), 25.1 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −107.2; **HRMS**: m/z calculated for $C_{39}H_{46}FN_2O$ $(M+H)^+$ 577.3589, found 577.3588.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(4-trifluoromethylphenyl)ethyl)benzimidamide **1.4h**.*

From 2-bromo-1-(4-trifluoromethylphenyl)ethanone (734 mg), **1.4h** was obtained as a white solid (770 mg, 49 % yield). **m.p.** 194°C; **^{1}H (300 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.14-7.22 (m, 1H), 6.92-7.10 (m, 7H), 6.79-6.91 (m, 3H), 4.98 (s, 2H), 4.00 (sept, *J* = 6.7 Hz, 2H), 3.10 (sept, *J* = 6.7 Hz, 2H), 1.26 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H), 0.95 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 192.8 (*C*O), 156.5 (C^q), 147.8 (C^q), 144.4 (C^q), 140.2 (C^q), 139.8 (C^q), 138.8 (C^q), 132.4 (q, $^2J_{(C-F)}$ = 132 Hz, C^q), 129.0 (*C*H_{ar}), 128.9 (*C*H_{ar}), 128.7 (*C*H_{ar}), 128.4 (*C*H_{ar}), 127.2 (*C*H_{ar}), 124.5 (*C*H_{ar}), 123.4 (q, $^1J_{(C-F)}$ = 272 Hz, C^q), 122.6 (*C*H_{ar}), 122.4 (*C*H_{ar}), 58.2 (*C*H_2), 28.3 (*C*H(CH_3)$_2$), 28.1 (*C*H(CH_3)$_2$), 26.5 (CH(*C*H_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −64.7; **HRMS**: m/z calculated for $C_{40}H_{45}F_3N_2O$ $(M+H)^+$ 626.3484, found 626.3481.

*N,N'-bis-(2,6-diisopropylphenyl)-N-(2-oxo-2-(3,5-bistrifluoromethylphenyl)ethyl)benzimidamide **1.4i**.*

From 2-bromo-1-(3,5-bistrifluoromethylphenyl)ethanone (921 mg), **1.4i** was obtained as a white solid (833 mg, 48 % yield). **m.p.** 180°C; **^{1}H (300 MHz, $CDCl_3$)** δ 8.49 (s, 2H), 8.01 (s, 1H), 7.15-7.22 (m, 1H), 6.97-7.08 (m, 7H), 6.78-6.88 (m, 3H), 4.95 (s, 2H), 3.99 (sept, *J* = 6.7 Hz, 2H), 3.03 (sept, *J* = 6.7 Hz, 2H), 1.29 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.94 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 190.8 (*C*O), 156.5 (C^q), 147.7 (C^q), 144.0 (C^q), 139.9 (C^q), 138.4 (C^q), 132.4 (q, $^2J_{(C-F)}$ = 34 Hz, C^q), 131.7 (C^q), 129.0 (*C*H_{ar}), 128.9 (*C*H_{ar}), 128.8 (*C*H_{ar}), 128.0 (*C*H_{ar}), 127.3 (*C*H_{ar}), 126.1 (*C*H_{ar}), 124.6 (*C*H_{ar}), 123.1 (q, $^1J_{(C-F)}$ = 271 Hz, C^q), 122.6 (*C*H_{ar}), 57.6 (*C*H_2), 28.3 (*C*H(CH_3)$_2$), 28.1 (*C*H(CH_3)$_2$), 26.5 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 23.1 (CH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −62.0; **HRMS**: m/z calculated for $C_{41}H_{45}F_6N_2O$ $(M+H)^+$ 695.3358, found 695.3528.

N,N'-bis(2,6-diisopropylphenyl)-N-(2-oxo-2-phenylethyl)-3,5-bis(trifluoromethyl)benzimidamide.

From 2-bromo-acetophenone (0.760 g), the title compound was obtained as a white solid (567 mg, 47% yield). **m.p.** 198°C. **^{1}H (300 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.41-7.60 (m, 6H), 7.17-7.22 (m, 1H), 7.05-7.10 (m, 2H), 6.77-6.89 (m, 3H), 5.11 (s, 2H), 3.93 (sept, *J* = 6.7 Hz, 2H), 3.06 (sept, *J* = 6.7 Hz, 2H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.21 (d, *J* = 6.7 Hz, 6H), 1.04 (d, *J* = 6.7 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H). **^{13}C (75 MHz, $CDCl_3$)** δ 192.9 (*C*O), 153.4 (C^q), 147.9 (C^q), 143.8 (C^q), 139.2 (C^q), 138.5 (C^q), 136.3 (C^q), 134.8 (C^q), 133.3 (CH_{ar}), 130.6 (q, $^{2}J_{(C-F)}$ = 33 Hz, C^q), 129.3 (CH_{ar}), 128.9 (CH_{ar}), 128.0 (CH_{ar}), 124.7 (CH_{ar}), 123.1 (CH_{ar}), 123.0 (q, $^{1}J_{(C-F)}$ = 271 Hz, C^q), 122.7 (CH_{ar}), 122.1 (CH_{ar}), 58.2 (CH_2), 28.6 ($CH(CH_3)_2$), 28.2 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$), 21.7 ($CH(CH_3)_2$). **^{19}F (282 MHz, $CDCl_3$)** δ −64.5. **HRMS**: m/z calculated for $C_{41}H_{45}F_6N_2O$ $(M+H)^+$ 695.3431, found 695.3428.

N,N'-bis-(2,6-diisopropylphenyl)-2-phenyl-4-(4-pyrrolidinophenyl)imidazolium (HCl_2^-) ***1.5a****.*

From **1.4a** (800 mg), **1.5a** was obtained as a white solid (290 mg, 33 % yield). **m.p.** 272°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.20-7.29 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.38 (d, *J* = 8.0 Hz, 2H), 3.14-3.22 (m, 4H), 2.48 (sept, *J* = 6.5 Hz, 2H), 2.40 (sept, *J* = 6.5 Hz, 2H), 1.90-1.98 (m, 4H), 1.27 (d, *J* = 6.5 Hz, 6H), 0.97 (d, *J* = 6.5 Hz, 6H), 0.88 (d, *J* = 6.5 Hz, 6H), 0.81 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 149.3 (C^q), 145.1 (C^q), 144.6 (C^q), 144.5 (C^q), 138.7 (C^q), 133.0 (CH_{ar}), 132.9 (CH_{ar}), 132.6 (CH_{ar}), 130.4 (C^q), 129.6 (CH_{ar}), 129.4 (CH_{ar}), 129.3 (CH_{ar}), 129.0 (C^q), 126.2 (CH_{ar}), 125.6 (CH_{ar}), 120.9 (C^q), 119.7 (CH_{ar}), 112.1 (CH_{ar}), 109.8 (C^q), 47.6 (NCH_2), 29.6 ($CH(CH_3)_2$), 29.4 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 25.5 (CH_2), 24.1 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{43}H_{52}N_3$ 610.4156, found 610.4149.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-methoxyphenyl)-2-phenylimidazolium (HCl_2^-) ***1.5b****.*

From **1.4b** (600 mg), **1.5b** was obtained as a white solid (585 mg, 89 % yield). **m.p.** 269°C decomp; **^{1}H (300 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.19-7.41 (m, 8H), 6.88-6.96 (m, 4H), 3.81 (s, 3H), 2.55 (sept, *J* = 6.7 Hz, 2H), 2.46 (sept, *J* = 6.7 Hz, 2H), 1.39 (d, *J* = 6.7 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H), 0.91 (d, *J* = 6.7 Hz, 6H), 0.87 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 161.6 (C^q), 144.9 (C^q), 144.6 (C^q), 137.2 (C^q), 137.2 (C^q), 132.9 (CH_{ar}), 132.5 (CH_{ar}), 130.1 (CH_{ar}), 129.6 (C^q), 129.3 (CH_{ar}), 128.7 (C^q), 126.2 (CH_{ar}), 125.5 (CH_{ar}), 122.2 (CH_{ar}), 120.8 (C^q), 116.5 (C^q), 115.0 (CH_{ar}), 55.7 (OCH_3), 29.5 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 22.6 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{40}H_{47}N_2O$ 571.3683, found 571.3670.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-methylphenyl)-2-phenylimidazolium (HCl_2^-) ***1.5c****.*

From **1.4c** (1120 mg), **1.5c** was obtained as a white solid (842 mg, 69 % yield). **m.p.** 302°C decomp; **^{1}H (300 MHz, $CDCl_3$)** δ 8.44 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.10-7.36 (m, 10H), 6.89 (d, *J* = 7.8 Hz, 2H), 2.49 (sept, *J* = 6.7 Hz, 2H), 2.39 (sept, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 1.32 (d, *J* = 6.7 Hz, 6H), 0.99 (d, *J* = 6.7 Hz, 6H), 0.85 (d, *J* = 6.7 Hz, 6H), 0.83 (d, *J* = 6.7 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 145.3 (C^q), 144.8 (C^q), 144.5 (C^q), 141.6 (C^q), 137.4 (C^q), 133.1 (CH_{ar}), 132.9 (CH_{ar}), 132.5 (CH_{ar}), 130.2 (CH_{ar}), 130.1 (C^q), 129.6 (CH_{ar}), 129.4 (CH_{ar}), 128.6 (C^q), 128.4 (CH_{ar}), 126.2 (CH_{ar}), 125.5 (CH_{ar}), 122.5 (CH_{ar}), 121.4 (C^q), 120.6 (C^q), 29.5 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 22.6 ($CH(CH_3)_2$), 21.4 (CH_3); **HRMS**: m/z calculated for $C_{40}H_{47}N_2$ 555.3734, found 555.3742.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-chlorophenyl)-2-phenylimidazolium (HCl_2^-) ***1.5e****.*

From **1.4e** (600 mg), **1.5e** was obtained as a white solid (502 mg, 79 % yield). **m.p.** 268°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 9.48 (s, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.20-7.29 (m, 6H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 2.46 (sept, *J* = 6.5 Hz, 2H), 2.36 (sept, *J* = 7.0 Hz, 2H), 1.31 (d, *J* = 6.5 Hz, 6H), 0.92 (d, *J* = 7.0 Hz, 6H), 0.81 (d, *J* = 6.5 Hz, 6H), 0.79 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 145.2 (C^q), 144.8 (C^q), 137.1 (C^q), 136.0 (C^q), 133.1 (CH_{ar}), 133.0 (CH_{ar}), 132.5 (CH_{ar}), 130.3 (C^q), 130.2 (CH_{ar}), 129.8 (CH_{ar}), 129.7 (CH_{ar}), 129.3 (CH_{ar}), 128.9 (C^q), 126.4 (CH_{ar}), 125.5 (CH_{ar}), 125.3 (CH_{ar}), 123.3 (C^q), 121.0 (C^q), 29.7 ($CH(CH_3)_2$), 29.4 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{39}H_{45}ClN_2$ 576.3266, found 576.3290.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-bromophenyl)-2-phenylimidazolium (HCl_2^-) ***1.5f****.*

From **1.4f** (800 mg), **1.5f** was obtained as a white solid (500 mg, 58 % yield). **m.p.** 182°C; **^{1}H (300 MHz, $CDCl_3$)** δ 9.56 (s, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.16-7.59 (m, 12H), 6.89 (d, *J* = 7.7 Hz, 2H), 2.45 (sept, *J* = 6.8 Hz, 2H), 2.38 (sept, *J* = 6.7 Hz, 2H), 1.36 (d, *J* = 6.7 Hz, 6H), 0.97 (d, *J* = 6.8 Hz, 6H), 0.81-0.88 (m, 12H); **^{13}C (75 MHz, $CDCl_3$)** δ 145.0 (C^q), 144.6 (C^q), 144.3 (C^q), 135.5 (C^q), 132.9 (CH_{ar}), 132.8 (CH_{ar}), 132.3 (CH_{ar}), 132.1 (CH_{ar}), 130.0 (CH_{ar}), 129.9 (C^q), 129.4 (CH_{ar}), 129.1 (CH_{ar}), 128.3 (C^q), 126.1 (CH_{ar}), 125.1 (CH_{ar}), 125.0 (C^q), 124.6 (CH_{ar}), 123.4 (C^q), 120.4 (C^q), 29.3 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 25.5 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{39}H_{45}BrN_2$ 620.2761/622.2748, found 620.2785/622.2770.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-fluorophenyl)-2-phenylimidazolium (HCl_2^-) ***1.5g****.*

From **1.4g** (1200 mg), **1.5g** was obtained as a white solid (1060 mg, 81 % yield). **m.p.** 287°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 9.34 (s, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39-7.46 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.18-7.29 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 2.46 (sept, *J* = 7.0 Hz, 2H), 2.36 (sept, *J* = 7.0 Hz, 2H), 1.31 (d, *J* = 7.0 Hz, 6H), 0.92 (d, *J* = 7.0 Hz, 6H), 0.81 (d, *J* = 7.0 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 163.9 (d, $^{1}J_{(C-F)}$ =

252 Hz, C^q), 145.1 (C^q), 145.0 (C^q), 144.7 (C^q), 136.1 (C^q), 133.0 (CH_{ar}), 132.9 (CH_{ar}), 132.4 (CH_{ar}), 131.3 (d, $^3J_{(C-F)}$ = 8 Hz, CH_{ar}), 130.3 (C^q), 129.8 (CH_{ar}), 129.3 (CH_{ar}), 128.8 (C^q), 126.3 (CH_{ar}), 125.5 (CH_{ar}), 124.8 (CH_{ar}), 121.0 (C^q), 116.8 (d, $^2J_{(C-F)}$ = 23 Hz, CH_{ar}), 29.7 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$). **^{19}F (282 MHz, C_6D_6)** δ −110.0; **HRMS**: m/z calculated for $C_{39}H_{45}FN_2$ 560.3561, found 560.3568.

N,N'-bis-(2,6-diisopropylphenyl)-2-phenyl-4-(4-trifluoromethylphenyl)imidazolium (HCl_2^-) ***1.5h****.*

From **1.4h** (700 mg), **1.5h** was obtained as a white solid (547 mg, 72 % yield). **m.p.** 224°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 9.40 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 2.52 (sept, *J* = 6.5 Hz, 2H), 2.43 (sept, *J* = 7.0 Hz, 2H), 1.39 (d, *J* = 6.5 Hz, 6H), 0.98 (d, *J* = 7.0 Hz, 6H), 0.85 (d, *J* = 7.0 Hz, 6H), 0.84 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 145.4 (C^q), 145.0 (C^q), 144.8 (C^q), 135.3 (C^q), 133.1 (CH_{ar}), 132.9 (CH_{ar}), 132.4 (CH_{ar}), 132.1 (q, $^2J_{(C-F)}$ = 33 Hz, C^q), 130.3 (C^q), 129.8 (CH_{ar}), 129.4 (CH_{ar}), 129.3 (CH_{ar}), 128.9 (C^q), 128.4 (C^q), 126.9 (CH_{ar}), 126.4 (CH_{ar}), 126.3 (CH_{ar}), 125.4 (CH_{ar}), 123.7 (q, $^1J_{(C-F)}$ = 273 Hz, C^q), 120.9 (C^q), 29.7 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −64.7; **HRMS**: m/z calculated for $C_{40}H_{44}F_3N_2$ 609.3451, found 609.3436.

N,N'-bis-(2,6-diisopropylphenyl)-4-(3,5-bistrifluoromethylphenyl)-2-phenylimidazolium (HCl_2^-) ***1.5i****.*

From **1.4i** (1000 mg), **1.5i** was obtained as a white solid (720 mg, 67 % yield). **m.p.** 264°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 10.72 (s, 1H), 8.17(s, 2H), 7.82 (s, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 2.54 (sept, *J* = 7.0 Hz, 2H), 2.44 (sept, *J* = 6.5 Hz, 2H), 1.42 (d, *J* = 6.5 Hz, 6H), 0.98 (d, *J* = 7.0 Hz, 6H), 0.86 (d, *J* = 7.0 Hz, 6H), 0.84 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 145.9 (C^q), 144.9 (C^q), 144.7 (C^q), 133.5 (C^q), 133.3 (CH_{ar}), 133.2 (CH_{ar}), 132.5 (q, $^2J_{(C-F)}$ = 33 Hz, C^q), 132.4 (CH_{ar}), 130.1 (C^q), 129.8 (CH_{ar}), 129.4 (CH_{ar}), 128.3 (C^q), 127.5 (CH_{ar}), 127.2 (C^q), 126.6 (CH_{ar}), 125.4 (CH_{ar}), 123.6 (CH_{ar}), 122.7 (q, $^1J_{(C-F)}$ = 272 Hz, C^q), 120.6 (C^q), 29.6 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −64.4; **HRMS**: m/z calculated for $C_{41}H_{43}F_6N_2$ 677.3325, found 677.3313.

N,N'-bis-(2,6-diisopropylphenyl)-2-(3,5-bistrifluoromethylphenyl)-4-phenylimidazolium (HCl_2^-).

From the corresponding open form (570 mg), the title compound was obtained as a white solid (475 mg, 86 % yield). **m.p.** 242°C decomp. **^{1}H (500 MHz, $CDCl_3$)** δ 10.3 (s, 1H), 7.69 (s, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49-7.54 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.20-7.31 (m, 9H), 2.39 (sept, *J* = 7.0 Hz, 2H), 2.29 (sept, *J* = 7.0 Hz, 2H), 1.32 (d, *J* = 7.0 Hz,

6H), 0.84 (d, *J* = 7.0 Hz, 6H), 0.75 (d, *J* = 7.0 Hz, 6H), 0.71 (d, *J* = 7.0 Hz, 6H). **^{13}C (125 MHz, $CDCl_3$)** δ 144.8 (C^q), 144.6 (C^q), 140.6 (C^q), 137.9 (C^q), 133.5 (CH_{ar}), 132.9 (CH_{ar}), 132.9 (q, $^2J_{(C-F)}$ = 35 Hz, C^q), 131.0 (CH_{ar}), 130.1 (CH_{ar}), 129.5 (CH_{ar}), 129.1 (CH_{ar}), 128.5 (C^q), 126.9 (C^q), 126.6 (CH_{ar}), 125.7 (CH_{ar}), 125.2 (CH_{ar}), 124.2 (C^q), 123.6 (C^q), 121.9 (q, $^1J_{(C-F)}$ = 272 Hz, C^q), 29.7 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$). **^{19}F (282 MHz, $CDCl_3$)** δ −64.0. **HRMS**: m/z calculated for $C_{41}H_{43}F_6N_2^+$ 677.3325, found 677.3331.

NHC **1.13** was prepared by a procedure adapted from that reported by K. Hirano, S. Urban, C. Wang, F. Glorius, *Org. Lett.* **2009**, *11*, 1019 – 1022. **^{1}H (300 MHz, C_6D_6)** δ 7.14-7.49 (m, 8H), 6.90-7.09 (m, 3H), 6.36 (s, 1H), 3.09-3.36 (m, 4H), 1.45 (d, *J* = 6.8 Hz, 6H), 1.43 (d, *J* = 6.8 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 6H), 1.11 (d, *J* = 6.8 Hz, 6H); **^{13}C (75 MHz, C_6D_6)** δ 222.3 (C_{carb}), 146.8 (C^q), 146.6 (C^q), 130.3 (C^q), 129.5 (CH_{ar}), 129.4 (CH_{ar}), 124.3 (CH_{ar}), 124.1 (CH_{ar}), 120.4 (CH_{ar}), 78.2 (*C*H), 29.4 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$).

N,N'-bis-(2,6-diisopropylphenyl)-2-benzoyl-4-phenylimidazolium chloride.

Benzoyl chloride (61 µL, 0.530 mmol) was added at room temperature to a solution of NHC **1.13** (247 mg, 0.530 mmol) in hexanes (20 mL). A white precipitate appeared instantaneously. The suspension was stirred for 1 hour. The solid was allowed to decant. Filtration of the solvent followed by drying under vacuum afforded the title compound as a white powder (316 mg, 99 % yield). **m.p.** 278°C decomp; **^{1}H (300 MHz, $CDCl_3$)** δ 10.04 (s, 1H), 7.55-7.67 (m, 7H), 7.22-7.43 (m, 7H), 7.15-7.19 (m, 2H), 2.58-2.74 (m, 4H), 1.44 (d, *J* = 6.5 Hz, 6H), 1.29 (d, *J* = 6.5 Hz, 6H), 1.10 (d, *J* = 6.5 Hz, 6H), 0.92 (d, *J* = 6.5 Hz, 6H); **^{13}C (75 MHz, $CDCl_3$)** δ 179.2 (*C*O), 145.3 (C^q), 144.9 (C^q), 141.5 (C^q), 136.7 (CH_{ar}), 133.5 (C^q), 133.0 (C^q), 132.7 (CH_{ar}), 132.6 (CH_{ar}), 131.1 (CH_{ar}), 129.6 (CH_{ar}), 129.4 (CH_{ar}), 129.1 (C^q), 128.8 (CH_{ar}), 128.5 (C^q), 125.8 (CH_{ar}), 125.4 (CH_{ar}), 125.2 (CH_{ar}), 123.9 (C^q), 29.8 ($CH(CH_3)_2$), 29.5 ($CH(CH_3)_2$), 27.1 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 22.2 ($CH(CH_3)_2$); **HRMS**: m/z calculated for $C_{40}H_{45}N_2O^+$ 569.3526, found 569.3530.

N,N'-bis-(2,6-diisopropylphenyl)-2-(4-(2,3,5,6-tetrafluoropyridine))-4-phenylimidazolium chloride.

A solution of pentafluoropyridine (50 µL, 0.33 mmol) in ether (2.5 mL) was added at −78°C to a solution of NHC **1.13** (215 mg, 0.33 mmol) in ether (5 mL). A brown precipitate appeared instantaneously. The suspension was stirred for 30 minutes at −78°C. A solution of trimethylsilylchloride (60 µL, 0.33 mmol) in ether (2.5 mL) was added at −78°C. The precipitate turned white. The solid was allowed to decant. Filtration of the solvent followed by drying under vacuum afforded the title compound as a white solid **(**170 mg, 84 % yield). **m.p.** 244°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 10.4 (s, 1H), 7.27-7.32 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.91-7.04 (m, 7H), 2.12 (sept, *J* = 6.5 Hz, 2H), 2.07 (sept, *J* = 6.5 Hz, 2H), 1.07 (d, *J* = 6.5 Hz, 6H), 0.80 (d, *J* = 6.5 Hz, 6H), 0.68 (d, *J* = 6.5 Hz, 6H), 0.42 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 145.3 (C^q), 145.2 (C^q), 143.8 (dm, $^1J_{(C-F)}$ = 248 Hz, CF_{ar}), 140.1 (C^q), 139.3 (dd, $^1J_{(C-F)}$ = 268 Hz, $^2J_{(C-F)}$ = 37 Hz, CF_{ar}), 133.5 (CH_{ar}), 132.9 (CH_{ar}), 131.9 (C^q), 131.3 (CH_{ar}), 129.6 (CH_{ar}), 128.8

(CH_{ar}), 128.7 (CH_{ar}), 128.4 (C^q), 127.7 (C^q), 126.6 (CH_{ar}), 125.2 (CH_{ar}), 124.0 (C^q), 116.6 (C^q), 114.9 (t, $^2J_{(C-F)}$ = 13 Hz, C^q), 29.6 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 27.0 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 22.2 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −84.6-−84.9 (m, 2F), −133.9-−134.3 (m, 2F). **HRMS**: m/z calculated for $C_{41}H_{43}F_6N_2^+$ 677.3325, found 677.3331.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-(1-pyrrolidino)phenyl)-2-phenylimidazol-5-ylidene ***1.7a*** and *1-(2,6-diisopropylphenyl)-5-isopropyl-9,9-dimethyl-9a-phenyl-2-(4-(pyrrolidin-1-yl)phenyl)-9,9a-dihydro-1H-imidazo[1,2-a]indole* ***1.8.***

From **1.5a** (200 mg), **1.7a** can be observed at −78°C by ^{1}H NMR as a 50/50 mixture with the rearranged product **1.8**. **1.7a**: **^{1}H (500 MHz, C_6D_6)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.11-7.18 (m, 2H), 7.02-7.07 (m, 2H), 6.91-6.98 (m, 4H), 6.53-6.62 (m, 3H), 6.30 (d, *J* = 8.5 Hz, 2H), 3.20 (br s, 2H), 2.94 (br s, 2H), 2.68-2.74 (m, 4H), 1.34 (d, *J* = 7.0 Hz, 6H), 1.28-1.32 (m, 4H), 0.95 (d, *J* = 7.0 Hz, 6H), 0.90 (d, *J* = 7.0 Hz, 6H), 0.75 (d, *J* = 7.0 Hz, 6H). Product **1.8** was obtained quantitatively after 5 minutes in benzene at room temperature. **1.8**: **m.p.** 45°C decomp; **^{1}H (300 MHz, C_6D_6)** δ 7.24-7.32 (m, 5H), 7.13-7.20 (m, 3H), 6.98-7.05 (m, 2H), 6.83-6.93 (m, 3H), 6.58 (s, 1H), 6.37 (d, *J* = 8.8 Hz, 2H), 4.62 (sept, *J* = 6.8 Hz, 1H), 3.89 (sept, *J* = 6.8 Hz, 1H), 3.76 (sept, *J* = 6.8 Hz, 1H), 2.78-2.92 (m, 4H), 2.26 (s, 3H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.53 (d, *J* = 6.8 Hz, 3H), 1.50 (d, *J* = 6.8 Hz, 6H), 1.49 (s, 3H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.27 (br s, 4H), 0.44 (d, *J* = 6.8 Hz, 3H); **^{13}C (75 MHz, C_6D_6)** δ 152.7 (C^q), 151.2 (C^q), 147.5 (C^q), 145.8 (C^q), 143.8 (C^q), 141.6 (C^q), 138.2 (C^q), 136.7 (C^q), 127.3 (CH_{ar}), 126.8 (CH_{ar}), 126.0 (C^q), 125.3 (CH_{ar}), 124.2 (CH_{ar}), 121.1 (CH_{ar}), 118.9 (CH_{ar}), 111.9 (*C*H), 103.8 (C^q), 55.3 (CH_3), 47.6 (NCH_2), 30.9 (CH_3), 29.0 ($CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 25.8 (CH_3), 25.7 (CH_2), 25.5 (CH_3), 25.4 (CH_3), 24.5 (CH_3), 24.4 (CH_3), 24.1 (CH_3), 24.0 (CH_3).

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-methoxyphenyl)-2-phenylimidazol-5-ylidene ***1.7b****.*

From **1.5b** (80 mg), **1.7b** was obtained as a brown foam (45 mg, 63% yield). **m.p.** 56°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.74-7.79 (m, 2H), 7.01-7.17 (m, 3H), 6.85-6.94 (m, 4H), 6.47-6.63 (m, 6H), 3.21 (sept, *J* = 6.5 Hz, 2H), 3.08 (s, 3H), 2.83 (sept, *J* = 6.5 Hz, 2H), 1.30 (d, *J* = 6.5 Hz, 6H), 0.91 (d, *J* = 6.5 Hz, 6H), 0.79 (d, *J* = 6.5 Hz, 6H), 0.69 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 200.2 (C_{carb}), 159.1 (C^q), 146.1 (C^q), 145.4 (C^q), 144.9 (C^q), 141.4 (C^q), 134.4 (C^q), 130.8 (CH_{ar}), 129.8 (CH_{ar}), 129.7 (CH_{ar}), 129.4 (CH_{ar}), 125.5 (CH_{ar}), 125.4 (C^q), 124.4 (CH_{ar}), 114.0 (CH_{ar}), 55.0 (OCH_3), 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$).

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-methylphenyl)-2-phenylimidazol-5-ylidene ***1.7c****.*

From **1.5c** (300 mg), **1.7c** was obtained as an ochre foam (255 mg, 85% yield). **m.p.** 42°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.10-7.17 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.88-6.95 (m, 4H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.52-6.60 (m, 3H), 3.14 (sept, *J* = 7.0 Hz, 2H), 2.85 (sept, *J* = 7.0 Hz, 2H), 1.92 (s, 3H), 1.32 (d, *J* = 7.0 Hz, 6H), 0.94 (d, *J* = 7.0 Hz, 6H), 0.81 (d, *J* = 7.0 Hz, 6H), 0.72(d, *J* = 7.0 Hz, 6H); **^{13}C (125**

MHz, C_6D_6) δ 200.0 (C_{carb}), 146.0 (C^q), 145.4 (C^q), 145.1 (C^q), 141.5 (C^q), 135.7 (C^q), 134.3 (C^q), 130.8 (CH_{ar}), 129.7 (CH_{ar}), 129.4 (CH_{ar}), 129.1 (CH_{ar}), 128.7 (CH_{ar}), 128.5 (CH_{ar}), 126.7 (C^q), 125.5 (CH_{ar}), 124.4 (CH_{ar}), 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$), 21.4 (CH_3).

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-chlorophenyl)-2-phenylimidazol-5-ylidene ***1.7e***.

From **1.5e** (200 mg), **1.7e** was obtained as a green foam (149 mg, 84% yield). **m.p.** 57°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.61-7.68 (m, 2H), 7.05-7.16 (m, 3H), 6.97-7.03 (m, 2H), 6.82-6.93 (m, 5H), 6.50-6.58 (m, 3H), 3.06 (sept, *J* = 7.0 Hz, 2H), 2.74 (sept, *J* = 7.0Hz, 2H), 1.30 (d, *J* = 7.0 Hz, 6H), 0.91 (d, *J* = 7.0 Hz, 6H), 0.73 (d, *J* = 7.0 Hz, 6H), 0.68 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 201.3 (C_{carb}), 145.9 (C^q), 145.7 (C^q), 145.2 (C^q), 140.6 (C^q), 139.7 (C^q), 134.7 (C^q), 133.9 (C^q), 132.3 (C^q), 131.0 (CH_{ar}), 129.7 (CH_{ar}), 129.6 (CH_{ar}), 129.4 (CH_{ar}), 129.3 (CH_{ar}), 128.6 (CH_{ar}), 128.4 (CH_{ar}), 126.4 (C^q), 125.6 (CH_{ar}), 124.5 (CH_{ar}), 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$).

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-bromophenyl)-2-phenylimidazol-5-ylidene ***1.7f***.

From **1.5f** (200 mg), **1.7f** was obtained as a yellow foam (73 mg, 41% yield). **m.p.** 52°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.59-7.67 (m, 2H), 6.81-7.16 (m, 11H), 6.49-6.58 (2H), 3.09 (sept, *J* = 7.0 Hz, 2H), 2.76 (sept, *J* = 6.5 Hz, 2H), 1.30 (d, *J* = 6.5 Hz, 6H), 0.93 (d, *J* = 7.0 Hz, 6H), 0.74 (d, *J* = 6.5 Hz, 6H), 0.68 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 202.9 (C_{carb}), 145.9 (C^q), 145.8 (C^q), 145.3 (C^q), 140.5 (C^q), 139.8 (C^q), 135.3 (C^q), 134.1 (C^q), 131.5 (CH_{ar}), 131.0 (CH_{ar}), 129.7 (CH_{ar}), 129.5 (CH_{ar}), 129.3 (CH_{ar}), 128.4 (CH_{ar}), 126.5 (C^q), 125.6 (CH_{ar}), 124.4 (CH_{ar}), 120.4, 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$).

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-fluorophenyl)-2-phenylimidazol-5-ylidene ***1.7g***.

From **1.5g** (200 mg), **1.7g** was obtained as an ochre foam (172 mg, 97% yield). **m.p.** 65°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.56-7.63 (m, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.75-6.82 (m, 4H), 6.42-6.51 (m, 5H), 2.99 (sept, *J* = 7.0 Hz, 2H), 2.66 (sept, *J* = 7.0 Hz, 2H), 1.18 (d, *J* = 7.0 Hz, 6H), 0.82 (d, *J* = 7.0 Hz, 6H), 0.62 (d, *J* = 7.0 Hz, 6H), 0.58 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 200.1 (C_{carb}), 162.4 (d, $^1J_{(C-F)}$ = 244 Hz, C^q), 145.9 (C^q), 145.6 (C^q), 145.3 (C^q), 140.5 (C^q), 139.8 (C^q), 134.0 (C^q), 132.4 (C^q), 131.1 (CH_{ar}), 130.0 (d, $^3J_{(C-F)}$ = 8 Hz, CH_{ar}), 129.7 (CH_{ar}), 129.5 (CH_{ar}), 129.4 (CH_{ar}), 128.9 (CH_{ar}), 128.7 (CH_{ar}), 128.4 (CH_{ar}), 126.5 (C^q), 125.6 (CH_{ar}), 124.4 (CH_{ar}), 115.2 (d, $^2J_{(C-F)}$ = 21 Hz, CH_{ar}), 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$); **^{19}F (282 MHz, C_6D_6)** δ −118.4.

N,N'-bis-(2,6-diisopropylphenyl)-4-(4-trifluoromethylphenyl)-2-phenylimidazol-5-ylidene ***1.7h***.

From **1.5h** (200 mg), **1.7h** was obtained as a green foam (95 mg, 54% yield). **m.p.** 61°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.12-7.22 (m, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.90-6.98 (m, 3H), 6.57-6.63 (m, 4H), 3.13 (sept, *J* = 7.0 Hz, 2H), 2.79 (sept, *J* = 7.0 Hz, 2H), 1.36 (d, *J* = 7.0 Hz, 6H), 0.98 (d, *J* = 7.0 Hz, 6H), 0.76 (d, *J* = 7.0 Hz, 6H), 0.74 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 204.9 (C_{carb}), 146.3 (C^q), 145.9 (C^q), 145.3 (C^q), 140.2 (C^q), 139.9 (C^q), 139.6 (C^q), 133.9 (C^q), 131.1 (q, $^{2}J_{(C-F)}$ = 35 Hz, C^q), 131.2 (CH_{ar}), 129.7 (CH_{ar}), 129.6 (CH_{ar}), 127.8 (CH_{ar}), 125.7 (CH_{ar}), 125.3 (CH_{ar}), 124.5 (CH_{ar}), 124.5 (q, $^{1}J_{(C-F)}$ = 274 Hz, C^q), 29.7 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$); **^{19}F (282 MHz, C_6D_6)** δ −63.3.

*N,N'-bis-(2,6-diisopropylphenyl)-4-(3,5-bistrifluoromethylphenyl)-2-phenylimidazol-5-ylidene **1.7i**.*

From **1.5i** (200 mg), **1.7i** was obtained as an ochre foam (44 mg, 24% yield). **m.p.** 54°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 8.32 (s, 2H), 7.47 (s, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.90-6.95 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.48-6.58 (m, 3H), 3.04 (sept, *J* = 7.0Hz, 2H), 2.70 (sept, *J* = 7.0Hz, 2H), 1.25 (d, *J* = 7.0 Hz, 6H), 0.89 (d, *J* = 7.0 Hz, 6H), 0.72 (d, *J* = 7.0 Hz, 6H), 0.67 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 205.8 (C_{carb}), 146.9 (C^q), 145.7 (C^q), 145.2 (C^q), 139.3 (C^q), 138.9 (C^q), 138.6 (C^q), 133.3 (C^q), 131.7 (q, $^{2}J_{(C-F)}$ = 33 Hz, C^q), 131.5 (CH_{ar}), 129.9 (CH_{ar}), 129.7 (CH_{ar}), 129.6 (CH_{ar}), 128.7 (CH_{ar}), 128.5 (CH_{ar}), 127.2 (CH_{ar}), 125.9 (CH_{ar}), 124.6 (CH_{ar}), 124.5 (q, $^{1}J_{(C-F)}$ = 272 Hz, C^q), 119.0 (CH_{ar}), 29.6 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$); **^{19}F (282 MHz, C_6D_6)** δ −64.4.

*N,N'-bis-(2,6-diisopropylphenyl)-2-(3,5-bistrifluoromethylphenyl)-4-phenylimidazol-5-ylidene **1.12b**.*

From the corresponding imidazolium salt (200 mg), the title compound was obtained as an ochre foam (88 mg, 48% yield). **m.p.** 71°C decomp; **^{1}H (500 MHz, C_6D_6)** δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 2H), 7.21 (s, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 2H), 6.75-6.82 (m, 3H), 2.95 (sept, *J* = 7.0 Hz, 2H), 2.65 (sept, *J* = 7.0 Hz, 2H), 1.21 (d, *J* = 7.0 Hz, 6H), 0.82 (d, *J* = 7.0 Hz, 6H), 0.65 (d, *J* = 7.0 Hz, 6H), 0.57 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, C_6D_6)** δ 202.9 (C_{carb}), 145.5 (C^q), 145.0 (C^q), 143.1 (C^q), 142.0 (C^q), 138.7 (C^q), 135.1 (C^q), 133.2 (C^q), 132.1 (q, $^{2}J_{(C-F)}$ = 33 Hz, C^q), 131.6 (CH_{ar}), 130.3 (CH_{ar}), 129.6 (CH_{ar}), 128.8 (CH_{ar}), 128.7 (CH_{ar}), 127.3 (CH_{ar}), 126.0 (CH_{ar}), 124.9 (CH_{ar}), 123.4 (q, $^{1}J_{(C-F)}$ = 272 Hz, C^q), 121.7 (CH_{ar}), 29.5 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 23.3 ($CH(CH_3)_2$), 22.4 ($CH(CH_3)_2$); **^{19}F (282 MHz, C_6D_6)** δ −63.6.

*chloro-MIC(4-(4-pyrrolidino))-Iridium(I)-cis-dicarbonyl complex **1.9a**.*

From **1.5a** (98 mg), **1.9a** was obtained as a yellow solid (128 mg, 89% yield). **m.p.** 255°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.40 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.16-7.21 (m, 4H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 8.0 Hz, 2H), 3.12-3.19 (m, 4H), 2.90 (sept,

J = 6.5 Hz, 2H), 2.51 (sept, *J* = 6.5 Hz, 2H), 1.85-1.92 (m, 4H), 1.46 (d, *J* = 6.5 Hz, 6H), 0.79 (d, *J* = 6.5 Hz, 6H), 0.64-0.74 (m, 12H); **^{13}C (125 MHz, $CDCl_3$)** δ 182.3 (*C*O), 169.9 (*C*O), 157.8 (*C*Ir), 147.7 (C^q), 145.6 (C^q), 145.4 (C^q), 143.6 (C^q), 143.1 (C^q), 135.5 (C^q), 132.9 (CH_{ar}), 131.7 (C^q), 131.0 (CH_{ar}), 130.5 (CH_{ar}), 130.2 (CH_{ar}), 130.0 (CH_{ar}), 128.3 (CH_{ar}), 125.3 (CH_{ar}), 125.2 (CH_{ar}), 124.2 (C^q), 117.2 (C^q), 110.6 (CH_{ar}), 47.6 (NCH_2), 29.0 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 25.6 (CH_2), 24.2 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$); **I.R. (CH_2Cl_2)** ν cm^{-1} 2048.9 and 1966.3 (CO).

*chloro-MIC(4-(4-methoxy))-Iridium(I)-cis-dicarbonyl complex **1.9b**.*

From **1.7b** (45 mg), **1.9b** was obtained as a yellow solid (38 mg, 57% yield). **m.p.** 251°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.43 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 2H, 7.17-7.24 (m, 2H), 7.09-7.14 (m, 3H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 3.71 (s, 3H), 2.89 (sept, *J* = 6.5 Hz, 2H), 2.49 (sept, *J* = 6.5 Hz, 2H), 1.47 (d, *J* = 6.5 Hz, 6H), 0.78 (d, *J* = 6.5 Hz, 6H), 0.72 (d, *J* = 6.5 Hz, 6H), 0.71 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.9 (*C*O), 169.6 (*C*O), 159.7 (*C*Ir), 158.9 (C^q), 145.6 (C^q), 145.3 (C^q), 144.2 (C^q), 142.0 (C^q), 135.4 (C^q), 133.3 (CH_{ar}), 131.4 (C^q), 131.3 (CH_{ar}), 130.7 (CH_{ar}), 130.5 (CH_{ar}), 130.0 (CH_{ar}), 128.4 (CH_{ar}), 125.5 (CH_{ar}), 125.3 (CH_{ar}), 124.1 (C^q), 123.0 (C^q), 113.0 (CH_{ar}), 55.3 (OCH_3), 29.1 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$); **I.R. (CH_2Cl_2)** ν cm^{-1} 2053.2 and 1968.6.

*chloro-MIC(4-(4-methyl))-Iridium(I)-cis-dicarbonyl complex **1.9c**.*

From **1.7c** (225 mg), **1.9c** was obtained as a yellow solid (262 mg, 77% yield). **m.p.** 231°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.41 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.16-7.21 (m, 2H), 7.07-7.12 (m, 3H), 6.94 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 2.87 (sept, *J* = 7.0 Hz, 2H), 2.47 (sept, *J* = 6.5 Hz, 2H), 2.18 (s, 3H), 1.45 (d, *J* = 7.0 Hz, 6H), 0.73 (d, *J* = 7.0 Hz, 6H), 0.66-0.71 (m, 12H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.9 (*C*O), 169.6 (*C*O), 159.2 (*C*Ir), 145.6 (C^q), 145.3 (C^q), 144.4 (C^q), 142.3 (C^q), 138.2 (C^q), 135.4 (C^q), 131.8 (CH_{ar}), 131.4 (C^q), 131.3 (CH_{ar}), 130.7 (CH_{ar}), 130.6 (CH_{ar}), 130.0 (CH_{ar}), 128.4 (CH_{ar}), 128.3 (CH_{ar}), 127.6 (C^q), 125.5 (CH_{ar}), 125.3 (CH_{ar}), 124.0 (C^q), 29.1 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 21.5 (CH_3); **I.R. (CH_2Cl_2)** ν cm^{-1} 2051.3 and 1968.2 (CO).

*chloro-MIC(4-(4-H))-Iridium(I)-cis-dicarbonyl complex **1.9d**.*

From **1.7d** (100 mg), **1.9d** was obtained as a yellow solid (120 mg, 79% yield). **m.p.** 242°C decomp; **^{1}H (300 MHz, $CDCl_3$)** δ 7.46-7.50 (m, 4H), 7.17-7.29 (m, 8H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 2H), 2.96 (sept, *J* = 6.7 Hz, 2H), 2.57 (sept, *J* = 6.7 Hz, 2H), 1.54 (d, *J* = 6.7 Hz, 6H), 0.77-0.83 (m, 18H); **^{13}C (75 MHz, $CDCl_3$)** δ 181.8 (*C*O), 169.5 (*C*O), 159.6 (*C*Ir), 145.5 (C^q), 145.2 (C^q), 144.6 (C^q), 142.1 (C^q), 135.4 (C^q), 132.0 (CH_{ar}), 131.4 (CH_{ar}), 131.2 (C^q), 130.8 (CH_{ar}), 130.7 (CH_{ar}), 130.5 (C^q), 130.0 (CH_{ar}), 128.4 (CH_{ar}), 127.5 (CH_{ar}), 125.5 (CH_{ar}), 125.3 (CH_{ar}), 123.9 (C^q), 29.1

(*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$); **I.R. (CH_2Cl_2)** ν cm^{-1} 2051.6 and 1968.3 (CO).

*chloro-MIC(4-(4-chloro))-Iridium(I)-cis-dicarbonyl complex **1.9e***.

From **1.7e** (149 mg), **1.9e** was obtained as a yellow solid (256 mg, 77% yield). **m.p.** 242°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.35 (t, *J* = 8.0 Hz, 2H), 7.25-7.31 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.97-7.09 (m, 5H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 2.71-2.84 (br sept, 2H), 2.38 (sept, *J* = 6.5 Hz, 2H), 1.37 (d, *J* = 6.5 Hz, 6H), 0.69 (d, *J* = 6.5 Hz, 6H), 0.65 (d, *J* = 7.0 Hz, 6H), 0.63 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.6 (*C*O), 169.4 (*C*O), 160.2 (*C*Ir), 145.4 (*C*^{q}), 145.2 (*C*^{q}), 144.9 (*C*^{q}), 140.9 (*C*^{q}), 135.3 (*C*^{q}), 134.4 (*C*^{q}), 133.0 (*C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 131.0 (*C*^{q}), 130.9 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 129.1 (*C*^{q}), 128.5 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 125.7 (*C*H$_{ar}$), 125.4 (*C*H$_{ar}$), 123.7 (*C*^{q}), 29.1 (*C*H(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$); **I.R. (CH_2Cl_2)** ν cm^{-1} 2053.2 and 1969.9 (CO).

*chloro-MIC(4-(4-bromo))-Iridium(I)-cis-dicarbonyl complex **1.9f***.

From **1.7f** (73 mg), **1.9f** was obtained as a yellow solid (85 mg, 80% yield). **m.p.** 230°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.35 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.19-7.23 (m, 2H), 7.14-7.18 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 2.71-2.82 (br sept, 2H), 2.37 (sept, *J* = 6.5 Hz, 2H), 1.37 (d, *J* = 6.5 Hz, 6H), 0.69 (d, *J* = 6.5 Hz, 6H), 0.64 (d, *J* = 7.0 Hz, 6H), 0.62 (d, *J* = 7.0 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.6 (*C*O), 169.4 (*C*O), 160.3 (*C*Ir), 145.5 (*C*^{q}), 145.2 (*C*^{q}), 144.9 (*C*^{q}), 141.0 (*C*^{q}), 135.4 (*C*^{q}), 133.3 (*C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 131.1 (*C*^{q}), 130.9 (*C*H$_{ar}$), 130.8 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 129.6 (*C*^{q}), 128.5 (*C*H$_{ar}$), 125.7 (*C*H$_{ar}$), 125.4 (*C*H$_{ar}$), 123.8 (*C*^{q}), 122.9 (*C*^{q}), 29.2 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$); **I.R. (CH_2Cl_2)** ν cm^{-1} 2053.1 and 1970.0 (CO).

*chloro-MIC(4-(4-fluoro))-Iridium(I)-cis-dicarbonyl complex **1.9g***.

From **1.7g** (172 mg), **1.9g** was obtained as a yellow solid (170 mg, 65% yield). Single crystals were obtained from a saturated chloroform solution at −20°C. **m.p.** 265°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.37-7.48 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.11-7.17 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.82 (t, *J* = 8.5 Hz, 2H), 2.83-2.93 (br sept, 2H), 2.48 (sept, *J* = 6.5 Hz, 2H), 1.46 (d, *J* = 7.0 Hz, 6H), 0.78 (d, *J* = 6.5 Hz, 6H), 0.73 (d, *J* = 7.0 Hz, 6H), 0.72 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.6 (*C*O), 169.4 (*C*O), 162.7 (d, $^1J_{(C\text{-}F)}$ = 252 Hz, *C*^{q}), 159.7 (*C*Ir), 145.5 (*C*^{q}), 145.2 (*C*^{q}), 144.7 (*C*^{q}), 141.1 (*C*^{q}), 135.3 (*C*^{q}), 133.7 (d, $^3J_{(C\text{-}F)}$ = 6 Hz, *C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 131.0 (*C*^{q}), 130.8 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 126.8 (*C*^{q}), 125.6 (*C*H$_{ar}$), 125.3 (*C*H$_{ar}$), 123.8 (*C*^{q}), 114.6 (d, $^2J_{(C\text{-}F)}$ = 21 Hz, *C*H$_{ar}$), 29.1 (*C*H(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −114.2; **I.R. (CH_2Cl_2)** ν cm^{-1} 2054.7 and 1970.9 (CO).

*chloro-MIC(4-(4-trifluoromethyl))-Iridium(I)-cis-dicarbonyl complex **1.9h***.

From **1.7h** (95 mg), **1.9h** was obtained as a yellow solid (71 mg, 51% yield). **m.p.** 228°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.19-7.31 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.93 (br s, 2H), 2.53 (sept, *J* = 6.5 Hz, 2H), 1.52 (d, *J* = 7.0 Hz, 6H), 0.75-0.83 (m, 18H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.4 (*C*O), 169.3 (*C*O), 161.3 (*C*Ir), 145.5 (C^q), 145.2 (C^q), 140.7 (C^q), 135.3 (C^q), 134.2 (C^q), 132.0 (CH_{ar}), 131.8 (CH_{ar}) 130.9 (CH_{ar}), 130.1 (CH_{ar}), 130.0 (q, $^{2}J_{(C-F)}$ = 32 Hz, C^q), 129.2 (C^q), 128.5 (CH_{ar}), 125.8 (CH_{ar}), 125.4 (CH_{ar}), 124.5 (CH_{ar}), 124.2 (q, $^{1}J_{(C-F)}$ = 270 Hz, C^q), 123.7 (C^q), 29.1 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −64.1; **I.R. (CH_2Cl_2)** ν cm^{-1} 2054.2 and 1970.81 (CO).

*chloro-MIC(4-(3,5-bistrifluoromethyl))-Iridium(I)-cis-dicarbonyl complex **1.9i**.*

From **1.7i** (44 mg), **1.9i** was obtained as a yellow solid (25 mg, 42% yield). **m.p.** 247°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.95 (s, 2H), 7.66 (s, 1H), 7.44-7.51 (m, 2H), 7.16-7.26 (m, 5H), 7.03 (t, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 2.86 (br s, 2H), 2.45 (sept, *J* = 7.0 Hz, 2H), 1.45 (d, *J* = 7.0 Hz, 6H), 0.69-0.78 (m, 18H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.0 (*C*O), 169.0 (*C*O), 162.9 (*C*Ir), 145.4 (C^q), 145.1 (C^q), 139.4 (C^q), 135.3 (C^q), 132.9 (C^q), 132.1 (CH_{ar}), 131.6 (CH_{ar}), 131.2 (CH_{ar}), 131.1 (CH_{ar}), 130.6 (q, $^{2}J_{(C-F)}$ = 31 Hz, C^q), 130.4 (C^q), 130.1 (CH_{ar}), 128.7 (CH_{ar}), 126.0 (CH_{ar}), 125.5 (CH_{ar}), 123.5 (C^q), 123.3 (q, $^{1}J_{(C-F)}$ = 274 Hz, C^q), 121.6 (CH_{ar}), 29.2 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.7 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −64.6; **I.R. (CH_2Cl_2)** ν cm^{-1} 2057.4 and 1973.4 (CO).

chloro-MIC(2-(3,5-bistrifluoromethyl))-Iridium(I)-cis-dicarbonyl complex.

From **1.12b** (88 mg), the title complex was obtained as a yellow solid (67 mg, 51% yield). **m.p.** 214°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.56 (s, 1H), 744-7.53 (m, 4H), 7.13-7.30 (m, 9H), 2.89 (sept, *J* = 6.5 Hz, 2H), 2.43 (sept, *J* = 6.5 Hz, 2H), 1.45 (d, *J* = 6.5 Hz, 6H), 0.78 (d, *J* = 6.5 Hz, 6H), 0.68 (d, *J* = 6.5 Hz, 6H), 0.66 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.4 (*C*O), 169.4 (*C*O), 161.5 (*C*Ir), 145.2 (C^q), 144.9 (C^q), 143.2 (C^q), 140.7 (C^q), 134.5 (C^q), 132.2 (CH_{ar}), 132.2 (q, $^{2}J_{(C-F)}$ = 33 Hz, C^q), 131.9 (CH_{ar}), 131.6 (CH_{ar}), 130.4 (C^q), 129.9 (CH_{ar}), 129.7 (C^q), 129.0 (CH_{ar}), 127.8 (CH_{ar}), 126.1 (CH_{ar}), 126.0 (C^q), 125.9 (CH_{ar}), 123.1 (q, $^{1}J_{(C-F)}$ = 270 Hz, C^q), 122.3 (CH_{ar}), 29.1 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −65.0; **I.R. (CH_2Cl_2)** ν cm^{-1} 2054.8 and 1971.6 (CO).

chloro-MIC(2-benzoyl)-Iridium(I)-cis-dicarbonyl complex.

From the corresponding imidazolium salt (240 mg), the title complex was obtained as a yellow solid (279 mg, 82% yield). **m.p.** 224°C decomp; **^{1}H (500 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.03-7.18 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.75 (sept, *J* = 6.5 Hz, 2H), 2.51 (sept, *J* = 6.5 Hz, 2H), 1.44 (d, *J* = 6.5 Hz, 6H), 1.04 (d, *J* = 6.5 Hz, 6H), 0.97 (d, *J* = 6.5 Hz, 6H), 0.60 (d, *J* = 6.5 Hz, 6H); **^{13}C (125 MHz, $CDCl_3$)** δ 181.3 (Ir*C*O), 180.3 (*C*O), 169.1

(Ir*C*O), 164.8 (*C*Ir), 145.3 (C^q), 144.9 (C^q), 143.7 (C^q), 142.7 (C^q), 135.3 (C^q), 134.9 (C^q), 134.5 (CH_{ar}), 131.9 (CH_{ar}), 131.5 (CH_{ar}), 130.6 (CH_{ar}), 130.4 (C^q), 129.8 (C^q), 129.6 (CH_{ar}), 129.1 (CH_{ar}), 128.7 (CH_{ar}), 128.2 (C^q), 128.0 (C^q), 127.7 (CH_{ar}), 125.4 (CH_{ar}), 124.8 (CH_{ar}), 29.3 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). **I.R. (CH_2Cl_2)** ν cm^{-1} 2054.7 (CO), 1971.7 (CO).

chloro-MIC(2-(4-(2,3,5,6-tetrafluoropyridine)))-Iridium(I)-cis-dicarbonyl complex.

From the corresponding imidazolium salt (170 mg), the title complex was obtained as a yellow solid (179 mg, 74% yield). **m.p.** 222°C decomp. **^{1}H (500 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.17-7.22 (m, 3H), 7.07-7.14 (m, 4H), 2.69 (br s, 2H), 2.45 (sept, *J* = 6.5 Hz, 2H), 0.91-1.02 (m, 12H), 0.72-0.84 (m, 12H). **^{13}C (125 MHz, $CDCl_3$)** δ 180.7 (*C*O), 168.9 (*C*O), 165.7 (*C*Ir), 146.0 (C^q), 145.8 (C^q), 144.0 (dm, $^1J_{(C-F)}$ = 247 Hz, *C*F_{ar}), 139.5 (dd, $^1J_{(C-F)}$ = 272 Hz, $^2J_{(C-F)}$ = 27 Hz, *C*F_{ar}), 133.6 (C^q), 132.4 (C^q), 132.1 (CH_{ar}), 131.9 (CH_{ar}), 131.4 (CH_{ar}), 128.9 (C^q), 129.3 (CH_{ar}), 129.2 (C^q), 128.6 (C^q), 127.8 (CH_{ar}), 125.9 (CH_{ar}), 125.8 (CH_{ar}), 117.8 (t, $^2J_{(C-F)}$ = 17 Hz, C^q), 29.0 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$); **^{19}F (282 MHz, $CDCl_3$)** δ −87.0-−87.2 (m, 2F), −132.5-−132.8 (m, 2F); **I.R. (CH_2Cl_2)** ν cm^{-1} 2054.8 and 1971.6 (CO).

4) Crystallographic Data

Crystal data and structure refinement for 1.9g.

Identification code	1.9g	
Empirical formula	$C_{82}H_{87}Cl_2F_2Ir_2N_4O_4$	
Formula weight	1685.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.4177(11) Å	α= 110.8870(10)°
	b = 17.9554(15) Å	β= 101.3940(10)°
	c = 18.2012(16) Å	γ = 90.0400(10)°
Volume	4004.0(6) $Å^3$	
Z	2	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	3.440 mm^{-1}	
F(000)	1690	
Crystal size	0.32 x 0.17 x 0.10 mm^3	
Theta range for data collection	1.90 to 22.01°	
Index ranges	-14<=h<=13, -18<=k<=17, 0<=l<=19	
Reflections collected	9604	
Independent reflections	9613 [R(int) = 0.0000]	
Completeness to theta = 22.01°	97.9 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.7248 and 0.4057	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9613 / 36 / 882	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1275	

R indices (all data)	R1 = 0.0772, wR2 = 0.1392
Extinction coefficient	0.0008(2)
Largest diff. peak and hole	2.038 and -1.113 e.Å^{-3}

B) Thiazol-5-ylidenes

1) General Information

All manipulations related to the synthesis of thiazolium salts **1.21a-c** were performed under air. For metal complexes, all experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *b* = broad signal. N-phenylbenzothiamide (**1.19a**), N-mesitylbenzothiamide (**1.19b**), and *N*-(2,6-diisopropylphenyl)benzothiamide (**1.19c**) were prepared following the literature procedure, while all other starting materials were purchased from commercial sources.

2) Synthesis and Characterization

*2-Oxo-2-phenylethyl-N-phenylbenzimidothioate **1.20a**.*

Triethylamine (1.30 g, 12.9 mmol) was added dropwise to a solution of N-phenylbenzothiamide (**1.19a**) (2.50 g, 11.7 mmol) and phenacyl bromide (2.33 g, 11.7 mmol) in 100 mL of acetonitrile. The resulting solution was stirred for 20 h at room temperature. The final yellow solution was cooled down to 0 °C and 50 mL of diethyl ether (Et_2O) was added to precipitate the ammonium salt. The mixture was filtered and the filtrate dried under vacuum, and further extracted with a mixture of toluene/hexane (1:1). The suspension obtained was then filtered and the filtrate was vacuum dried to yield 2.95 g of **1.20a** as a yellow solid. Yield 76% (8.90 mmol). **m.p.** 80-82 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 4.69 (bs, 2 H, C*H*$_2$), 6.63 (bs, 2 H, Ar*H*), 6.94 (bs, 1 H, Ar*H*), 7.13 (bs, 2 H, Ar*H*), 7.19 (bm, 5 H, Ar*H*), 7.48 (bs, 2 H, Ar*H*), 7.59 (bs, 1 H, Ar*H*), 8.10 (bs, 2 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 38.2 (*C*H$_2$), 121.3 (*C*H$_{ar}$), 123.4 (*C*$_{ar}$), 127.3 (*C*$_{ar}$), 129.0 (*C*H$_{ar}$, two signals overlapping), 129.3 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$, three signals overlapping), 131.4 (*C*H$_{ar}$), 133.8 (*C*H$_{ar}$), 135.2 (*C*$_{ar}$), 149.5 (S*C*N), 191.4 (*C*=O).

*2-Oxo-2-phenylethyl-N-(2,4,6-trimethylphenyl)benzimidothioate **1.20b**.*

The procedure described for the preparation of compound **1.20a** was followed using in this case N-mesitylbenzothiamide (**1.19b**). After purification by column chromatography on silica gel (DCM/Hex 1:1), **1.20b** was obtained as a yellow oil. Yield 63% (2.75 g, 7.37 mmol). **^{1}H (300 MHz, $CDCl_3$)** δ 1.96 (bs, 6 H, *o*-C*H*$_3$), 2.18 (bs, 3 H, *p*-C*H*$_3$), 4.67 (bs, 2 H, C*H*$_2$), 6.73 (bs, 2 H, Ar*H*), 7.18-7.38 (bm, 4 H, Ar*H*), 7.45-7.60 (bm, 4 H, Ar*H*), 8.03 (bs, 2 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 18.3 (*o*-*C*H$_3$), 20.8 (*p*-*C*H$_3$), 38.5 (*C*H$_2$), 126.5 (*C*$_{ar}$), 127.4 (*C*$_{ar}$), 128.5 (*C*H$_{ar}$), 128.7 (*C*H$_{ar}$, two signals overlapping), 128.8 (*C*H$_{ar}$, two signals overlapping), 129.4 (*C*$_{ar}$), 130.3 (*C*H$_{ar}$), 131.4 (*C*$_{ar}$), 133.5 (*C*H$_{ar}$), 135.4 (*C*$_{ar}$), 145.2 (S*C*N), 194.0 (*C*=O).

*2-Oxo-2-phenylethyl-N-(2,6-diisopropylphenyl)benzimidothioate **1.20c**.*

The procedure described for the preparation of compound **1.20a** was followed using in this case N-(2,6-diisopropylphenyl) benzothiamide (**1.19c**). After purification by column chromatography on silica gel (DCM/Hex 1:1), **1.20c** was obtained as a yellowish oil. Yield 55% (2.67 g, 6.43 mmol). **^{1}H (300 MHz, $CDCl_3$)** δ 1.04 (bs, 6 H, CH(CH_3)$_2$), 1.17 (bs, 6 H, CH(CH_3)$_2$), 2.91 (bs, 2 H, CH(CH$_3$)$_2$), 4.57 (bs, 2 H, CH_2), 7.08 (bs, 4 H, CH$_{ar}$), 7.27-7.35 (bs, 3 H, CH_{ar}), 7.43-7.49 (bs, 4 H, CH_{ar}), 8.01-8.04 (bs, 2 H, CH_{ar}). **^{13}C (75 MHz, $CDCl_3$)** δ 22.6, 23.4 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 38.6 (*C*H$_2$), 123.1 (*C*H$_{ar}$), 123.9 (*C*H$_{ar}$), 124.0 (*C*$_{ar}$), 126.9 (*C*$_{ar}$), 127.8 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$, two signals overlapping), 128.7 (*C*H$_{ar}$), 130.2 (*C*H$_{ar}$), 131.5 (*C*$_{ar}$), 133.5 (*C*H$_{ar}$), 136.9 (*C*$_{ar}$), 145.1 (S*C*N), 193.5 (*C*=O).

*2,3,4-Triphenylthiazolium bromide **1.21a**.*

Hydrobromic acid (47% in H_2O, 10 mL, 88.9 mmol) was added slowly to a pre-cooled (0 °C) toluene (50 mL) solution of **1.20a** (1.00 g, 3.02 mmol) in acetic anhydride (8.7 g, 85.2 mmol). The resulting yellow mixture was heated at 90 °C for 48 h. The reaction mixture was quenched with 50 mL of water, and the aqueous layer was extracted with 100 mL of dichloromethane (DCM). The organic layer was washed twice with water (50 mL), dried over $MgSO_4$, filtered, and evaporated under vacuum to yield the crude product as a yellow solid. **1.21a** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Yield 60% (0.720 g, 1.82 mmol). **m.p.** 222-224 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 7.23 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.28 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.32-7.36 (m, 6 H, Ar*H*), 7.46 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 7.51-7.54 (m, 4 H, Ar*H*), 8.64 (s, 1 H, CH_{thiaz}). **^{13}C (75 MHz, $CDCl_3$)** δ 125.1 (*C*H$_{thiaz}$), 126.9 (*C*$_{ar}$), 127.7 (*C*$_{ar}$), 128.2 (*C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$), 130.5 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$, two signals overlapping), 131.1 (*C*H$_{ar}$), 133.0 (*C*H$_{ar}$), 135.9 (*C*$_{ar}$), 153.1 (N*C*C), 172.9 (N*C*S).

*3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazolium bromide **1.21b**.*

The procedure described for the preparation of salt **1.21a** was followed using in this case **1.20b**. **1.21b** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Single crystals were obtained by the slow evaporation of a concentrated acetone solution of **1.21b**. Yield 44% (0.579 g, 1.33 mmol). **m.p.** > 273 °C (decomp). **^{1}H (300 MHz, $CDCl_3$)** δ 1.83 (s, 6 H, *o*-CH$_3$), 2.28 (s, 3 H, *p*-CH$_3$), 6.88 (s, 2 H, Ar*H*), 7.10 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.24-7.30 (m, 4 H, Ar*H*), 7.35-7.39 (m, 3 H, Ar*H*), 7.55 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 9.10 (s, 1 H, CH_{thiaz}). **^{13}C (75 MHz, $CDCl_3$)** δ 18.0 (*o*-*C*H$_3$), 21.3 (*p*-*C*H$_3$), 125.7 (*C*$_{ar}$), 126.9 (*C*$_{ar}$), 128.6 (*C*H$_{thiaz}$), 129.0 (*C*H$_{ar}$, two signals overlapping), 130.0 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 131.6 (*C*$_{ar}$), 133.8 (*C*H$_{ar}$), 134.2 (*C*H$_{ar}$), 142.4 (*C*$_{ar}$), 148.0 (N*C*C), 170.4 (N*C*S).

*3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazolium bromide **1.21c**.*

The procedure described for the preparation of salt **1.21a** was followed using in this case **1.20c**. **1.21c** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Yield 42% (0.606 g, 1.27 mmol). **m.p.** 246-248 °C. **^{1}H (300 MHz, $CDCl_3$)** δ

0.71 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.74 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.16 (sept, *J* = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.11 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.22-7.28 (m, 6 H, Ar*H*), 7.35 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.38 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 7.56 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 9.20 (s, 1 H, C*H*$_{thiaz}$). **^{13}C (75 MHz, CDCl$_3$)** δ 23.6, 23.7 (CH(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 126.1 (*C*$_{ar}$), 126.4 (*C*H$_{ar}$), 127.1 (*C*$_{ar}$), 127.8 (*C*H$_{thiaz}$), 129.1 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.7 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 133.1 (*C*H$_{ar}$), 134.0 (*C*H$_{ar}$), 144.6 (*C*$_{ar}$), 148.8 (N*C*C), 171.0 (N*C*S).

2,3,4-Triphenylthiazolium trifluoromethanesulfonate.

DCM (15 mL) was added at room temperature to a Schlenk flask charged with silver trifluoromethanesulfonate (0.326 g, 1.27 mmol) and the thiazolium salt **1.21a** (0.500 g, 1.27 mmol). The reaction mixture was stirred for 4 h. After cannula filtration, the supernatant was dried under vacuum yielding the crude product as a pale yellow solid. The title compound was obtained as a white solid after washing the crude material with Et$_2$O (3 x 10 mL). Yield 93% (0.547 g, 1.18 mmol). **m.p.** 182-184 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 7.20-7.24 (m, 2 H, Ar*H*), 7.26-7.34 (m, 10 H, Ar*H*), 7.42-7.45 (m, 3 H, Ar*H*), 8.13 (s, 1 H, C*H*$_{thiaz}$). **^{13}C (75 MHz, CDCl$_3$)** δ 120.9 (q, *J*(C,F) = 319 Hz), 121.9 (*C*H$_{thiaz}$), 125.7 (*C*$_{ar}$), 127.5 (*C*$_{ar}$), 128.0 (*C*H$_{ar}$), 128.7 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 130.3 (*C*H$_{ar}$, two signals overlapping), 130.6 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 132.9 (*C*H$_{ar}$), 135.5 (*C*$_{ar}$), 150.4 (N*C*C), 172.1 (N*C*S). **^{19}F (282 MHz, CDCl$_3$)** δ −79.5.

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazolium trifluoromethanesulfonate.

The procedure described for the preparation of trifluoromethanesulfonyl salt was followed using in this case **1.21b**. The title compound was obtained as a white solid after washing the crude material with Et$_2$O (3 x 10 mL). Yield 87% (0.559 g, 1.10 mmol). **m.p.** 166-168 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 1.85 (s, 6 H, *o*-CH$_3$), 2.29 (s, 3 H, *p*-CH$_3$), 6.91 (s, 2 H, Ar*H*), 7.13 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.27-7.32 (m, 4 H, Ar*H*), 7.38-7.45 (m, 3 H, Ar*H*), 7.59 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 8.60 (s, 1 H, C*H*$_{thiaz}$). **^{13}C (75 MHz, CDCl$_3$)** δ 18.0 (*o*-*C*H$_3$), 21.3 (*p*-*C*H$_3$), 120.8 (q, *J*(C,F) = 318 Hz), 124.2 (*C*H$_{thiaz}$), 125.5 (*C*$_{ar}$), 126.7 (*C*$_{ar}$), 129.2 (*C*H$_{ar}$, two signals overlapping), 130.1 (*C*H$_{ar}$), 130.7 (*C*H$_{ar}$), 131.3 (*C*H$_{ar}$), 131.8 (*C*$_{ar}$), 134.1 (*C*H$_{ar}$), 134.3 (*C*H$_{ar}$), 142.6 (*C*$_{ar}$), 149.7 (N*C*C), 171.7 (N*C*S). **^{19}F (282 MHz, CDCl$_3$)** δ −77.2.

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazolium trifluoromethanesulfonate.

The procedure described for the preparation of trifluoromethanesulfonyl salt was followed using in this case **1.21c**. The title compound was obtained as a white solid after washing the crude material with Et$_2$O (3 x 10 mL). Yield 90% (0.625 g, 1.14 mmol). **m.p.** 188-190 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 0.75 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.77 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.21 (sept, *J* = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.16 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.26-7.32 (m, 6 H, Ar*H*), 7.41-7.45 (m, 3 H, Ar*H*), 7.57-7.65 (m, 2 H, Ar*H*), 8.78 (s, 1 H, C*H*$_{thiaz}$). **^{13}C (75 MHz, CDCl$_3$)** δ 23.7, 23.8 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 121.0 (q, *J*(C,F) = 318 Hz), 123.9 (*C*H$_{thiaz}$), 126.0 (*C*$_{ar}$), 126.5 (*C*H$_{ar}$), 127.0 (*C*$_{ar}$), 129.3

(*C*H$_{ar}$), 129.6 (*C*H$_{ar}$), 129.8 (*C*H$_{ar}$), 130.2 (*C*H$_{ar}$), 131.3 (*C*H$_{ar}$), 133.2 (*C*H$_{ar}$), 134.4 (*C*H$_{ar}$), 144.8 (*C*$_{ar}$), 150.5 (N*C*C), 172.4 (N*C*S). **^{19}F (282 MHz, CDCl$_3$)** δ −76.9.

*2,3,4-Triphenylthiazol-5-ylidene gold(I) chloride **1.22a**.*

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **1.22a** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 71% (0.167 g, 0.306 mmol). **m.p.** 276-278 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 7.05 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.16-7.23 (m, 5 H, Ar*H*), 7.24-7.26 (m, 2 H, Ar*H*), 7.29-7.35 (m, 5 H, Ar*H*), 7.44 (t, *J* = 7.0 Hz, 1 H, Ar*H*). No ^{13}C NMR spectrum is available due to limited solubility of the title product.

*3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene gold(I) chloride **1.22b**.*

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **1.22b** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 79% (0.200 g, 0.340 mmol). **m.p.** 303-305 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 1.66 (s, 6 H, *o*-CH$_3$), 2.06 (s, 3 H, *p*-CH$_3$), 6.69 (s, 2 H, Ar*H*), 6.99-7.05 (m, 5 H, Ar*H*), 7.12 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.35 (t, *J* = 7.4 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, CDCl$_3$)** δ 16.4 (*o*-*C*H$_3$), 19.6 (*p*-*C*H$_3$), 125.2 (*C*$_{ar}$), 126.6 (*C*H$_{ar}$), 127.0 (*C*H$_{ar}$), 127.8 (*C*$_{ar}$), 128.2 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 128.6 (*C*H$_{ar}$), 130.5 (*C*$_{ar}$), 131.0 (*C*H$_{ar}$), 132.4 (*C*$_{ar}$), 132.6 (*C*$_{ar}$), 139.5 (*C*H$_{ar}$), 149.5 (Au=*C*), 150.1 (N*C*C), 170.3 (N*C*S).

*3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene gold(I) chloride **1.22c**.*

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **1.22c** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 90% (0.244 g, 0.388 mmol). **m.p.** 138-140 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 0.56 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.68 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.14 (sept, *J* = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.01-7.09 (m, 7 H, Ar*H*), 7.17-7.22 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 7.26-7.34 (m, 3 H, Ar*H*), 7.39 (t, *J* = 7.6 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, CDCl$_3$)** δ 23.7, 24.0 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 126.0 (*C*H$_{ar}$), 127.4 (*C*$_{ar}$), 128.1 (*C*H$_{ar}$), 129.0 (*C*H$_{ar}$), 129.2 (*C*$_{ar}$), 129.8 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$), 131.7 (*C*$_{ar}$), 132.2

(*C*H$_{ar}$), 132.6 (*C*H$_{ar}$), 133.0 (*C*$_{ar}$), 144.7 (*C*H$_{ar}$), 151.4 (Au=*C*), 152.3 (N*C*C), 170.6 (N*C*S).

*2,3,4-Triphenylthiazol-5-ylidene palladium(II) allyl chloride **1.23a***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **1.23a** was obtained after washing the crude material with Et$_2$O (3 x 5 mL). Yield 58% (0.124 g, 0.250 mmol). **m.p.** 220-222 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 2.44 (b, 1 H, CH(C*H*$_2$)$_2$), 3.04 (b, 1 H, CH(C*H*$_2$)$_2$), 3.45 (d, *J* = 7.2 Hz, 1 H, CH(C*H*$_2$)$_2$), 4.11 (b, 1 H, CH(C*H*$_2$)$_2$), 5.11 (pentet, *J* = 6.9 Hz, 1 H, C*H*(CH$_2$)$_2$), 6.88 (d, *J* = 6.9 Hz, 2 H, Ar*H*), 7.03-7.07 (m, 3 H, Ar*H*), 7.15-7.19 (m, 4 H, Ar*H*), 7.22-7.26 (m, 4 H, Ar*H*), 7.38 (d, *J* = 7.4 Hz, 2 H, Ar*H*). **^{13}C (75 MHz, CDCl$_3$)** δ 59.9, 65.9 (CH(*C*H$_2$)$_2$), 117.7 (*C*H(CH$_2$)$_2$), 125.6 (*C*$_{ar}$), 127.4 (*C*H$_{ar}$), 127.6 (*C*H$_{ar}$), 127.7 (*C*H$_{ar}$) 128.3 (*C*H$_{ar}$), 128.6 (*C*H$_{ar}$), 129.1 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 130.3 (*C*$_{ar}$), 131.5 (*C*H$_{ar}$), 134.0 (*C*$_{ar}$), 136.9 (*C*H$_{ar}$), 149.2 (N*C*C), 159.2 (Pd=*C*), 172.4 (N*C*S).

*3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene palladium(II) allyl chloride **1.23b***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **1.23b** was obtained after washing the crude material with Et$_2$O (3 x 5 mL). Yield 51% (0.118 g, 0.220 mmol). **m.p.** 198-200 °C. **^{1}H (300 MHz, CDCl$_3$)** δ 1.56 (s, 6 H, *o*-CH$_3$), 2.05 (s, 3 H, *p*-CH$_3$), 2.29 (d, *J* = 13.1 Hz, 1 H, CH(C*H*$_2$)$_2$), 2.84 (b, 1 H, CH(C*H*$_2$)$_2$), 3.24 (d, *J* = 7.1 Hz, 1 H, CH(C*H*$_2$)$_2$), 3.90 (b, 1 H, CH(C*H*$_2$)$_2$), 4.97 (pentet, *J* = 6.8 Hz, 1 H, C*H*(CH$_2$)$_2$), 6.62 (s, 2 H, Ar*H*), 6.77-6.84 (m, 2 H, Ar*H*), 6.96-7.00 (m, 3 H, Ar*H*), 7.11-7.18 (m, 4 H, Ar*H*), 7.27 (t, *J* = 7.4 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, CDCl$_3$)** δ 17.9 (*o*-*C*H$_3$), 21.1 (*p*-*C*H$_3$), 59.9, 67.9 (CH(*C*H$_2$)$_2$), 117.5 (*C*H(CH$_2$)$_2$), 126.9 (C$_{ar}$), 127.6 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.6 (*C*$_{ar}$), 129.1 (*C*$_{ar}$), 129.4 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 130.2 (*C*H$_{ar}$), 130.7 (*C*H$_{ar}$), 131.4 (*C*$_{ar}$), 133.7 (*C*$_{ar}$), 141.0 (*C*H$_{ar}$), 149.1 (N*C*C), 156.0 (Pd=*C*), 171.8 (N*C*S).

*3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene palladium(II) allyl chloride **1.23c***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **1.21c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10

mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **1.23c** was obtained after washing the crude material with Et_2O (3 x 5 mL). Yield 53% (0.133 g, 0.228 mmol). **m.p.** 212-214 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 0.58 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.62 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.97 (sept, *J* = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 2.25 (b, 1 H, CH(C*H*$_2$)$_2$), 2.39 (b, 1 H, CH(C*H*$_2$)$_2$), 3.04 (d, *J* = 11.5 Hz, 1 H, CH(C*H*$_2$)$_2$), 4.03 (b, 1 H, CH(C*H*$_2$)$_2$), 5.02 (pentet, *J* = 6.9 Hz, 1 H, C*H*(CH$_2$)$_2$), 7.03-7.09 (m, 4 H, Ar*H*), 7.12-7.18 (m, 4 H, Ar*H*), 7.26-7.31 (m, 4 H, Ar*H*), 7.42 (t, *J* = 7.6 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 23.6, 23.9 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 51.8, 69.9 (CH(*C*H$_2$)$_2$), 113.8 (*C*H(CH$_2$)$_2$), 125.6 (*C*H$_{ar}$), 125.7 (*C*$_{ar}$), 127.1 (*C*H$_{ar}$), 127.8 (*C*$_{ar}$), 128.4 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 129.2 (*C*H$_{ar}$), 130.9 (*C*$_{ar}$), 131.4 (*C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 133.5 (*C*$_{ar}$), 144.5 (*C*H$_{ar}$), 150.8 (N*C*C), 159.5 (Pd=*C*), 171.8 (N*C*S).

*2,3,4-Triphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride **1.24a***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium salt **1.21a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Rh(COD)Cl]$_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **1.24a** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 45% (0.098 g, 0.193 mmol). **m.p.** 238-240 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 7.00 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.16 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.19-7.24 (m, 3 H, Ar*H*), 7.28-7.35 (m, 8 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 127.6 (C$_{ar}$), 127.7 (*C*H$_{ar}$), 127.9 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$, two signals overlapping), 129.3 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$), 130.4 (*C*$_{ar}$), 132.1 (*C*H$_{ar}$), 133.2 (*C*$_{ar}$), 137.2 (*C*H$_{ar}$), 150.9 (N*C*C), 157.8 (d, *J* = 37.1 Hz, Rh=*C*), 172.4 (N*C*S), 183.3 (d, *J* = 76.3 Hz, Rh-*C*O), 185.9 (d, *J* = 55.6 Hz, Rh-*C*O). **IR (C_6H_6)** *v* 2070.8, 1996.0 (CO).

*3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride **1.24b***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium salt **1.21b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Rd(COD)Cl]$_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **1.24b** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 41% (0.098 g, 0.177 mmol). **m.p.** 218-220 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 1.83 (s, 6 H, *o*-CH$_3$), 2.24 (s, 3 H, *p*-CH$_3$), 6.80 (s, 2 H, Ar*H*), 7.15 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.28-7.35 (m, 5 H, Ar*H*), 7.44 (t, *J* = 6.9 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 18.2 (*o*-*C*H$_3$), 21.3 (*p*-*C*H$_3$), 127.5 (C$_{ar}$), 127.7 (*C*H$_{ar}$), 128.3 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 129.3 (*C*$_{ar}$), 129.5 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 132.0 (*C*$_{ar}$), 132.7 (*C*$_{ar}$), 134.3 (*C*$_{ar}$), 140.9 (*C*H$_{ar}$), 150.5 (N*C*C), 158.6 (d, *J*

= 40.1 Hz, Rh=*C*), 171.6 (N*C*S), 183.3 (d, *J* = 79.5 Hz, Rh-*C*O), 185.6 (d, *J* = 57.6 Hz, Rh-*C*O). **IR (C_6H_6)** *v* 2071.9, 1998.1 (CO).

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride ***1.24c***.

THF (12 mL) was added at −78 °C to a Schlenk flask charged with the thiazolium salt **1.21c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and $[Rd(COD)Cl]_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **1.24c** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 47% (0.120 g, 0.202 mmol). **m.p.** 270-272 °C. **^{1}H (300 MHz, $CDCl_3$)** δ 0.68 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.78 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.27 (sept, *J* = 6.4 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.08-7.20 (m, 6 H, Ar*H*), 7.21-7.28 (m, 4 H, Ar*H*), 7.40 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.50 (t, *J* = 7.4 Hz, 1 H, Ar*H*). **^{13}C (75 MHz, $CDCl_3$)** δ 23.7, 24.0 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 125.8 (*C*H$_{ar}$), 127.5 (*C*H$_{ar}$), 128.4 (*C*$_{ar}$), 128.8 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 131.4 (*C*$_{ar}$), 132.0 (*C*H$_{ar}$), 132.2 (*C*H$_{ar}$), 132.5 (*C*$_{ar}$), 133.1 (*C*$_{ar}$), 144.6 (*C*H$_{ar}$), 151.9 (N*C*C), 157.7 (d, *J* = 37.7 Hz, Rh=*C*), 172.7 (N*C*S), 183.2 (d, *J* = 76.1 Hz, Rh-*C*O), 186.0 (d, *J* = 54.6 Hz, Rh-*C*O). **IR (C_6H_6)** *v* 2069.7, 1996.9 (CO).

3) Crystallographic Data

Crystallographic Data and Summary of Data Collection and Structure Refinement

	3b	**5b**
Formula	$C_{27}H_{30}BrNO_2S$	$C_{24}H_{21}AuClNS$
Fw	512.49	587.89
cryst syst	Monoclinic	Monoclinic
space group	*P*2$_1$/c	*C*2/c
Size (mm^3)	0.32 x 0.17 x 0.10	0.27 x 0.17 x 0.10
T, K	100(2)	200(2)
a, Å	9.4960(14)	18.170(4)
b, Å	28.054(4)	9.7695(15)
c, Å	9.6399(14)	24.734(4)
a, deg	90	90
b, deg	104.693(2)	99.134(3)
g, deg	90	90
V, Å^3	2484.1(6)	4334.9(12)
Z	4	8
d_{calcd} g·cm^{-3}	1.370	1.802
m, mm^{-1}	1.763	7.016
Refl collected	20859	11994
T_{min}/ T_{max}	0.714	0.468
N$_{measd}$	6277	4607

[R_{int}]	[0.0276]	[0.0501]
R [I>2sigma(I)]	0.0319	0.0648
R_w[I>2sigma(I)]	0.0887	0.2058
GOF	1.120	1.174
Largest diff peak/hole[e·Å^{-3}]	0.476/-0.361	2.279/-2.230

C) Oxazol-5-ylidenes

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Coupling constants *J* are given in Hz.

2) Synthesis and Characterization

*3-methyl-2,4-diphenyloxazolium trifluoromethanesulfonate **1.30**.*

Methyl trifluoromethanesulfonate (0.20 mL, 0.98 mmol) was added to a solution of oxazole **1.29** (180 mg, 0.81 mmol) in dichloromethane (20 mL). The mixture was stirred overnight. The solution was concentrated under vacuum and the residue was washed with diethyl ether. The white powder obtained was recrystallized by layering diethyl ether on top of a saturated solution of **1.30** in chloroform. 172 mg were obtained (55 % yield). **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 3.97 (s, 3H), 7.50-7-81 (m, 8H), 8.03-8.10 (m, 2H), 8.14 (s, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 35.7 (CH3), 129.8 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 130.4 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$), 131.9 (*C*H$_{ar}$), 135.1 (*C*H$_{ar}$), 138.0 (*C*H$_{ar}$), quarternary were not observed due to low solubility; **^{19}F (282 MHz, $CDCl_3$)** δ −79.0.

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CHAPTER 2:

Simple alkynes as mesoionic carbenes equivalents

Adapted from:

G. Ung, D. Mendoza-Espinosa, J. Bouffard, G. Bertrand, *Angew. Chem. Int. Ed.* **2011**, *50*, 4215–4218

and G. Ung, D. Mendoza-Espinosa, G. Bertrand, *Chem. Commun.* **2012**, *48*, 7088–7090

Introduction

We observed in Chapter 1 that thiazol-5-ylidenes and oxazol-5-ylidenes were not stable as free species. Although they are not prone to dimerize, some degree of steric protection seemed to be required for the isolation of these highly basic species. In continuation with the work done on Chapter 1, we targeted the isomeric thiazol-4-ylidenes **2.A** and oxazol-4-ylidenes **2.B**, which introduce some steric bulk at the nitrogen atom. In this chapter, we demonstrate that oxazol-4-ylidenes are not stable, and ring open to the corresponding ynamide **2.C**. Nevertheless, the oxazol-4-ylidene transition metal complexes can be obtained by an unusual transition metal induced ring closure reaction. This concept was also exploited with the dithiol-5-ylidene/alkynyldithioate **2.D**/**2.E** couple. It is noteworthy to mention that the synthesis of triaryl substituted thiazol-4-ylidenes and oxazol-4-ylidene rhodium complexes was published by Zhang, Shi and co-workers shortly after our report on oxazol-4-ylidenes.[1] However, no studies of the stability of the free carbene were described.

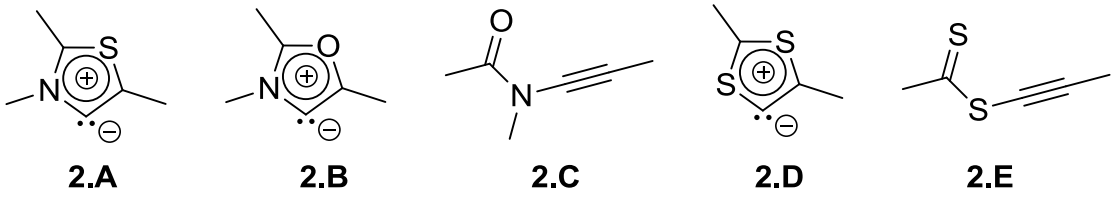
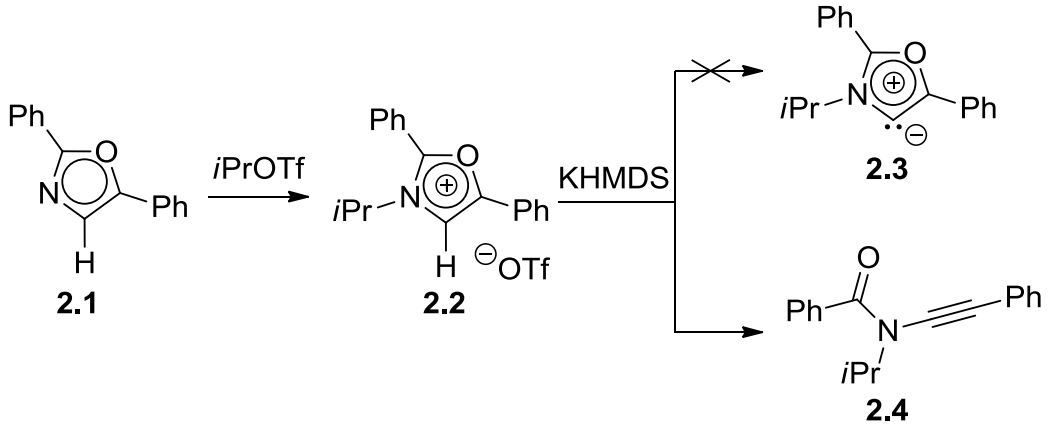


Figure F2. 1: Carbenes and alkynes discussed in this chapter.

A) Ynamides as ligand equivalents of oxazol-4-ylidenes.

By analogy with the synthetic route used for the preparation of the mesoionic carbenes presented in Chapter 1, the oxazolium salt **2.2** was chosen as a potential precursor for oxazol-4-ylidene **2.3**. The cationic heterocycle **2.2** was obtained by alkylation of the nitrogen atom of the readily available oxazole **2.1**[2] (Scheme **S2. 1**).



Scheme S2. 1: Synthesis and deprotonation of oxazolium salt **2.2**.

Clean deprotonation of **2.2** with potassium bis(trimethylsilyl)amide was achieved, as shown by the disappearance of the oxazolium proton in the ^{1}H NMR spectrum. However, the $^{13}C\{^{1}H\}$ NMR spectrum displayed signals at 75.7 and 83.7 ppm, far from the range expected for mesoionic carbenes (~200 ppm). These data are consistent with the presence of *sp* hybridized carbons, leading to the conclusion that the deprotonation of **2.2** yields the ynamide **2.4** and not the expected oxazol-4-ylidene **2.3**.

Ynamides are known to be very electron rich alkynes.[3] We envisioned that this feature would facilitate its complexation to electrophilic transition metal precursor. To

validate our hypothesis, ynamide **2.4** was reacted with half an equivalent of $\{Rh(COD)Cl\}_2$. The appearance of a doublet ($^1J_{(C–Rh)}$ = 48 Hz) at 156 ppm in the $^{13}C\{^1H\}$ NMR spectrum indicated that a complexation occurred. However, its chemical shift did not fit with an ynamide coordination. In addition, no acetylene carbon resonances were detected. After treatment of the obtained complex **2.5** with excess carbon monoxide, the corresponding rhodium chloride *cis*-dicarbonyl complex **2.6** was quantitatively obtained. Single crystals of **2.6** were grown from $CHCl_3$/pentane and the X-ray diffraction study revealed the cyclic structure of an oxazol-4-ylidene ligand (Figure **F2. 2**).

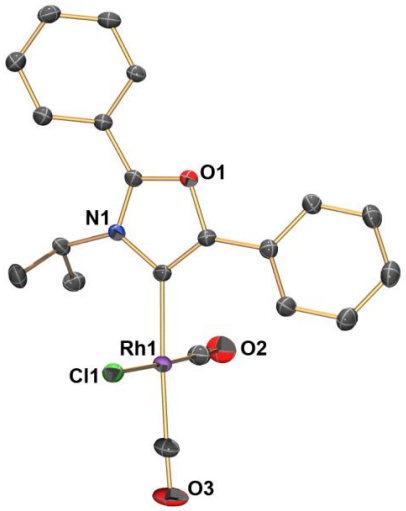
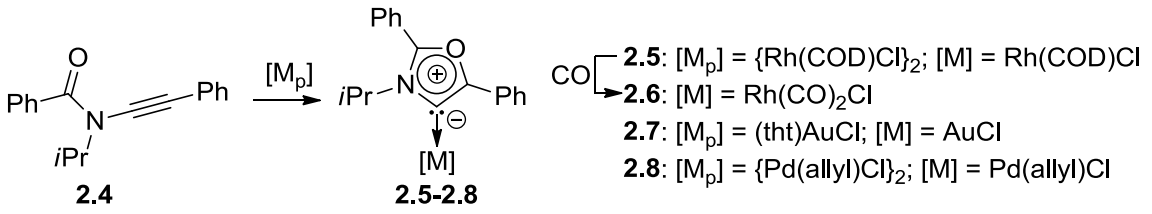


Figure F2. 2: Structure of **2.6·($CHCl_3$)** in the solid state, hydrogen atoms and co-crystallized solvent molecule are omitted for clarity, thermal ellipsoids are drawn at 50% probability.



Scheme S2. 2: Reaction of ynamide **2.4** with various transition metal fragments.

The transition metal fragment not only coordinated to the ynamide but also triggered a ring closure to yield the cyclic oxazol-4-ylidene ligand. To test the scope of this ring closing process, ynamide **2.4** was reacted with other electrophilic metal precursors. Complexes of gold **2.7** and palladium **2.8** were readily obtained (Scheme **S2. 2**). Ynamide **2.4** can therefore act as a synthetic ligand equivalent of mesoionic oxazol-4-ylidene **2.3**. The TEP for **2.6** (2048.4 cm^{-1}) indicates that ligand **2.3** is a stronger electron donor than classical imidazol-2-ylidenes (2051 cm^{-1}),[4] but is the weakest donor of the mesoionic carbene family (2033–2045 cm^{-1}).[5]

B) Alkynyldithioates as ligand equivalents of dithiol-5-ylidenes.

No derivatives of the dithiol-2-ylidene **2.9** are known owing to their dimerization into derivatives of tetrathiafulvalene **2.10**.[6] In continuation of the work presented in Chapter 1 on carbenes with decreased steric protection, we targeted the mesoionic dithiol-5-ylidenes of type **2.11** which should in principle be unable to dimerize (Figure **F2. 3**).

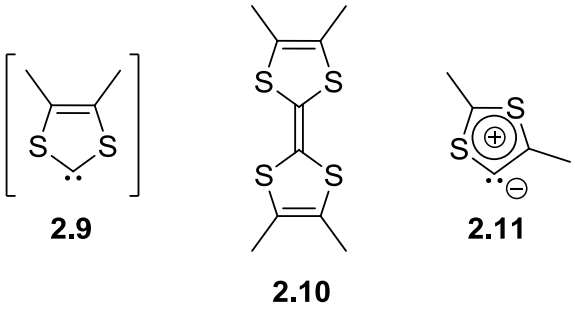
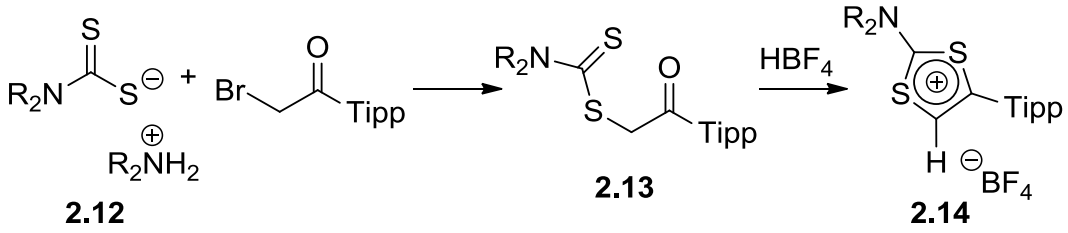


Figure F2. 3: Unknown dithiol-2-ylidene **2.9**, its dimer tetrathiafulvalene **2.10**, and the targeted dithiol-5-ylidene **2.11**.

Following the traditional route for the synthesis of mesoionic carbenes, we designed the dithiolium salt **2.14** as precursor. We have observed in Chapter 1 that thiazol-5-ylidenes were not stable. In order to provide some steric and electronic protection for the targeted dithiol-5-ylidene, we included a bulky triisopropylphenyl substituent adjacent to the carbene center, as well as an electron donating amino substituent on the backbone. Dithiolium tetrafluoroborate salt **2.14** was obtained in two steps from the dithiocarbamate **2.12** (Scheme **S2. 3**).



Scheme S2. 3: Synthesis of dithiolium tetrafluoroborate salt **2.14**; NR_2 = *N*-piperidinyl; Tipp = 2,4,6-triisopropylphenyl.

Deprotonation with potassium bis(trimethylsilyl)amide proceeded cleanly, as shown by the disappearance of the signals for the dithiolium proton in the ^{1}H NMR

spectrum and the corresponding *C*–H resonance in the $^{13}C\{^1H\}$ spectrum. However, no carbene carbon peaks were detected in the $^{13}C\{^1H\}$ spectrum, but two new quaternary signals appeared at 81.5 and 103.2 ppm typical for *sp* hybridized carbons. Single crystals of the deprotonation product were obtained from an ether/hexanes mixture, and an X-ray diffraction study revealed that it was not the expected cyclic dithiol-5-ylidene **2.15**, but the acyclic ethynyl dithiocarbamate **2.16** (Figure **F2. 4** left).

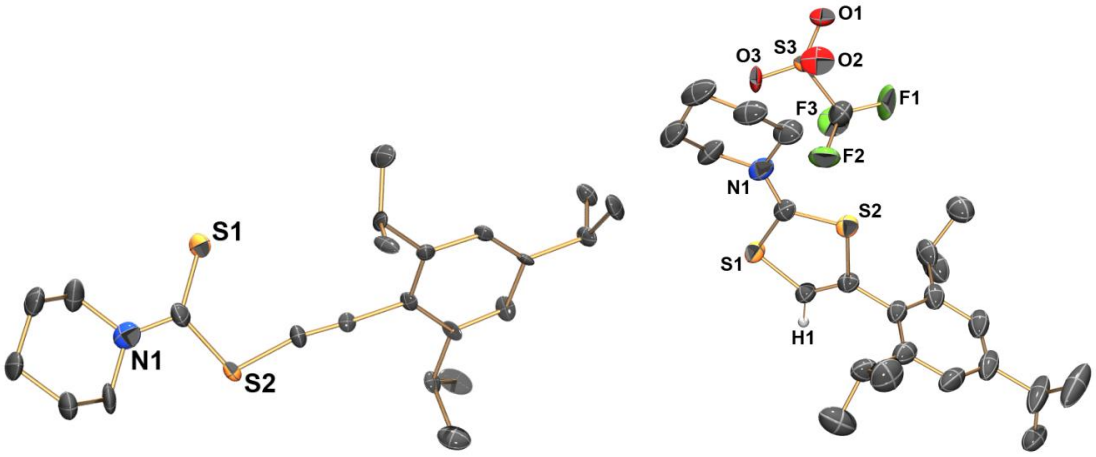
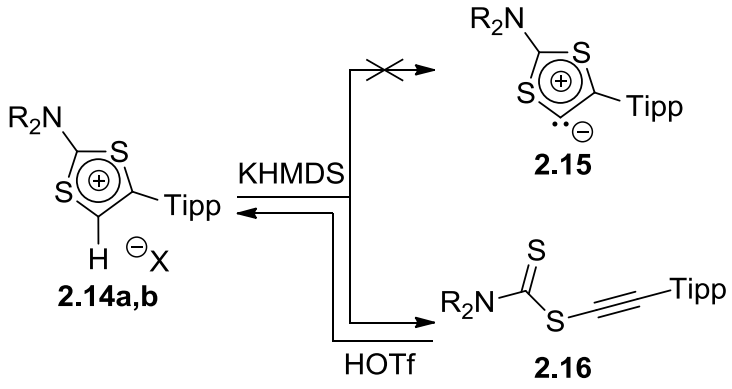
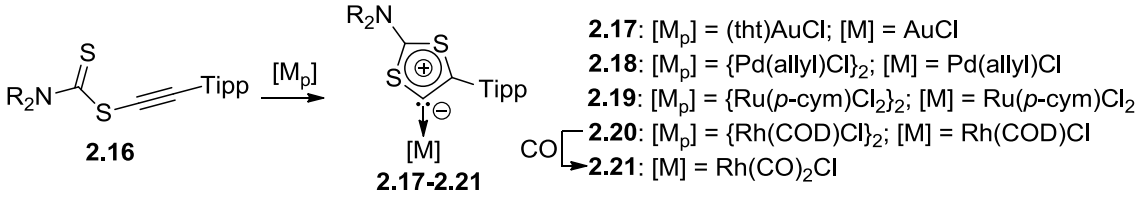


Figure F2. 4: Structure of **2.16** (left) and **2.14b** (right) in the solid state, hydrogen atoms except the dithiolium C–H are omitted for clarity, thermal ellipsoids are drawn at 50% probability.



Scheme S2. 4: Deprotonation of dithiolium salts **2.14a,b**; **a**: X = BF_4, **b**: X = OTf.

Interestingly, alkyne **2.16** reacted instantaneously with trifluoromethanesulfonic acid to yield the cyclic dithiolium salt **2.14b** (Scheme **S2. 4**, Figure **F2. 4** right). This result prompted us to investigate its reactivity with gold complexes, which are well-known alkynophilic π-acids.[7] The reaction of **2.16** with (tht)AuCl proceeded cleanly, and the dithiol-5-ylidene-gold complex **2.17** was isolated (Figure **F2. 5** left). These results show that with a gold complex, ethynyl dithiocarbamate **2.16** acts as a ligand equivalent of dithiol-5-ylidene **2.15**. To test the scope of this finding, we treated compound **2.16** with the less alkynophilic complexes $\{Pd(allyl)Cl\}_2$ and $\{Ru(p\text{-cym})Cl_2\}_2$ (Scheme **S2. 5**). Complexes **2.18** (Figure **F2. 5** middle) and **2.19** were isolated in 69 and 83% yield, respectively. To evaluate the donor properties of the dithiol-5-ylidene ligand **2.15**, we prepared the corresponding rhodium chloride *cis*-dicarbonyl complex **2.21** by the addition of half an equivalent of $\{Rh(COD)Cl\}_2$ to **2.16**, followed by treatment with excess carbon monoxide (Figure **F2. 5** right). The TEP for **2.21** (2044.8 cm^{-1}) indicates that **2.15** is a stronger electron donor than classical imidazol-2-ylidenes (TEP ~ 2050 cm^{-1}) and oxazol-4-ylidenes (TEP = 2048.4 cm^{-1}), but is weaker than other imidazol-5-ylidenes (TEP ~ 2038 cm^{-1}).



Scheme S2. 5: Reactivity of ethynyl dithiocarbamate **2.16** with various transition metals.

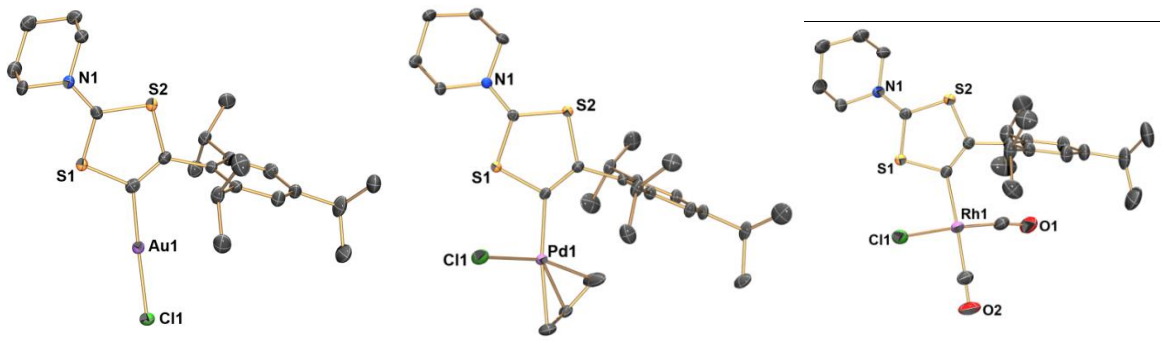


Figure F2. 5: Structure of **2.17** (left), **2.18·(CHCl$_3$)** (middle) and **2.21·(CHCl$_3$)** (right) in the solid state, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

Conclusion

In this chapter, we have discovered that the variety of isolable free mesoionic carbenes is limited by their propensity to undergo ring opening reactions. Indeed, we observed that the deprotonation of oxazolium and dithiolium salts do not yield the cyclic mesoionic carbene, but instead alkynes, namely an ynamide and alkynyldithioate, respectively. Nevertheless, we have shown that a reverse ring closure process, triggered by transition metals, provides the corresponding mesoionic carbene-metal complexes in both cases. This demonstrates that simple alkynes can act as synthetic equivalents of the free mesoionic carbene, opening the door for the design and synthesis of other ligand equivalents, which we will discuss in Chapter 4.

Chapter 2 has been adapted from materials published in G. Ung, D. Mendoza-Espinosa, J. Bouffard, G. Bertrand, *Angew. Chem. Int. Ed.* **2011**, *50*, 4215–4218 and G. Ung, D. Mendoza-Espinosa, G. Bertrand, *Chem. Commun.* **2012**, *48*, 7088–7090. The dissertation author was the primary investigator of these papers.

Appendix: Experimental section

A) Ynamides as ligand equivalent of oxazol-4-ylidenes.

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Varian Inova 500, Varian Inova 400 and Bruker 300 spectrometers at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

2) Synthesis and characterization

*3-isopropyl-2,5-diphenyloxazolium trifluoromethanesulfonate **2.2**.*

In a Schlenk are dissolved isopropanol (210 µL, 2.7 mmol, 2 eq) and pyridine (220 µL, 2.7 mmol, 2 eq) in dry CH_2Cl_2 (10 mL). The reaction mixture is cooled to −78 °C and trifluoromethanesulfonate anhydride (460 µL, 2.7 mmol, 2 eq) is added. The reaction mixture is stirred for 30 min at −78 °C then for an additional 30 min at room temperature. Dry hexanes (10 mL) are added. The supernatant solution is filtered into a Schlenk containing a solution of 2,5-diphenyloxazole **2.1** in dry CH_2Cl_2 (5 mL). Reaction mixture is stirred for 14 hours at room temperature. All volatiles are removed under vacuum and the white residue is washed with diethyl ether. 826 mg (2.00 mmol, yield = 74%) are obtained. **m.p.** 247 °C. **^{1}H (300 MHz, C_6D_6) δ** 1.53 (d, *J* = 6.6 Hz, 6H), 4.89 (sept, *J* = 6.6 Hz, 1H), 7.45-7.53 (m, 3H), 7.53-7.70 (m, 2H), 7.71-7.80 (m, 3H), 7.84-7.89 (m, 2H), 8.22 (s, 1H). **^{13}C (75 MHz, C_6D_6) δ** 22.3 (CH(*C*H$_3$)$_2$), 54.8 (*C*H(CH$_3$)$_2$), 115.1 (*C*H$_{oxa}$), 117.4 (*C*^{q}), 121.2 (*C*^{q}), 125.3 (*C*^{q}), 126.2 (*C*H$_{ar}$), 130.7 (*C*H$_{ar}$), 130.9 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 132.6 (*C*H$_{ar}$), 135.8 (*C*H$_{ar}$), 155.1(*C*^{q}). **^{19}F{^{1}H} (282 MHz, C_6D_6) δ** −78.4 **HRMS:** m/z calculated for $C_{18}H_{18}NO$ $(M-OTf)^{+}$ 264.1383, found 264.1391.

*N-isopropyl-N-(phenylethynyl)benzamide **2.4**.*

Diethyl ether (15 mL) is added to cold (–78°C) potassium bis(trimethylsilyl)amide (48 mg, 0.242 mol, 1 eq) and oxazolium salt (100 mg, 0.242 mmol, 1 eq). The solution is stirred 15 min at −78°C then allowed to warm to room temperature. Diethyl ether is evaporated and the residue extracted with hexanes (30 mL). Hexanes are evaporated under vacuum yielding a white powder. 49 mg (0.186 mmol, yield = 77%) are obtained. **m.p.** 74 °C (dec). **^{1}H (300 MHz, C_6D_6) δ** 1.21 (d, *J* = 6.6 Hz, 6H), 4.93 (sept, *J* = 6.6 Hz, 1H), 6.86-6.98 (m, 3H), 7.00-7.17 (m, 5H), 8.14-8.21 (m, 2H). **^{13}C (75 MHz, C_6D_6) δ** 20.5 (CH(*C*H$_3$)$_2$), 48.1 (*C*H(CH$_3$)$_2$), 75.7 (*C*≡C), 83.8 (C≡*C*), 124.3 (*C*^{q}), 127.7 (*C*H$_{ar}$),

128.7 (*C*H$_{ar}$), 128.9 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 130.9 (*C*H$_{ar}$), 131.5 (*C*H$_{ar}$), 135.5 (*C*^{q}), 170.4 (*C*=O). **HRMS:** m/z calculated for $C_{18}H_{18}NO$ $(M+H)^+$ 264.1383, found 264.1388.

L-RhCl(COD) ***2.5****.*

THF (5 mL) is added to a solid mixture of ynamide **2.4** (52 mg, 0.197 mmol, 1 eq) and 1,5-cyclooctadiene rhodium chloride dimer (49 mg, 0.098 mmol, 0.5 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the light yellow residue washed with diethyl ether (4x10 mL). The resulting light yellow powder is dried under vacuum. 81 mg (0.160 mmol, yield = 81 %) are obtained. **m.p.** 164°C (dec). **^{1}H (500 MHz, $CDCl_3$) δ** 1.56-1.67 (m, 1H), 1.69 (d, *J* = 7.0 Hz, 3H), 1.75 (d, *J* = 7.0 Hz, 3H), 1.77-1.90 (m, 3H), 2.10-2.20 (m, 1H), 2.20-2.32 (m, 2H), 2.35-2.45 (m, 1H), 2.98-3.04 (m, 1H), 3.14-3.20 (m, 1H), 4.88-4.96 (m, 1H), 5.03-5.10 (m, 1H), 5.90 (sept, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.47-7.53 (m, 4H), 7.54-7.60 (m, 1H), 8.62 (d, *J* = 7.5 Hz, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.9 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 29.2 (*C*H$_2$), 29.4 (*C*H$_2$), 32.5 (*C*H$_2$), 33.1 (*C*H$_2$), 57.3 (*C*H(CH$_3$)$_2$), 67.4 (d, $J_{C\text{-}Rh}$ = 14.4 Hz, *C*H, COD), 71.3 (d, $J_{C\text{-}Rh}$ = 14.4 Hz, *C*H, COD), 95.9 (d, $J_{C\text{-}Rh}$ = 6.3 Hz, *C*H, COD), 96.4 (d, $J_{C\text{-}Rh}$ = 6.3 Hz, *C*H, COD), 124.0 (*C*^{q}), 126.3 (*C*H$_{ar}$), 127.9 (*C*H$_{ar}$), 128.2 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.7 (*C*^{q}), 132.6 (*C*H$_{ar}$), 152.5 (*C*^{q}), 155.6 (d, $J_{C\text{-}Rh}$ = 47.5 Hz, *C*-Rh), 158.8 (*C*^{q}).

L-RhCl(CO)$_2$ ***2.6****.*

Carbon monoxide is bubbled in a solution of L-RhCl(COD) **2.5** (81 mg, 0.197 mmol) in $CHCl_3$ (5 mL) for 20 minutes. Solvent is evaporated and the residue washed with hexanes (2x10 mL). The resulting light yellow powder is dried under vacuum. Single crystals were obtained by slow evaporation of a saturated solution of chloroform/hexanes (8:1) at room temperature. 88 mg (0.193 mmol, yield = 98 %) are obtained. **m.p.** 178 °C (dec). **^{1}H (500 MHz, $CDCl_3$) δ** 1.76 (br s, 3H), 1.83 (br s, 3H), 5.06 (sept, *J* = 7.0 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.55-7.68 (m, 5H), 8.39 (d, *J* = 7.5 Hz, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 23.2 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 54.9 (*C*H(CH$_3$)$_2$), 122.7 (*C*^{q}), 128.6 (*C*H$_{ar}$), 128.7 (*C*^{q}), 128.8 (*C*H$_{ar}$), 129.0 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 129.8 (*C*H$_{ar}$), 133.3 (*C*H$_{ar}$), 144.1 (d, $J_{C\text{-}Rh}$ = 39.3 Hz, *C*-Rh), 155.8 (*C*^{q}), 159.4 (*C*^{q}), 183.7 (d, $J_{C\text{-}Rh}$ = 76.3 Hz, *C*O), 185.9 (d, $J_{C\text{-}Rh}$ = 55.6 Hz, *C*O). **IR (CH_2Cl_2): ν (cm^{-1})** 2074.87 (CO), 1995.64 (CO).

L-AuCl ***2.7****.*

THF (5 mL) is added to a solid mixture of ynamide **2.4** (45 mg, 0.171 mmol, 1 eq) and tetrahydrothiophene gold chloride (54 mg, 0.171 mmol, 1 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the light yellow residue washed with diethyl ether (4x10 mL). The resulting light pink powder is dried under vacuum. 65 mg (0.132 mmol, yield = 77 %) are obtained. **m.p.** 155 °C. **^{1}H (300 MHz, $CDCl_3$) δ** 1.96 (d, *J* = 6.6 Hz, 6H), 5.00 (sept, *J* = 6.6 Hz, 1H), 7.35-7.43 (m, 3H), 7.66-7.77 (m, 5H), 8.30-8.39 (m, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 22.9 (CH(*C*H$_3$)$_2$), 53.3 *C*H(CH$_3$)$_2$), 121.7 (*C*^{q}), 125.3 (*C*H$_{ar}$), 127.9 (*C*^{q}), 128.9 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 133.7 (*C*H$_{ar}$), 138.4 (*C*^{q}), 157.9 (*C*^{q}), 158.4 (*C*^{q}).

L-PdCl(η^3-allyl) ***2.8****.*

THF (5 mL) is added to a solid mixture of ynamide **2.4** (49 mg, 0.186 mmol, 1 eq) and η^3-allyl palladium chloride dimer (34 mg, 0.093 mmol, 0.5 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the light yellow residue washed with diethyl ether (4x10 mL). The resulting white powder is dried under vacuum. 76 mg (0.169 mmol, yield = 91 %) are obtained. **m.p.** 187 °C. **^{1}H (500 MHz, $CDCl_3$) δ** 1.65-1.74 (m, 3H), 1.76 (d, *J* = 7.0 Hz, 3H), 2.25 (d, *J* = 11.5 Hz, 1H), 3.12 (d, *J* = 7.0 Hz, 1H), 3.30 (d, *J* = 13.5 Hz, 6H), 4.18 (d, *J* = 7.0 Hz, 1H), 4.90 (sept, *J* = 7.0 Hz, 1H), 5.17-5.28 (m, 1H), 7.15-7.20 (m, 1H), 7.24-7.30 (m, 2H), 7.50-7.60 (m, 5H), 8.22-8.28 (m, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.9 (CH(*C*H_3)$_2$), 23.1 (CH(*C*H_3)$_2$), 49.5 (*C*H_2-allyl), 53.7 (*C*H(CH$_3$)$_2$), 71.7 (*C*H_2-allyl), 113.4 (*C*H-allyl), 122.8 (*C*^{q}), 125.6 (*C*H$_{ar}$), 128.1 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 129.0 (*C*H$_{ar}$), 129.7 (*C*H$_{ar}$), 129.8 (*C*^{q}), 132.9 (*C*H$_{ar}$), 146.3 (*C*-Pd), 154.8 (*C*^{q}), 159.1 (*C*^{q}).

3) Crystallographic Data

Crystal data and structure refinement for 2.6.

Identification code	GU1188	
Empirical formula	$C_{21}H_{18}Cl_4NO_3Rh$	
Formula weight	577.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.7427(9) Å	α= 90°
	b = 19.1083(12) Å	β= 91.668(2)°
	c = 8.2340(5) Å	γ = 90°
Volume	2318.6(2) Å^3	
Z	4	
Density (calculated)	1.653 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	1152	
Theta range for data collection	2.13 to 41.65°	
Index ranges	-20<=h<=27, -35<=k<=32, -12<=l<=15	
Reflections collected	33043	
Independent reflections	14858 [R(int) = 0.0406]	
Completeness to theta = 41.65°	93.6 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14858 / 0 / 273	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0995	
R indices (all data)	R1 = 0.0737, wR2 = 0.1150	
Largest diff. peak and hole	2.028 and -1.808 e.Å^{-3}	

B) Alkynyldithioate as ligand equivalent of dithiol-5-ylidenes.

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectra were recorded on Varian Inova 500 and Bruker 300 spectrometers at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system.

2) Synthesis and characterization

*Piperidinium piperidine-1-carbodithioate **2.12**.*

Carbon disulfide (6.3 mL, 105 mmol, 1 eq) is added to a cold (0°C) solution of piperidine (21 mL, 215 mmol, 2.05 eq) in acetone (180 mL) under vigorous stirring. A white precipitate appears after a few minutes. Suspension is stirred for 30 min at 0°C. Precipitate is collected through filtration and washed with cold acetone (3x50 mL). White powder is dried under vacuum for 10 min. 21.2 g (86 mmol, yield = 82%) are obtained. **M.P.** 105°C. **^{1}H (300 MHz, $CDCl_3$) δ** 1.59-1.75 (m, 8H), 1.75-1.97 (m, 4H), 3.22-3.34 (m, 4H), 4.30-4.38 (m, 4H), 8.86 (br s, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 22.7 (CH_2), 30.0 (CH_2), 24.6 (CH_2), 26.3 (CH_2), 45.3 (NCH_2), 52.1 (NCH_2), 208.8 (C^q).

*2-oxo-2-(2,4,6-triisopropylphenyl)ethyl piperidine-1-carbodithioate **2.13**.*

Acetonitrile (50 mL) is added to piperidinium piperidine-1-carbodithioate (2.46 g, 10 mmol, 1 eq) and 2-bromo-1-(2,4,6-triisopropylphenyl)ethanone (3.25 g, 10 mmol, 1 eq). The suspension is heated to 80°C for 2 hours (all solids solubilize). The clear solution is cooled to room temperature and diethyl ether (50 mL) is added to precipitate piperidinium bromide. Precipitate is filtered and the filtrate concentrated under vacuum yielding a white powder (3.94 g, 9.7 mmol, yield = 97%) *N.B:* If piperidinium bromide has not been totally removed, product can be resolubilized in diethyl ether and the piperidinium bromide filtered. **M.P.** 178°C. **^{1}H (300 MHz, $CDCl_3$) δ** 1.27 (d, *J* = 6.8 Hz, 18H), 1.69-1.78 (m, 6H), 2.82 (sept, *J* = 6.8 Hz, 2H), 2.91 (sept, *J* = 6.8 Hz, 1H), 4.03 (br s, 2H), 4.33 (br s, 2H), 4.89 (s, 2H), 7.04 (s, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 24.2 ($CH(CH_3)_2$), 24.5 (CH_2), 24.7 ($CH(CH_3)_2$), 25.6 (br, CH_2), 26.3 (br, CH_2), 31.3 ($CH(CH_3)_2$), 34.6 ($CH(CH_3)_2$), 51.9 (CH_2), 54.0 (br, NCH_2), 121.4 (CH_{ar}), 136.2 (C^q), 144.5 (C^q), 150.4 (C^q), 193.9 (C^q), 203.5 (C^q). **HRMS:** m/z calculated for $C_{23}H_{36}NOS_2$ $(M+H)^+$ 406.2233, found 406.2243.

*1-(4-(2,4,6-triisopropylphenyl)-1,3-dithiol-2-ylidene)piperidinium tetrafluoroborate **2.14**.*

HBF_4 (48% in water, 18 mL) is added dropwise to a suspension of 2-oxo-2-(2,4,6-triisopropylphenyl)ethyl piperidine-1-carbodithioate (3 g, 7.4 mmol) in acetic anhydride (30 mL). After addition, clear slightly yellow solution is stirred 20 min at room

temperature. Water (30 mL) is added (white precipitate appears). Mixture is extracted with dichloromethane. Combined organic layers are washed with water, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting foam is triturated in diethyl ether (90 mL) for 30 min then precipitate is collected through filtration. White solid is washed with diethyl ether (3x30 mL) and dried under vacuum. 3.15 g (6.6 mmol, yield = 90%) are obtained. **M.P.** 242°C (dec). **^{1}H (300 MHz, $CDCl_3$) δ** 1.21 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.84-1.90 (m, 2H), 1.96-2.10 (m, 4H), 2.91 (sept, *J* = 6.8 Hz, 3H), 3.91 (t, *J* = 5.6 Hz, 2H), 4.00 (t, *J* = 5.6 Hz, 2H), 6.99 (s, 1H), 7.09 (s, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 21.5 (CH_2), 24.0 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 25.0 (CH_2), 25.1 ($CH(CH_3)_2$), 25.2 (CH_2), 31.1 ($CH(CH_3)_2$), 34.7 ($CH(CH_3)_2$), 56.6 (NCH_2), 57.7 (NCH_2), 119.8 ($CH_{dithiolium}$), 121.7 (C^q), 121.9 (CH_{ar}), 138.1 (C^q), 149.5 (C^q), 152.5 (C^q), 187.5 (C^q). **^{11}B (96 MHz, $CDCl_3$) δ** −1.1. **^{19}F (282 MHz, $CDCl_3$) δ** −154.2. **HRMS:** m/z calculated for $C_{23}H_{34}NS_2$ (M^+) 388.2127, found 388.2135.

*(2,4,6-triisopropylphenyl)ethynyl piperidine-1-carbodithioate **2.16**.*

THF (35 mL) is added to cold (–78°C) potassium bis(trimethylsilyl)amide (336 mg, 1.68 mol, 1 eq) and dithiolium salt (800 mg, 1.68 mmol, 1 eq). The solution is stirred 5 min at −78°C then allowed to warm to room temperature. THF is evaporated and the residue extracted with pentane (40 mL). Pentane is evaporated under vacuum yielding a pale yellow powder. Single crystals were obtained by slow evaporation of a saturated hexanes/diethyl ether (9:1) solution. 627 mg (1.62 mmol, yield = 96%) are obtained. **M.P.** 101°C. **^{1}H (500 MHz, C_6D_6) δ** 0.76-0.84 (m, 2H), 0.84-1.00 (m, 4H), 1.05 (d, *J* = 7.0 Hz, 6H), 1.23 (d, *J* = 7.0 Hz, 12H), 2.61 (sept, *J* = 7.0 Hz, 1H), 2.96 (br s, 2H), 3.73 (br s, 2H), 3.93 (sept, *J* = 7.0 Hz, 2H), 6.95 (s, 2H). **^{13}C (125 MHz, C_6D_6) δ** 24.1 ($CH(CH_3)_2$), 24.2 (CH_2), 24.4 ($CH(CH_3)_2$), 25.8 (br, CH_2), 32.8 ($CH(CH_3)_2$), 35.4 ($CH(CH_3)_2$), 52.5 (br, NCH_2), 53.4 (br, NCH_2), 81.5 (C^q), 103.2 (C^q), 119.4 (C^q), 121.2 (CH_{ar}), 150.8 (C^q), 152.8 (C^q), 190.3 (C^q). **IR (THF): ν (cm^{-1})** 2160.4 (C≡C). **HRMS:** m/z calculated for $C_{23}H_{34}NS_2$ $(M+H)^+$ 388.2127, found 388.2133.

*1-(4-(2,4,6-triisopropylphenyl)-1,3-dithiol-2-ylidene)piperidinium trifluoromethanesulfonate **2.14b**.*

Triflic acid (25 µL, 0.29 mmol, 1 eq) is added to a solution of ethynylcarbamodithioate **2** (112 mg, 0.29 mmol, 1 eq) in benzene (5 mL). Reaction is stirred 5 minutes then solvent is evaporated. Residue is washed with 3x15 mL of diethyl ether. Resulting white powder is dried under vacuum. Single crystals were obtained by vapor diffusion of diethyl ether in a solution of chloroform. 145 mg (0.27 mmol, yield = 93 %) are obtained. ^{1}H and ^{13}C NMR are identical to tetrafluoroborate salt. **^{19}F (282 MHz, $CDCl_3$) δ** −78.2.

*L-AuCl **2.17**.*

THF (5 mL) is added to a solid mixture of ethynylcarbamodithioate **2** (186 mg, 0.48 mmol, 1 eq) and tetrahydrothiophene gold chloride (154 mg, 0.48 mmol, 1 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the red residue washed with diethyl ether (4x10 mL). The resulting light pink powder is

dried under vacuum. Single crystals were obtained by slow evaporation of a saturated solution of chloroform. 203 mg (0.33 mmol, yield = 68 %) are obtained. **M.P.** 272°C. **^{1}H (500 MHz, $CDCl_3$) δ** 1.09 (d, *J* = 7.0 Hz, 6H), 1.21 (d, *J* = 7.0 Hz, 6H), 1.24 (d, *J* = 7.0 Hz, 6H), 1.66-1.72 (m, 2H), 1.74-1.86 (m, 4H), 2.82 (sept, *J* = 7.0 Hz, 1H), 2.94 (sept, *J* = 7.0 Hz, 2H), 3.60 (br s, 2H), 3.72 (br s, 2H), 6.92 (s, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.1 (*C*H_2), 24.1 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 25.1 (br, *C*H_2), 25.3 (CH(*C*H_3)$_2$), 30.6 (*C*H(CH$_3$)$_2$), 34.5 (*C*H(CH$_3$)$_2$), 55.1 (br, NCH$_2$), 57.5 (br, NCH$_2$), 121.5 (*C*H$_{ar}$), 126.9 (*C*^{q}), 131.4 (*C*^{q}), 146.9 (*C*-Au), 149.4 (*C*^{q}), 150.4 (*C*^{q}), 194.3 (*C*^{q}).

L-PdCl(η^3-allyl) ***2.18***.

THF (5 mL) is added to a solid mixture of ethynylcarbamodithioate **2** (119 mg, 0.31 mmol, 1 eq) and η^3-allyl palladium chloride dimer (56 mg, 0.16 mmol, 0.5 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the dark brown residue washed with diethyl ether (4x10 mL). The resulting white powder is dried under vacuum. Single crystals were obtained by layering hexanes on top of a saturated solution of chloroform. 146 mg (0.26 mmol, yield = 83 %) are obtained. **M.P.** 219°C. **^{1}H (500 MHz, $CDCl_3$) δ** 1.00 (d, *J* = 6.5 Hz, 6H), 1.07 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 9H), 1.60-1.67 (m, 2H), 1.69-1.78 (m, 4H), 2.25-2.30 (m, 1H), 2.76 (sept, *J* = 6.5 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.95 (sept, *J* = 6.5 Hz, 1H), 3.11 (sept, *J* = 6.5 Hz, 1H), 3.41-3.76 (m, 5H), 3.80 (d, *J* = 7.5 Hz, 1H), 4.71-4.82 (m, 1H), 6.86 (s, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.2 (*C*H_2), 23.8 (CH(*C*H_3)$_2$), 24.0 (CH(*C*H_3)$_2$), 25.0 (*C*H_2), 25.2 (CH(*C*H_3)$_2$), 25.3 (CH(*C*H_3)$_2$), 30.2 (*C*H(CH$_3$)$_2$), 34.3 (*C*H(CH$_3$)$_2$), 50.2 (*C*H_2-allyl), 54.2 (br, NCH$_2$), 57.2 (br, NCH$_2$), 70.5 (*C*H_2-allyl), 113.1 (*C*H-allyl), 120.7 (*C*H$_{ar}$), 120.8 (*C*H$_{ar}$), 128.1 (*C*^{q}), 129.9 (*C*^{q}), 149.0 (*C*^{q}), 149.5 (*C*^{q}), 150.0 (*C*^{q}), 160.3 (*C*-Pd), 196.1 (*C*^{q}).

L-$RuCl_2$(p-cym) ***2.19***.

THF (5 mL) is added to a solid mixture of ethynylcarbamodithioate **2** (192 mg, 0.49 mmol, 1 eq) and *p*-cymene ruthenium dichloride dimer (151 mg, 0.23 mmol, 0.5 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the dark brown residue washed with diethyl ether (4x10 mL). The resulting orange powder is dried under vacuum. 238 mg (0.34 mmol, yield = 69 %) are obtained. **M.P.** 217°C. **^{1}H (500 MHz, $CDCl_3$) δ** 1.14 (d, *J* = 7.0 Hz, 6H), 1.15 (d, *J* = 7.0 Hz, 6H), 1.30 (d, *J* = 7.0 Hz, 6H), 1.44 (d, *J* = 7.0 Hz, 6H), 1.66-1.72 (m, 2H), 1.75-1.83 (m, 4H), 1.79 (s, 3H), 2.73 (sept, *J* = 7.0 Hz, 1H), 2.97 (sept, *J* = 7.0 Hz, 1H), 3.47 (sept, *J* = 7.0 Hz, 1H), 3.60 (br s, 4H), 4.22 (sept, *J* = 7.0 Hz, 1H), 4.41-4.52 (m, 2H), 5.27 (d, *J* = 6.0 Hz, 2H), 7.13 (s, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 18.6 (*C*H_3), 22.2 (*C*H_2), 22.6 (CH(*C*H_3)$_2$), 23.0 (CH(*C*H_3)$_2$), 24.1 (CH(*C*H_3)$_2$), 25.0 (*C*H_2), 27.7 (CH(*C*H_3)$_2$), 30.2 (*C*H(CH$_3$)$_2$), 30.4 (*C*H(CH$_3$)$_2$), 34.4 (*C*H(CH$_3$)$_2$), 53.6 (br, NCH$_2$), 55.6 (br, NCH$_2$), 82.4 (br, *C*H$_{ar}$), 86.9 (br, *C*H$_{ar}$), 97.6 (*C*$^{q}_{p\text{-cym}}$), 98.0 (*C*$^{q}_{p\text{-cym}}$), 120.9 (*C*H$_{ar}$), 124.7 (*C*^{q}), 129.3 (*C*^{q}), 150.8 (*C*^{q}), 157.8 (*C*-Ru), 192.7 (*C*^{q}).

L-RhCl(COD) ***2.20***.

THF (5 mL) is added to a solid mixture of ethynylcarbamodithioate **2** (166 mg, 0.43 mmol, 1 eq) and 1,5-cyclooctadiene rhodium chloride dimer (105 mg, 0.21 mmol, 0.5 eq) at room temperature. Solution is stirred 14 hours at room temperature. Solvent is evaporated and the dark brown residue washed with diethyl ether (4x10 mL). The resulting light yellow powder is dried under vacuum. 181 mg (0.28 mmol, yield = 66 %) are obtained. **M.P.** 194°C (dec). **^{1}H (500 MHz, $CDCl_3$) δ** 1.01 (d, *J* = 7.0 Hz, 6H), 1.18 (d, *J* = 7.0 Hz, 6H), 1.28 (d, *J* = 7.0 Hz, 6H), 1.47-1.55 (m, 2H), 1.55-1.62 (m, 2H), 1.62-1.67 (m, 2H), 1.68-1.77 (m, 4H), 1.78-1.87 (m, 2H), 1.94-2.04 (m, 2H), 2.83 (sept, *J* = 7.0 Hz, 1H), 3.14 (sept, *J* = 7.0 Hz, 2H), 3.18-3.23 (m, 2H), 3.53 (br s, 4H), 4.58-4.66 (m, 2H), 6.93 (s, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.5 (CH_2), 24.2 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 25.1 (CH_2), 26.1 ($CH(CH_3)_2$), 29.1 (CH_2, COD), 30.6 ($CH(CH_3)_2$), 32.9 (CH_2, COD), 34.6 ($CH(CH_3)_2$), 54.1 (br, NCH_2), 56.8 (br, NCH_2), 69.6 (d, $J_{C\text{-}Rh}$ = 13.6 Hz, *C*H, COD), 94.7 (d, $J_{C\text{-}Rh}$ = 7.6 Hz, *C*H, COD), 121.1 (CH_{ar}), 122.6 (C^q), 128.1 (C^q), 150.0 (C^q), 150.4 (C^q), 164.2 (d, $J_{C\text{-}Rh}$ = 41 Hz, *C*-Rh), 196.4 (C^q).

L-RhCl(CO)$_2$ ***2.21***.

Carbon monoxide is bubbled in a solution of L-RhCl(COD) **8** (181 mg, 0.28 mmol) in CH_2Cl_2 (5 mL) for 20 minutes. Solvent is evaporated and the residue washed with hexanes (2x10 mL). The resulting light yellow powder is dried under vacuum. Single crystals were obtained by slow evaporation of a saturated solution of chloroform/hexanes (5:1) at room temperature. 156 mg (0.27 mmol, yield = 96 %) are obtained. **M.P.** 186°C (dec). **^{1}H (500 MHz, $CDCl_3$) δ** 1.06 (d, *J* = 6.5 Hz, 6H), 1.18 (d, *J* = 6.5 Hz, 6H), 1.26 (d, *J* = 6.5 Hz, 6H), 1.67-1.74 (m, 2H), 1.75-1.88 (m, 4H), 2.83 (sept, *J* = 6.5 Hz, 1H), 3.09 (sept, *J* = 6.5 Hz, 2H), 3.57 (br s, 2H), 3.71 (br s, 2H), 6.95 (s, 2H). **^{13}C (125 MHz, $CDCl_3$) δ** 22.3 (CH_2), 23.9 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 25.1 (CH_2), 25.9 ($CH(CH_3)_2$), 30.4 ($CH(CH_3)_2$), 34.4 ($CH(CH_3)_2$), 54.5 (br, NCH_2), 57.2 (br, NCH_2), 121.5 (CH_{ar}), 127.8 (C^q), 130.2 (C^q), 149.9 (C^q), 150.7 (C^q), 157.9 (d, $J_{C\text{-}Rh}$ = 35 Hz, *C*-Rh), 182.9 (d, $J_{C\text{-}Rh}$ = 78 Hz, *C*O), 185.6 (d, $J_{C\text{-}Rh}$ = 54 Hz, *C*O), 195.1 (C^q). **IR (CH_2Cl_2): ν (cm^{-1})** 2068.4 (CO), 1993.2 (CO).

3) Crystallographic Data

Crystal data and structure refinement for 2.14b.

Empirical formula	$C_{24}H_{34}F_3NO_3S_3$	
Formula weight	537.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2(1)	
Unit cell dimensions	a = 8.337(4) Å	α= 90°
	b = 18.426(9) Å	β= 103.526(6)°
	c = 8.901(4) Å	γ = 90°
Volume	1329.3(11) Å^3	
Z	2	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.326 mm^{-1}	
F(000)	568	

Crystal size	0.32 x 0.17 x 0.13 mm^3
Theta range for data collection	2.35 to 29.07°
Index ranges	-9<=h<=11, -24<=k<=24, -11<=l<=10
Reflections collected	10208
Independent reflections	6054 [R(int) = 0.0310]
Completeness to theta = 29.07°	90.2 %
Max. and min. transmission	0.9589 and 0.9029
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6054 / 1 / 376
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1238
R indices (all data)	R1 = 0.0559, wR2 = 0.1300
Absolute structure parameter	0.01(8)
Largest diff. peak and hole	0.549 and -0.474 e.$Å^{-3}$

Crystal data and structure refinement for 2.16.

Empirical formula	C40.90 H59.10 N2 O0.30 S3.70	
Formula weight	702.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna21	
Unit cell dimensions	a = 17.6150(8) Å	α= 90°.
	b = 10.6460(7) Å	β= 90°.
	c = 23.5500(14) Å	γ = 90°.
Volume	4416.3(4) $Å^3$	
Z	4	
Density (calculated)	1.056 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	1520	
Crystal size	0.24 x 0.11 x 0.07 mm^3	
Theta range for data collection	1.44 to 21.09°.	
Index ranges	-17<=h<=17, -10<=k<=10, -23<=l<=23	
Reflections collected	13379	
Independent reflections	4642 [R(int) = 0.0621]	
Completeness to theta = 21.09°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4642 / 593 / 591	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1843	
R indices (all data)	R1 = 0.0906, wR2 = 0.1967	
Absolute structure parameter	0(6)	
Largest diff. peak and hole	0.572 and -0.335 e.$Å^{-3}$	

Crystal data and structure refinement for 2.17.

Empirical formula	$C_{23}H_{33}AuClNS_2$
Formula weight	620.04
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	C2/c	
Unit cell dimensions	a = 36.3520(17) Å	α= 90°
	b = 8.4521(4) Å	β= 104.142(2)°
	c = 16.2723(7) Å	γ = 90°
Volume	4848.2(4) $Å^3$	
Z	8	
Density (calculated)	1.699 Mg/m^3	
Absorption coefficient	6.361 mm^{-1}	
F(000)	2448	
Crystal size	0.32 x 0.14 x 0.10 mm^3	
Theta range for data collection	2.31 to 30.51°	
Index ranges	-51<=h<=48, -12<=k<=12, -22<=l<=23	
Reflections collected	20276	
Independent reflections	7333 [R(int) = 0.0367]	
Completeness to theta = 30.51°	99.1 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.5688 and 0.2354	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7333 / 0 / 259	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0902	
R indices (all data)	R1 = 0.0504, wR2 = 0.0954	
Largest diff. peak and hole	4.372 and -1.729 $e.Å^{-3}$	

Crystal data and structure refinement for 2.18.

Empirical formula	$C_{27}H_{37}Cl_4NPdS_2$	
Formula weight	687.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.4843(11) Å	α= 90°
	b = 15.8792(11) Å	β= 95.076(4)°
	c = 12.6282(10) Å	γ = 90°
Volume	3092.8(4) $Å^3$	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	1.098 mm^{-1}	
F(000)	1408	
Crystal size	0.97 x 0.32 x 0.14 mm^3	
Theta range for data collection	1.84 to 30.51°	
Index ranges	-22<=h<=21, -22<=k<=22, -18<=l<=11	
Reflections collected	41320	
Independent reflections	9447 [R(int) = 0.0356]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.8615 and 0.4156	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9447 / 0 / 374	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0688	
R indices (all data)	R1 = 0.0407, wR2 = 0.0750	

Largest diff. peak and hole	0.776 and -0.543 e.Å^{-3}

Crystal data and structure refinement for 2.21.

Empirical formula	$C_{26}H_{34}Cl_4NO_2RhS_2$	
Formula weight	701.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.568(6) Å	α= 90°
	b = 16.027(6) Å	β= 96.226(3)°
	c = 12.709(5) Å	γ = 90°
Volume	3152(2) Å^3	
Z	4	
Density (calculated)	1.478 Mg/m^3	
Absorption coefficient	1.037 mm^{-1}	
F(000)	1432	
Crystal size	0.28 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.83 to 29.32°	
Index ranges	-21<=h<=20, -21<=k<=17, -17<=l<=17	
Reflections collected	26018	
Independent reflections	8042 [R(int) = 0.0343]	
Completeness to theta = 29.32°	93.1 %	
Max. and min. transmission	0.9034 and 0.7600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8042 / 0 / 358	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0562	
R indices (all data)	R1 = 0.0264, wR2 = 0.0597	
Largest diff. peak and hole	0.545 and -0.507 e.Å^{-3}	

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CHAPTER 3:

Bond activation with a simple alkynyldithioate

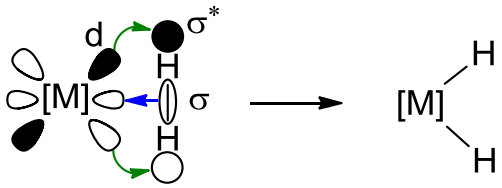
Adapted from:

G. Ung, G. D. Frey, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2011**, *50*, 9923–9925

and G. Ung, G. Bertrand, *Chem. Eur. J.* **2012**, *18*, 12955–12957

Introduction

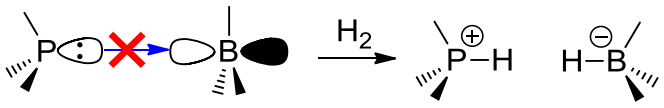
Strong bond splitting is the key step in most catalytic chemical transformations. For many years, it has been a task performed quasi-exclusively by transition metal complexes, and it is of paramount importance to find alternatives that are less costly and more environmentally friendly. The activation of a strong bond requires that the pair of bonding electrons is perturbed in some way so as to form a chemically active species. For transition metal complexes the bond splitting results from the primary interaction between a vacant orbital at the metal and a bonding orbital of the substrate, with concomitant backdonation from a filled d orbital at the metal to an antibonding orbital of the bound substrate (Scheme **S3. 1**).[1]



Scheme S3. 1: Schematic representation of the activation of dihydrogen with a transition metal.

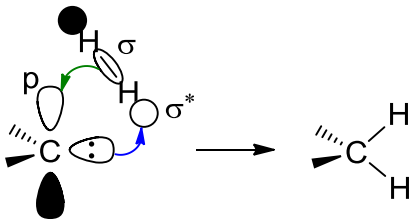
Recent works have shown that besides transition metals, other reactive chemical species are able to split enthalpically strong bonds, using various modes of activation. The discovery by Stephan and co-workers in 2006[2] of the so-called frustrated Lewis pairs (FLPs) has led to the emergence of a new era in the chemistry of bond activation.[3] The concept of FLPs is astonishingly simple: they consist of a combination of a Lewis base and a Lewis acid, which have a low binding affinity. The "frustration" is mainly achieved by preventing the lone pair of the Lewis base to interact with the empty orbital of the

Lewis acid either with steric encumbrance or by placing both components in a rigid environment. Additionally, these systems always involve, with one exception,[4] strongly acidic polyfluorinated boranes or alanes, in combination with rather weak bases. The activation of the substrates is therefore likely to be electrophilic in nature, similar to transition metals, although the true mechanism is still a source of debate.[5]



Scheme S3. 2: Schematic representation of a frustrated Lewis pair and activation of dihydrogen.

In contrast, singlet carbenes[6] and heavier analogues[7] are strongly basic, and consequently act first as nucleophiles towards the substrates. DFT calculations have demonstrated that the lone pair of a singlet cyclic (alkyl)(amino) carbene initially interacts with the σ* orbital of dihydrogen, allowing splitting of the latter.[8]

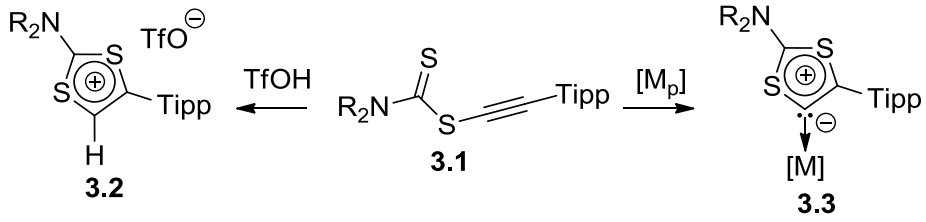


Scheme S3. 3: Schematic representation of the activation of dihydrogen with a singlet carbene.

In this chapter, we will show that an apparently benign ethynyl dithiocarbamate is able to cleave a variety of enthalpically strong bonds. The mode of activation involves the cooperative effect of both a nucleophilic and an electrophilic carbon center.

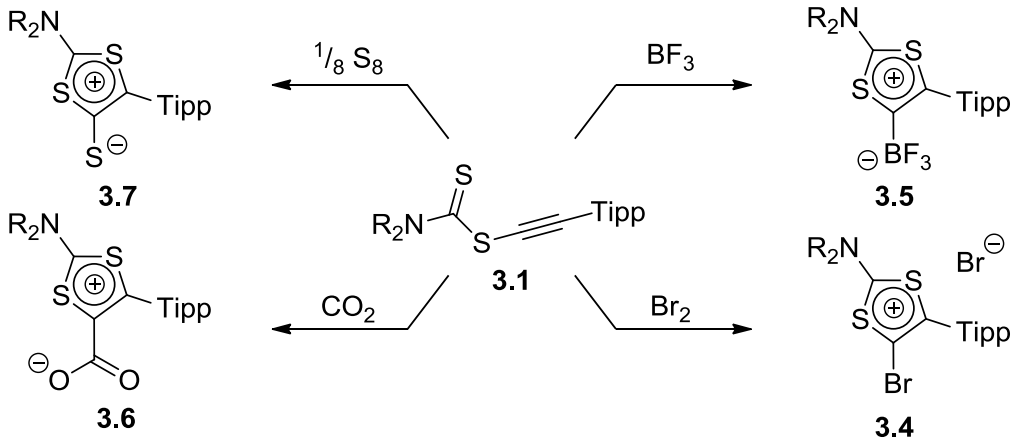
A) Bond activation with ethynyl dithiocarbamate.

We have shown in Chapter 2 that trifluoromethanesulfonic acid and a variety of transition metal complexes induce the ring closure of ethynyl dithiocarbamate **3.1**, affording the dithiolium salt **3.2** and transition metal complexes **3.3**, respectively (Scheme **S3. 4**).



Scheme S3. 4: Reactivity of ethynyl dithiocarbamate **3.1** with a strong acid and transition metals observed in Chapter 2.

These results prompted us to study the extent of the electrophile-induced ring closing process of ethynyl dithiocarbamate (Scheme **S3. 5**). As expected, strong electrophiles such as bromine and trifluoroborane instantaneously react with **3.1** at room temperature giving the corresponding dithiolium salt **3.4** (Figure **F3. 1**, left) and zwitterion **3.5**. More surprisingly, carbon dioxide and elemental sulfur, which are far less electrophilic, also induce the cyclization to zwitterions **3.6** (Figure **F3. 1**, middle) and **3.7** (Figure **F3. 1**, right).



Scheme S3. 5: Reaction of ethynyl dithiocarbamate **3.1** with electrophiles.

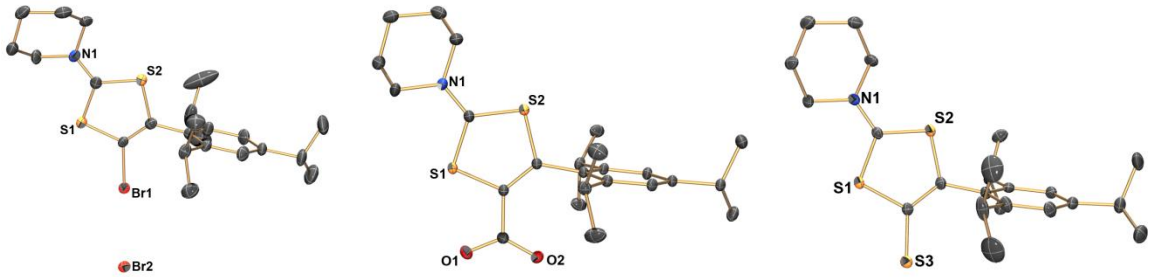


Figure F3. 1: Structure of **3.4** (left), **3.6·(CH_2Cl_2)** (middle) and **3.7** (right) in the solid state, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

The reaction with carbon dioxide and elemental sulfur, which are known to readily react with singlet carbenes[9] and mesoionic carbenes[10] and very unlikely to interact with the carbon–carbon triple bond of **3.1**, at least at room temperature,[11] prompted us to reconsider the true nature of ethynyl dithiocarbamate **3.1**. Thus, we postulated the existence of an equilibrium between the linear **3.1** and the cyclic dithiol-5-ylidene **3.1'**. Calculations at the M05-2X/dev2-SVP level of theory predict that **3.1'** is 11.4 kcal.mol^{-1}

higher in energy than its acyclic form **3.1**, with a small energy barrier (1.6 kcal.mol^{-1}) for the ring opening process (Figure **F3. 2**).

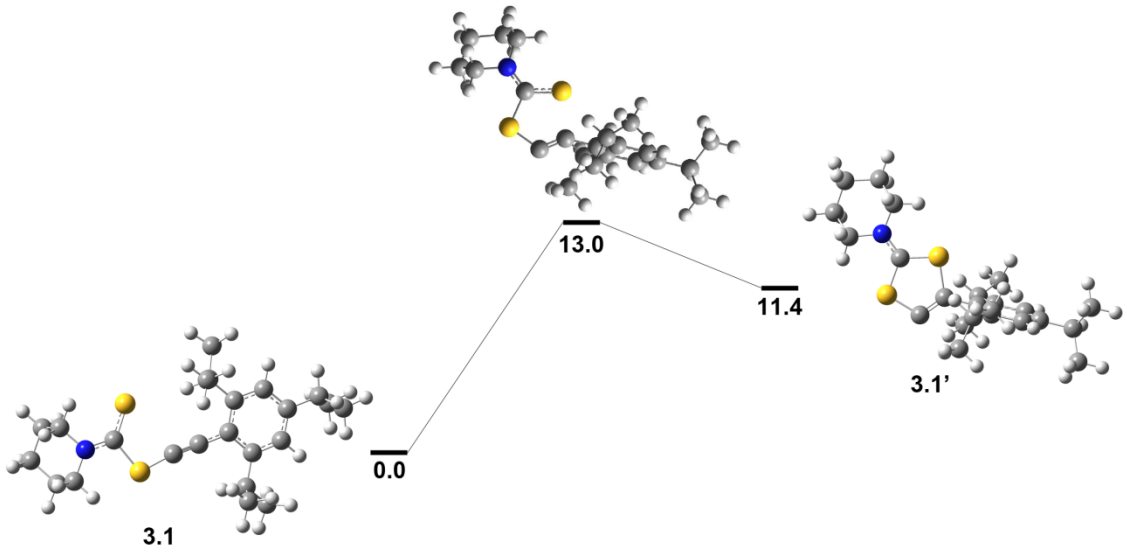
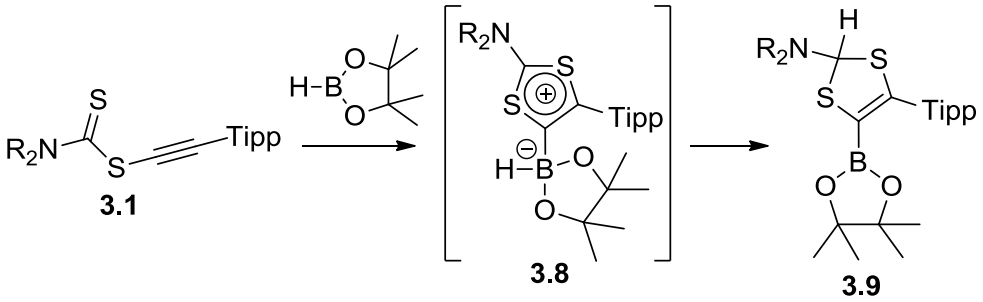


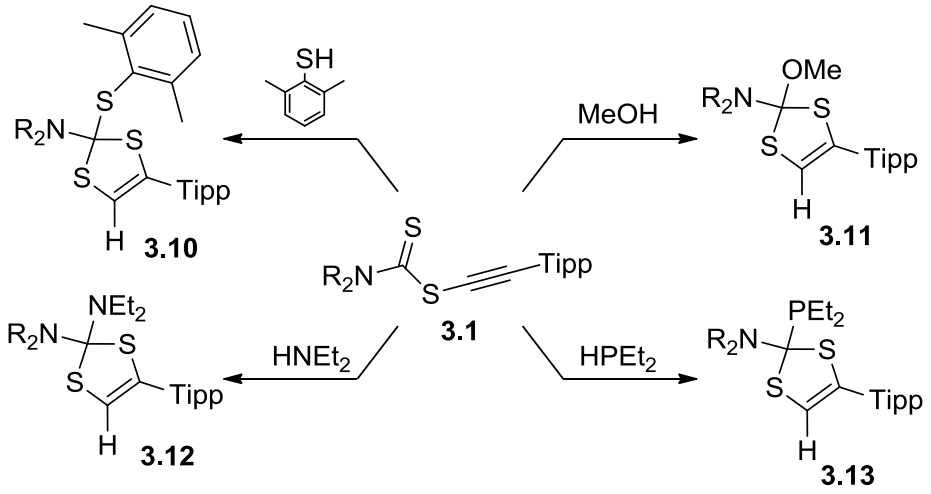
Figure F3. 2: Calculated energies for the equilibrium between ethynyl dithiocarbamate **3.1** and dithiol-5-ylidene **3.1'**.

Decreasing further the electrophilicity of the substrate, pinacolborane was tested and, at room temperature, it does not only induce the cyclisation of **3.1**, but a B–H bond cleavage also occurs (Scheme **S3. 6**). In the ^{11}B NMR spectrum, no coupling was detected with any protons, and in the ^{1}H NMR spectrum, all signals were inequivalent, indicating the creation of a stereogenic center. Lastly, in the ^{13}C{^{1}H} NMR spectrum, a new *C*–H signal was observed at 83.1 ppm. The formation of adduct **3.9** can be explained by a hydride migration from the putative, first formed, zwitterion **3.8**. This pointed us towards the electrophilic nature of the carbon center at position 2 (in between the two sulfur atoms).



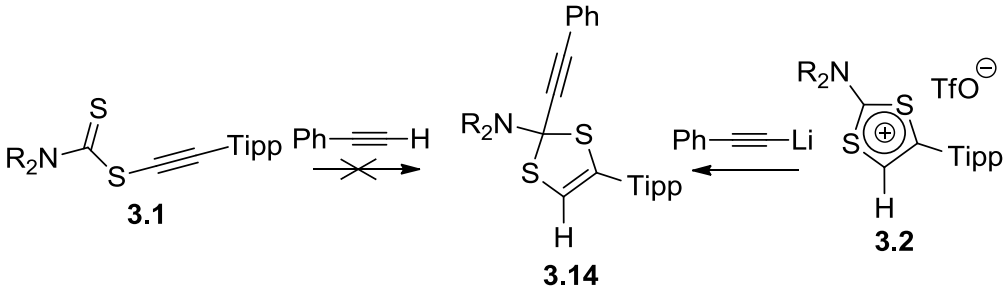
Scheme S3. 6: B–H bond activation with ethynyl dithiocarbamate.

The stupefying ring closure process observed with very weak Lewis acids encouraged us to examine the reactivity of **3.1** with weak Brønsted acids. We reacted **3.1** with 2,6-dimethylthiophenol and observed the clean formation of adduct **3.10** where the thiophenolate is bonded to the carbon at position 2 (Scheme **S3. 7**). In the ^{13}C NMR spectrum, we observed a new *C*–H resonance at 114.1 ppm as well as a new quaternary signal at 83.8 ppm. In addition, both ^{1}H and $^{13}C\{^{1}H\}$ spectra displayed inequivalent signals, indicating the sp^3 hybridization of the carbon at position 2. With this promising result, we reduced the acidity of the substrate and reacted **3.1** with methanol, and observed the activation of the O–H bond yielding adduct **3.11**. To test the limits of ethynyl dithiocarbamate, we targeted the very weakly Brønsted acidic diethylamine and even diethylphosphine, and adducts **3.12** and **3.13** were obtained in moderate to good yields (Scheme **S3. 7**).



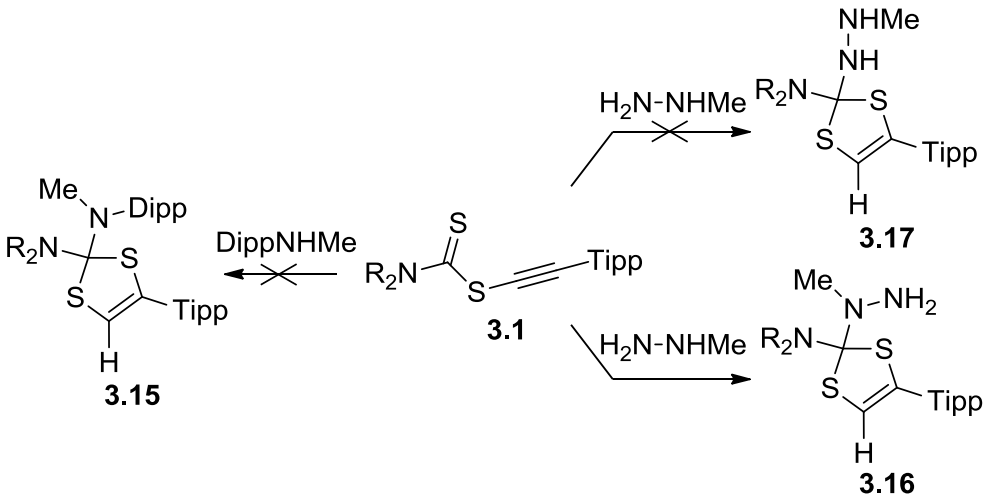
Scheme S3. 7: Reaction of ethynyl dithiocarbamate **3.1** with weak Brønsted acids.

It is difficult to believe that methanol, and even diethyl-amine or -phosphine are acidic enough to protonate the carbon–carbon triple bond of **3.1** or the putative dithiol-5-ylidene **3.1'** in equilibrium. Additionally, phenylacetylene, which is more acidic, does not react with **3.1** even in forcing conditions. We verified that lithium phenylacetylide reacts with dithiolium salt **3.2** to give **3.14**, demonstrating that the activation process does not occur by deprotonation followed by addition (Scheme **S3. 8**).



Scheme S3. 8: Reactivity of ethynyl dithiocarbamate **3.1** with phenylacetylene.

Since the observed reactivity of **3.1** does not parallel the acidity of the substrates, we postulated that there is a collaborative effect between the nucleophilic and electrophilic centers of **3.1**. Indeed, all the substrates that were tested previously possess lone pairs, with the exception of phenylacetylene. This suggests that a heteroatom lone pair of the substrate has to interact with the electrophilic center of **3.1** to allow for a reaction. We chose to react **3.1** with a more bulky and more acidic amine such as *N*-(2,6-diisopropylphenyl)-*N*-methylamine, and no reaction was observed (Scheme **S3. 9**). A confirmation of this hypothesis was brought by the reaction of **3.1** with methyl hydrazine, which cleanly led to the formation of **3.16**. This adduct, which has been characterized by single crystal X-ray diffraction studies (Figure **F3. 3**), features the more basic nitrogen atom bonded to the electrophilic C-2 center. Clearly, a simple deprotonation of hydrazine would occur at the non-substituted nitrogen, which would have led to adduct **3.17** (Scheme **S3. 9**).



Scheme S3. 9: Reaction of ethynyl dithiocarbamate with various amines, demonstrating the need of an available lone pair to allow activation.

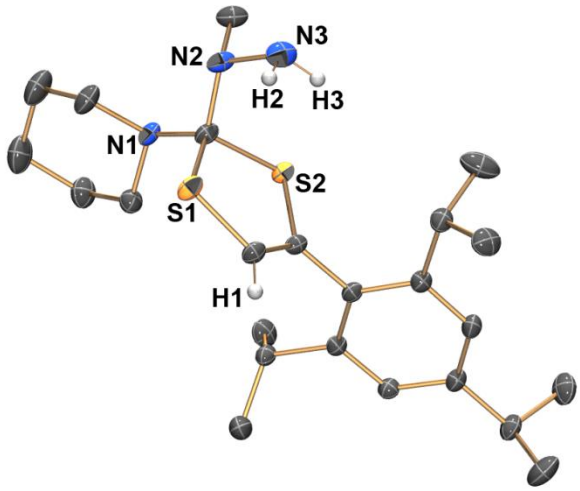
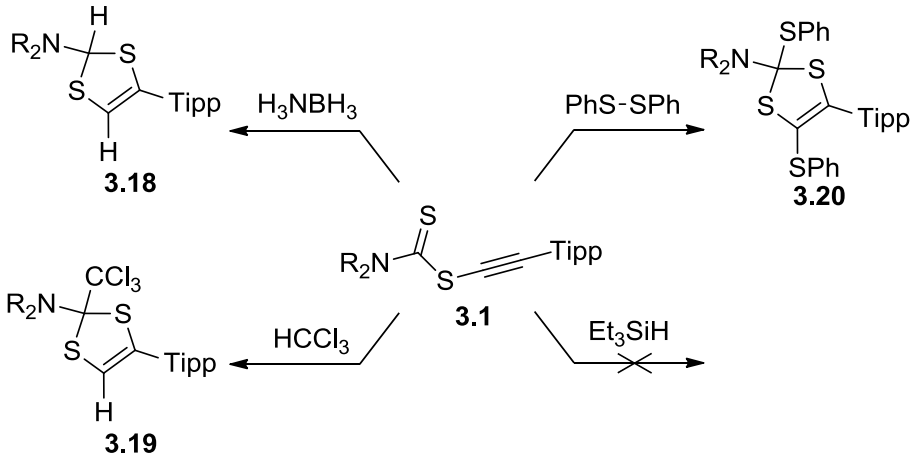


Figure F3. 3: Structure of **3.16** in the solid state, hydrogen atoms, except H1, H2 and H3 are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

Having uncovered some clues about the mode of activation of ethynyl dithiocarbamate, we sought to activate other types of strong bonds. Not surprisingly, the reaction of **3.1** with the non-polarized dihydrogen did not occur. However, reaction of **3.1** with ammonia-borane (a source of "polar" H_2) proceeded cleanly to afford adduct **3.18**. The more polar C–H bond of chloroform is also activated by **3.1** to yield adduct **3.19** (Scheme **S3. 10**). Reaction with non-polarized bonds is also possible, provided the substrate possesses a heteroatom lone pair: for example, compound **3.1** is able to cleave diphenyldisulfide to give adduct **3.20** which structure was proven by X-ray crystallography (Figure **F3. 4**). In contrast, triethylsilane, possessing neither a sufficiently polarized bond nor a heteroatom lone pair, is totally inert towards **3.1**.



Scheme S3. 10: Activation of small molecules with ethynyl dithiocarbamate **3.1**.

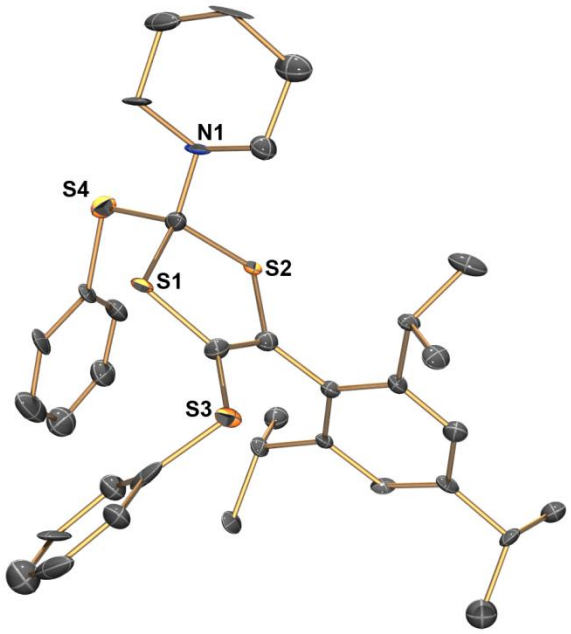
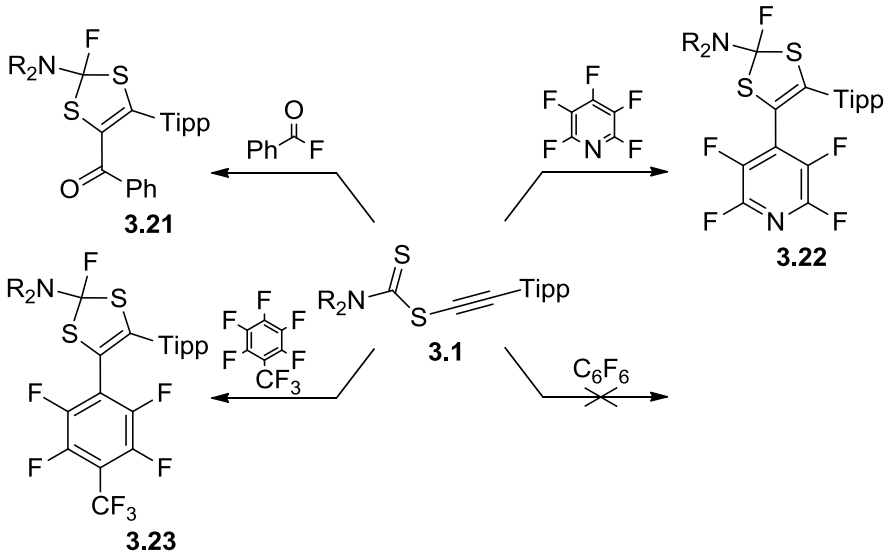


Figure F3. 4: Structure of **3.20** in the solid state, hydrogen atoms are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

To test the limits of our activator, we then targeted C–F bonds, which are among the strongest organic bonds, significantly stronger than C–H bonds, yet more polarized. Their activation usually requires transition metals[12,13] or strong Lewis acids.[14] Addition of

the very polarized benzoyl fluoride to ethynyl dithiocarbamate **3.1** yielded adduct **3.21** (Scheme **S3. 11**). In the ^{19}F NMR spectrum, a new singlet was detected at −33 ppm. Additionally, a doublet ($^{1}J_{C–F}$ = 274 Hz) was observed in the $^{13}C\{^{1}H\}$ NMR spectrum at 135.7 ppm. Finally, both ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra displayed unsymmetrical signals. Decreasing the polarity of the C–F bond, we reacted **3.1** with pentafluoropyridine and octafluorotoluene, yielding adducts **3.22** and **3.23**, respectively (Scheme **S3. 11**). Both compounds exhibit similar resonances in ^{19}F NMR (singlets at −36 and −38 ppm, respectively) and in $^{13}C\{^{1}H\}$ NMR (doublets $^{1}J_{C–F}$ = 274 and 272 Hz at 136.4 and 136.2 ppm, respectively). Ethynyl dithiocarbamate **3.1** was however unable to activate hexafluorobenzene, which was ascribed to the lack of polarity of the latter. Single crystals of **3.23** were obtained from a saturated solution in 1,4-dioxane and the X-ray diffraction study revealed that the fluorine atom F1 is covalently bonded to the carbon atom ($d_{C–F}$ = 1.404(5) Å) (Figure **F3. 5**).



Scheme S3. 11: C–F bond activation with ethynyl dithiocarbamate **3.1**.

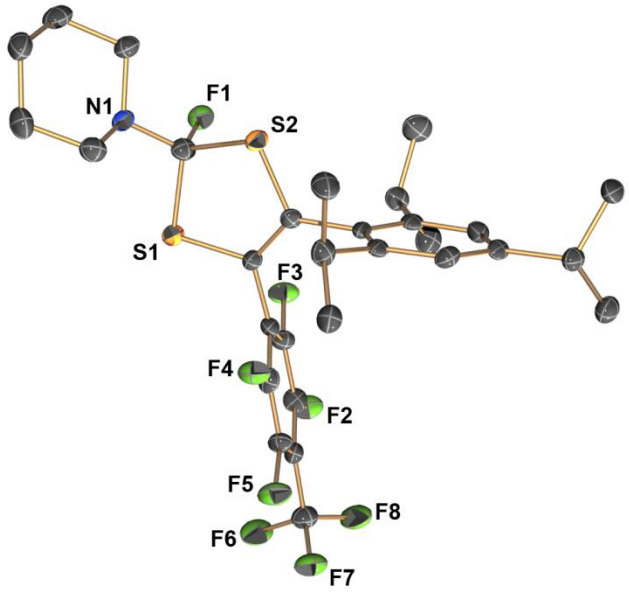


Figure F3. 5: Structure of **3.23·($C_4H_8O_2$)** in the solid state, hydrogen atoms and co-crystallized solvent molecule are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

B) Chemistry of the adducts.

Having in hands a large variety of products of activation, we sought to examine their potential as reagents. Two categories of reagents can be distinguished: the betaine adducts such as **3.6** and **3.7**, and the 2,2-disubstituted dithioles schematically represented by **3.A** (Figure **F3. 6**). Because of the presence of three heteroatoms surrounding the carbon center at position 2, the substituent X of **3.A** should be rather labile. On the other hand, the bond between the carbon at position 5 and the other part of the substrate (Y) should be easily cleaved because of the ring-opening process, which leads to the non-basic ethynyl dithiocarbamate **3.1**.

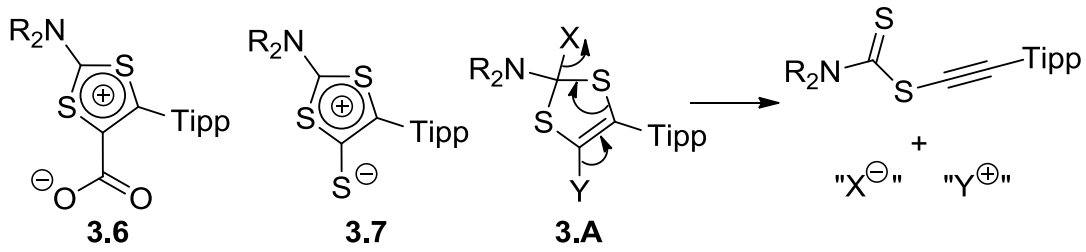
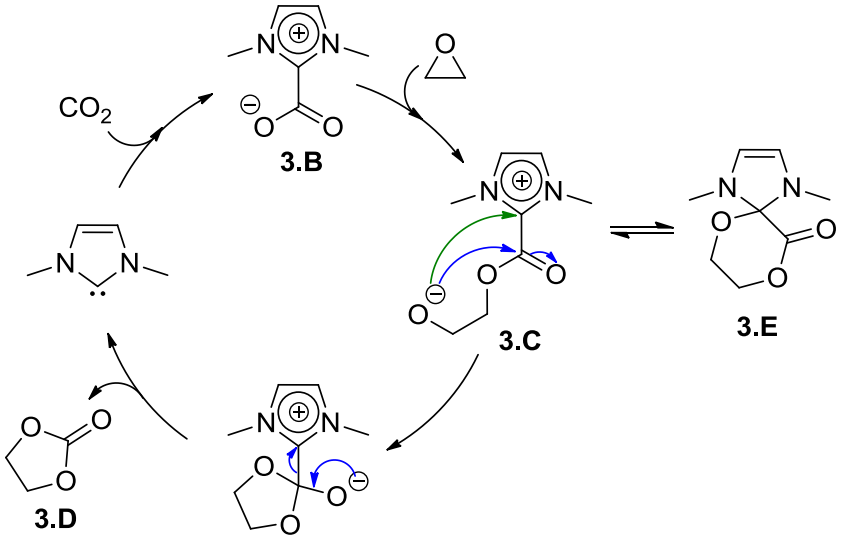


Figure F3. 6: Adducts discussed in this chapter and schematic representation of the potential release of both X and Y fragments.

1) Betaine adducts.

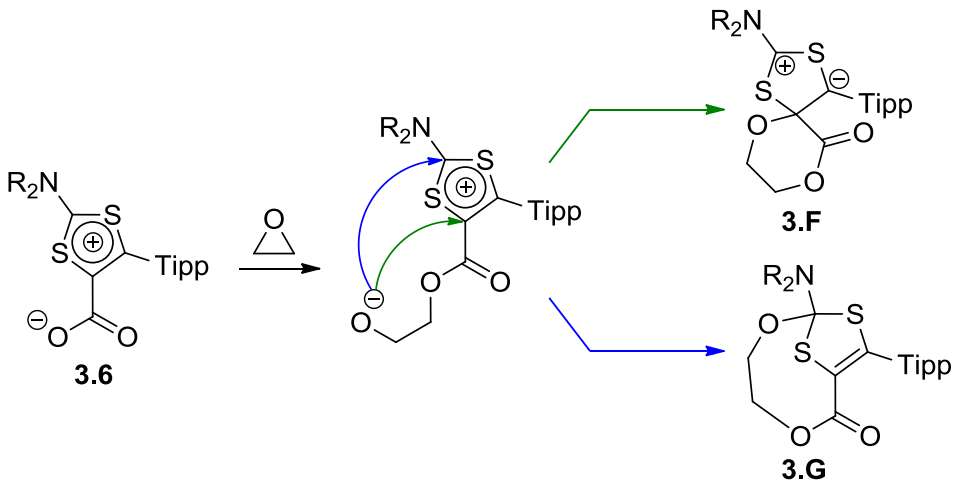
a) CO_2 adduct

The synthesis and reactivity of imidazol-2-ylidenes·CO_2 betaines **3.B** has been studied and reviewed recently.[15] One elegant use of these types of adduct is the catalytic coupling of carbon dioxide with epoxides.[16] In the proposed mechanism, the betaine **3.B** attacks the epoxide generating the zwitterion **3.C**. The anion can then attack the carbonyl group, and after addition-elimination, the product **3.D** is generated, liberating the free imidazol-2-ylidene that can react with carbon dioxide to complete the catalytic cycle (Scheme **S3. 12**).



Scheme S3. 12: Catalytic formation of cyclic carbonate **3.D**.

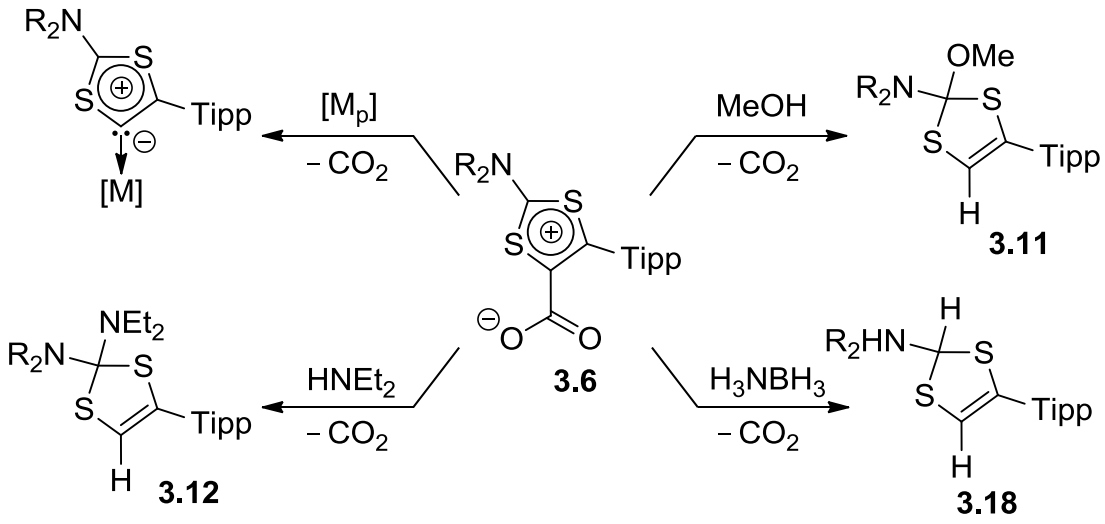
Although rather efficient, this reaction is conducted in harsh conditions (*e.g.* 2.0 MPa of CO_2 at 120 °C for 24 hours), which are required to overcome the reversible formation of the thermodynamically favored spiro compound **3.E** (Scheme **S3. 12**). Because of the mesoionic character of the dithiol-5-ylidene-betaine **3.6**, the formation of a zwitterionic spiro adduct **3.F** is very unlikely. In addition, the attack to the previously observed electrophilic center, yielding a very strained [5.2.1]bicyclic compound **3.G**, is also unfavored (Scheme **S3. 13**).



Scheme S3. 13: Unlikely ring closing pathways with a mesoionic carbene-betaine adduct.

The reaction of betaine **3.6** with 1 equivalent of 2,2-dimethyloxirane was very sluggish and only 5% of a new product could be observed. The conversion was increased slightly under heating conditions and with excess epoxide, but completion was never observed. This is probably due to the reversibility of the epoxide opening reaction. In order to drive the equilibrium, we used the betaine **3.6** in catalytic conditions using excess epoxide and CO_2, but no new products were detected.

Similarly to imidazol-2-ylidenes·CO_2 betaine,[17] adduct **3.6** can also react with transition metals yielding the corresponding dithiol-5-ylidene-transition metal complex with the loss of carbon dioxide. More surprisingly, the reaction with small molecules such as diethylamine, methanol or ammonia-borane also yields the decarboxylated cyclic adducts **3.12**, **3.11** and **3.18**, respectively (Scheme **S3. 14**).

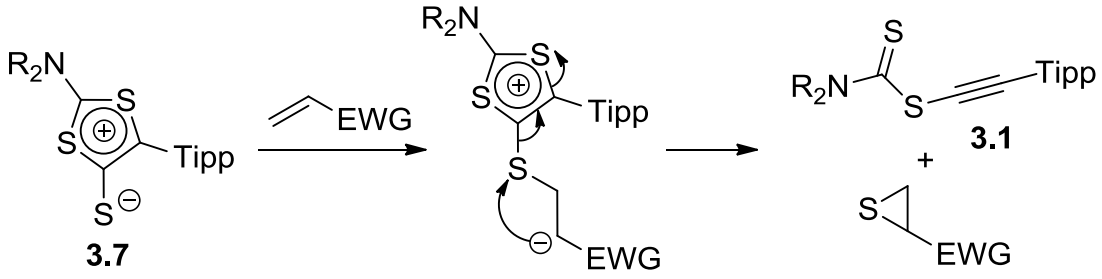


Scheme S3. 14: Decarboxylative reactivity of betaine adduct **3.6** with transition metals and small molecules.

The loss of CO_2 prompted us to study other catalytic systems that would involve the use of **3.6** as an activated CO_2 source. The major drawback of such system is that it requires substrates that do not react with ethynyl dithiocarbamate **3.1** to allow for the regeneration of **3.6**. Since the scope of bond activation with compound **3.1** is very broad, we were limited to only a few substrates. We envisioned studying the hydrosilylation of carbon dioxide into silyl esters of formic acid, using various silanes. Stoichiometric reaction of betaine **3.6** with triethylsilane, triethoxysilane, or diphenylsilane did not occur, even under heating conditions. However, compound **3.6** reacted rather cleanly with phenylsilane at 65 °C, yielding a new product exhibiting unsymmetrical ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Additionally, a singlet at 5.92 ppm indicated that a hydride attacked the electrophilic carbon at the position 2 of the dithiole ring. This carbon center is therefore more electrophilic than the carboxylate carbon, which obviously limits the applications of the adduct **3.6** as an organocatalyst.

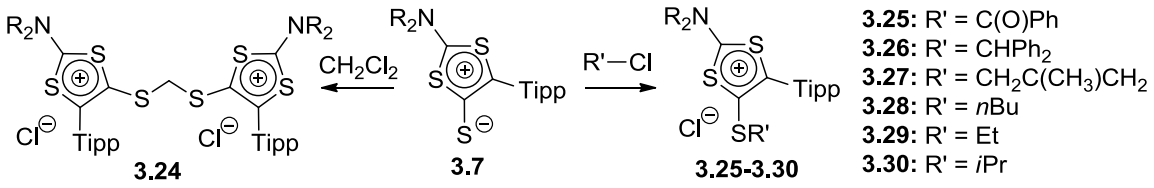
b) Sulfur adduct

Parallel to the study done with betaine **3.6**, we also examined the reactivity of the sulfur adduct **3.7** as a potential sulfur transferring reagent. Because of the munchnone-type structure of adduct **3.7**, the nucleophilicity of the negatively charged sulfur atom should be enhanced. Additionally, nucleophilic attack on that sulfur atom can potentially release the non-basic ethynyl dithiocarbamate **3.1**. The ambiphilic nature of betaine **3.7** prompted us to study its reactivity as a thiiranation reagent (Scheme **S3. 15**).



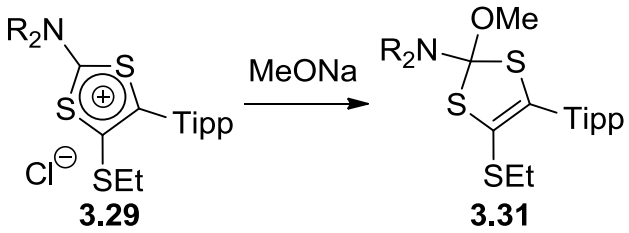
Scheme S3. 15: Targeted thiiranation with betaine **3.7**.

The nucleophilicity of adduct **3.7** was discovered serendipitously. Dissolving betaine **3.7** in dichloromethane led to a rapid change of color from bright red to pale yellow. After work-up, the product displayed a new singlet at 4.59 ppm in the ^{1}H spectrum and a new CH_2 signal at 42.9 ppm in the $^{13}C\{^{1}H\}$ spectrum, indicating that betaine **3.7** displaced both chlorine atoms of dichloromethane, yielding bis-salt **3.24** (Scheme **S3. 16**). The nucleophilic potential of **3.7** was further assessed by reaction with various electrophiles such as benzoyl chloride, diphenylmethyl chloride, 2-methylallyl chloride, n-butyl chloride, ethyl chloride and even isopropyl chloride to form dithiolium salts **3.25-3.30**, respectively (Scheme **S3. 16**).



Scheme S3. 16: Reactivity of betaine **3.7** as a nucleophile.

These results prompted us to study the reactivity of betaine **3.7** with Michael acceptors, in the hope of obtaining the thiirane. Unfortunately, reaction of adduct **3.7** with electron poor alkenes such as acrylonitrile, methyl acrylate or methyl vinyl ketone did not proceed. Since the betaine **3.7** is such a good nucleophile, we reasoned that the limiting step in the thiiranation is the attack on the sulfur by the carbanion. The introduction of electron withdrawing groups on the dithiole ring could enhance the electrophilicity of the sulfur atom. However, a fine tuning has to be found since the carbon at position 2 of the dithiole ring is still electrophilic, as shown by the prompt addition of sodium methoxide to salt **3.29** (Scheme **S3. 17**).



Scheme S3. 17: Addition of methoxide to alkylated betaine **3.29**.

2) 2,2-disubstituted dithioles.

Despite the presence of three surrounding heteroatoms and the driving rearomatization force of the dithiole ring, none of the 2,2-disubstituted dithioles **3.A**

obtained in Part A could release the nucleophilic fragment X cleanly, with the exception of fluorine adducts **3.21-3.23** (Figure **F3. 7**), which were utilized as fluorine transfer reagents.

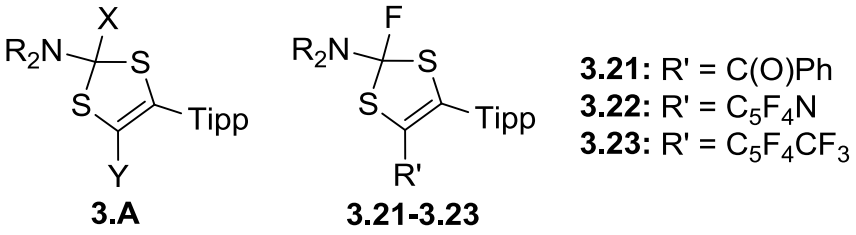
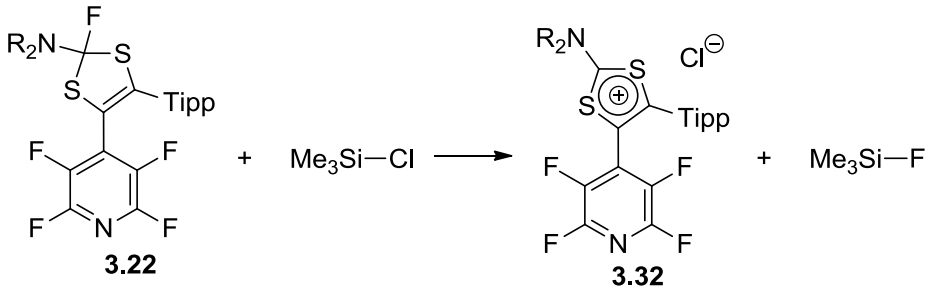


Figure F3. 7: 2,2-disubstituted dithioles discussed in this section.

Fluorine is a key functional group in biologically active molecules.[18] Although electrophilic fluorination reactions have been extensively developed,[19] nucleophilic substitution using fluoride remains limited.[20] This is mainly due to the fact that fluoride anions form very strong ion pairs in non-protic solvents and are highly solvated in protic solvents.[21] To overcome these problems, fluoride anions have been associated with large cations, which reduce the ion pairing effect,[22] as exemplified by the widely used tetrabutylammonium fluoride (TBAF). However, this salt is highly hygroscopic, and methods to obtain water-free TBAF are limited.[23] It is therefore of primary interest to develop novel convenient anhydrous fluoride sources.

We have shown in Part A of this chapter that ethynyl dithiocarbamate **3.1** was able to activate C–F bonds yielding adducts **3.21-3.23**. Because of four heteroatoms surrounding the carbon atom of the activation adducts **3.21-3.23**, their C_{sp^3}–F bond is strongly polarized. For example, in the solid state, the C1–F1 bond of adduct **3.23** is significantly elongated [1.404(5) Å] compared to other typical C_{sp^3}–F bonds (1.32-1.35

Å)[24] (Figure **F3. 5**). This prompted us to investigate the lability of the fluorine atom. Chlorotrimethylsilane was added to a dioxane solution of **3.22** and a precipitate appeared immediately. Analysis of the supernatant revealed the presence of fluorotrimethylsilane, while the precipitate was identified as the dithiolium salt **3.32(Cl)** (Scheme **S3. 18**; Figure **F3. 8**).



Scheme S3. 18: Fluorine transfer to chlorotrimethylsilane.

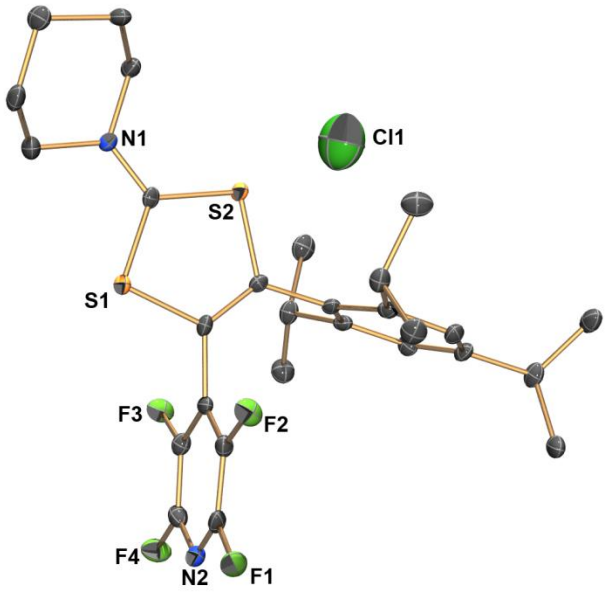
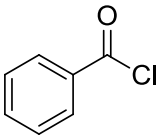
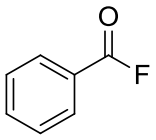
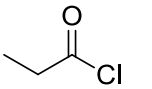
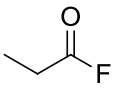
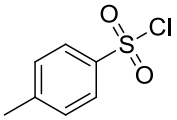
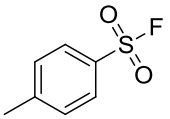
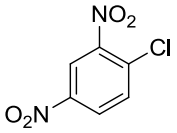
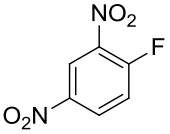
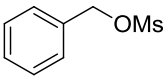
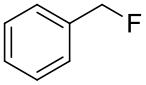
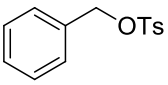
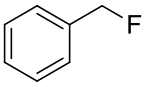
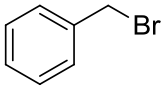
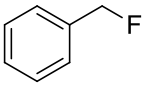
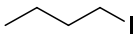
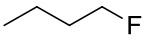


Figure F3. 8: Structure of **3.32·(H_2O)** in the solid state, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

Compound **3.22** also reacts almost instantaneously with strong electrophiles such as acyl chlorides or *para*-toluenesulfonyl chloride. All fluorinated products were isolated in very good yields (Table **T3. 1**: entries 2 to 4; 83 to 95 %). Nucleophilic aromatic substitutions can as well be achieved in good yields with the electron poor 1-chloro-2,4-dinitrobenzene (Table **T3. 1**: entry 4). Additionally, benzyl mesylate, tosylate and bromide were also successfully converted to their fluorinated counterparts (Table **T3. 1**: entries 5 to 7) at a higher temperature. Lastly, the fluorine anion can even be transferred to secondary alkyl triflate, and primary and secondary alkyl iodides (Table **T3. 1**: entries 8 to 10), although these transformations require higher temperatures and longer times, which affect their yields. Compound **3.22** is therefore able to release a fluoride anion even though the fluorine atom is always covalently bound to the heterocycle, regardless of the polarity of the solvent ($^{1}J_{C\text{-}F}\{C_6D_6\} = {}^{1}J_{C\text{-}F}\{THF\text{-}d_8\} = 274$ Hz). Note that salt **3.32(X)** precipitates from the solution, allowing for an easy separation of the fluorinated product by simple filtration. Moreover, **3.22** is soluble in ethereal solvents and aromatic hydrocarbons, and is remarkably stable in solution at room temperature. In order to assess the power of our newly discovered fluorinating reagent, we compared our results with those obtained using Olah's reagent (hydrogen fluoride·pyridine),[25] a widely used fluorinating compound (Table **T3. 1**).

Table T3. 1: Scope of the fluorine transfer reaction.[a]

	Reagent	Product	t	T	Conv.[b]	Yield[c]	Yield[d]
1	$Me_3Si—Cl$	$Me_3Si—F$	5 min	RT	100 %	95 %	Quant.
2			5 min	RT	100 %	87 %	93 %
3			5 min	RT	100 %	83 %	91 %
4			5 min	RT	100 %	95 %	96 %
5			2 h	RT	100 %	92 %	N.R.
6			10 h	45 °C	100 %	86 %	43 %
7			10 h	45 °C	100 %	85 %	52 %
8			14 h	45 °C	85 %[e]	73 %	N.R.
9			14 h	45 °C	74 %[e]	74 %	N.R.
10			14 h	45 °C	70 %[e]	54 %	N.R.
11			14 h	45 °C	64 %[e]	64 %	N.R.

[a] Reaction conducted using **3.22** (0.26 mmol), reagent (0.26 mmol) in 1,4-dioxane (4 mL). [b] Determined by 19F NMR spectroscopy using fluorobenzene as internal standard. [c] Yield of isolated product. [d] Yield of the product using Olah's reagent. [e] Longer reaction times lead to decomposition of the starting material without yielding more product.

Our reagent has a similar reactivity than Olah's reagent with strong electrophiles (Table **T3. 1**: entries 1 to 4) but it is much more efficient for the other substrates. In addition, adduct **3.22** is far less corrosive and is an easy-to-handle crystalline material.

Conclusion

We have shown in this chapter that the apparently benign ethynyl dithiocarbamate **3.1** can activate a large variety of small molecules and enthalpically strong bonds. This is partly due to the existence of an equilibrium with the non-observable dithiol-5-ylidene isomer **3.1'**, and also to the cooperative effect of the nucleophilic and electrophilic centers of the ethynyl dithiocarbamate **3.1**. While the resulting adducts gave some hopes for the applications of **3.1** as an organocatalyst, its high reactivity towards a large variety of substrates limited the scope of feasible reactions. In addition, all betaine adducts were not able to transfer their activated moieties (*e.g.* CO_2 or S). Nevertheless, the fluorinated adducts proved to be excellent fluorine transfer reagents towards a large variety of electrophiles.

Chapter 3 has been adapted from materials published in G. Ung, G. D. Frey, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2011**, *50*, 9923–9925 and G. Ung, G. Bertrand, *Chem. Eur. J.* **2012**, *18*, 12955–12957. The dissertation author was the primary investigator of these papers.

Appendix: Experimental section

A) Bond activation with ethynyl dithiocarbamate.

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{31}P, ^{19}F, ^{11}B and ^{13}C NMR spectra were recorded on Varian Inova 500, Varian Inova 400 and Bruker 300 spectrometers at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system.

2) Synthesis and characterization

*4-bromo-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium bromide **3.4**.*

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Bromine (6.6 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 min). All volatiles are removed under vacuum yielding a red powder. 67 mg (0.123 mmol, yield = 95 %) are obtained. **m.p.** 177 °C. **^{1}H (300 MHz, C_6D_6) δ** 1.20-1.37 (m, 18H), 1.89-1.97 (m, 2H), 1.98-2.14 (m, 4H), 2.79-3.01 (m, 3H), 3.97-4.15 (m, 4H), 7.12 (s, 2H). **^{13}C (75 MHz, C_6D_6) δ** 21.2 (CH_2), 23.9 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 25.0 ($CH(CH_3)_2$), 25.1 (CH_2), 25.2 (CH_2), 31.5 ($CH(CH_3)_2$), 34.6 ($CH(CH_3)_2$), 57.1 (NCH_2), 57.4 (NCH_2), 103.4 (C^qBr), 120.3 (C^q), 122.3 (CH_{ar}), 135.2 (C^q), 149.5 (C^q), 152.9 (C^q), 185.0 (C^q). **HRMS:** m/z calculated for $C_{23}H_{33}BrNS_2$ $(M)^+$ 466.1232, found 466.1241.

*2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium-4-trifluoroborate **3.5**.*

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). A solution of $BF_3{\cdot}OEt_2$ (0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 min). All volatiles are removed under vacuum yielding an orange powder. 54 mg (0.119 mmol, yield = 92 %) are obtained. **m.p.** 185 °C. **^{1}H (300 MHz, CD_3CN) δ** 1.18 (d, *J* = 6.8 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.29 (d, *J* = 6.8 Hz, 6H), 1.71-1.82 (m, 6H), 2.96 (sept, *J* = 6.8 Hz, 1H), 3.05 (sept, *J* = 6.8 Hz, 2H), 3.68 (t, *J* = 5.4 Hz, 2H), 3.80 (t, *J* = 5.4 Hz, 2H), 7.14 (s, 2H). **^{13}C (75 MHz, CD_3CN) δ** 22.4 (CH_2), 24.0 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 25.3 (CH_2), 25.4 ($CH(CH_3)_2$), 31.5 ($CH(CH_3)_2$), 35.1 ($CH(CH_3)_2$), 56.2 (NCH_2), 58.2 (NCH_2), 117.4 (C^q), 122.1 (CH_{ar}), 122.8 (C^q), 150.2 (C^q), 151.4 (C^q), 190.6 (C^q). **^{11}B{^{1}H} (96 MHz, CD_3CN) δ** 0.21 (q, $J_{B\text{-}F}$ = 36 Hz). **^{19}F{^{1}H} (282 MHz, CD_3CN) δ** −137.3 (q, $J_{F\text{-}B}$ = 36 Hz). **HRMS:** m/z calculated for $C_{23}H_{34}BF_3NS_2$ $(M+H)^+$ 456.2172, found 456.2161.

*2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium-4-carboxylate **3.6**.*

In a Schlenk, carbon dioxide is bubbled into a solution of ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in CH_2Cl_2 (1 mL) during 30 min. Solvent is evaporated yielding a yellow powder. 55 mg (0.126 mmol, yield = 98 %) are obtained. Single crystals are obtained by layering pentane on top of a saturated solution in CH_2Cl_2 at −20°C (Figure S.1). **m.p.** 82 °C. **^{1}H (300 MHz, CD_2Cl_2) δ** 1.25 (d, *J* = 6.8 Hz, 6H), 1.26 (d, *J* = 6.8 Hz, 6H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.77-2.02 (m, 6H), 2.92-3.09 (m, 3H), 3.68 (t, *J* = 5.8 Hz, 2H), 3.85 (t, *J* = 5.8 Hz, 2H), 7.12 (s, 2H). **^{13}C (75 MHz, CD_2Cl_2) δ** 22.2 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 25.5 (*C*H$_2$), 25.6 (*C*H$_2$), 31.9 (*C*H(CH$_3$)$_2$), 34.9 (*C*H(CH$_3$)$_2$), 55.6 (N*C*H$_2$), 56.2 (N*C*H$_2$), 121.9 (*C*H$_{ar}$), 123.6 (*C*^{q}), 133.3 (*C*^{q}), 144.6 (*C*^{q}), 148.8 (*C*^{q}), 151.2 (*C*^{q}), 159.6 (*C*^{q}OO), 185.0 (*C*^{q}).

*2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium-4-thiolate **3.7**.*

In a Schlenk are loaded ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) and precipitated sulfur (4 mg, 0.129 mmol). C_6H_6 is added at room temperature, the solution turns immediately deep red. Reaction is stirred 15 min at room temperature, then the solvent is evaporated under vacuum. The resulting red foam is triturated in hexanes. Filtration followed by vacuum drying yields to a yellow-orange powder. 53 mg (0.125 mmol, yield = 97 %) are obtained. Single crystals are obtained from a solution pentane/ether/acetonitrile (2/5/3) at −20°C (Figure S.2). **m.p.** 127 °C. **^{1}H (300 MHz, CD_3CN) δ** 1.20 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.62-1.88 (m, 6H), 2.94 (sept, *J* = 6.8 Hz, 1H), 3.18 (sept, *J* = 6.8 Hz, 2H), 3.60 (br s, 4H), 7.12 (s, 2H). **^{13}C (75 MHz, C_6D_6) δ** 22.0 (*C*H$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.7 (*C*H$_2$), 25.4 (CH(*C*H$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 32.0 (*C*H(CH$_3$)$_2$), 35.1 (*C*H(CH$_3$)$_2$), 53.6 (N*C*H$_2$), 111.5 (*C*^{q}), 121.9 (*C*H$_{ar}$), 126.9 (*C*^{q}), 150.4 (*C*^{q}), 151.5 (*C*^{q}), 158.9 (*C*^{q}), 183.9 (*C*^{q}). **HRMS:** m/z calculated for $C_{23}H_{33}NNaS_3$ $(M+Na)^+$ 442.1667, found 442.1686.

*2-(piperidin-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.9**.*

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Pinacol-borane (19 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 3 hours). All volatiles are removed under vacuum yielding a yellow oil. 62 mg (0.121 mmol, yield = 94 %) are obtained. **^{1}H (300 MHz, C_6D_6) δ** 0.94 (s, 6H), 0.97 (s, 6H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.51-1.61 (m, 6H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 2.58-2.69 (m, 2H), 2.70-2.83 (m, 2H), 2.91 (sept, *J* = 6.8 Hz, 1H), 3.52 (sept, *J* = 6.8 Hz, 1H), 3.78 (sept, *J* = 6.8 Hz, 1H), 6.41 (s, 1H), 7.20 (s, 1H), 7.24 (s, 1H) **^{13}C (75 MHz, C_6D_6) δ** 24.4 (CH(*C*H$_3$)$_2$), 24.6 (*C*H$_3$), 24.7 (*C*H$_3$), 24.9 (*C*H$_2$), 25.0 (CH(*C*H$_3$)$_2$), 26.2 (*C*H$_2$), 26.3 (CH(*C*H$_3$)$_2$), 31.1 (*C*H(CH$_3$)$_2$), 31.6 (*C*H(CH$_3$)$_2$), 35.1 (*C*H(CH$_3$)$_2$), 48.4 (N*C*H$_2$), 83.1 (SSN*C*H), 83.2 (O*C*(CH$_3$)$_2$), 83.8 (O*C*(CH$_3$)$_2$), 120.9 (*C*H$_{ar}$), 121.4 (*C*H$_{ar}$), 127.7 (q, $^1J_{BC}$ = 24 Hz, *C*^{q}), 129.6 (*C*^{q}), 145.4 (*C*^{q}), 148.1 (*C*^{q}), 149.1 (*C*^{q}), 149.4 (*C*^{q}). **^{11}B{^{1}H} (96 MHz, C_6D_6) δ** 21.7.

2-S-(2,6-dimethylphenylthio)-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole ***3.10***.

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). 2,6-dimethylthiophenol (17 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 min). All volatiles are removed under vacuum yielding an orange oil. 59 mg (0.113 mmol, yield = 88 %) are obtained. **^{1}H (300 MHz, $CDCl_3$) δ** 1.28 (d, *J* = 6.8 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 6.8 Hz, 6H), 1.40-1.52 (m, 2H), 1.55-1.68 (m, 4H), 2.61 (br s, 6H), 2.87 (sept, *J* = 6.8 Hz, 1H), 3.38 (m, 6H), 5.49 (s, 1H), 7.05-7.10 (m, 3H), 7.18 (s, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 23.6 (CH_3), 24.6 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 25.3 (CH_2), 25.6 ($CH(CH_3)_2$), 26.8 (CH_2), 31.0 ($CH(CH_3)_2$), 35.2 ($CH(CH_3)_2$), 50.3 (NCH_2), 83.8 ($NSSSC^q$), 114.1 (*C*H), 121.6 (CH_{Tipp}), 127.3 (C^q), 128.8 (CH_{ar}), 129.9 (C^q), 131.4 (C^q), 132.5 (C^q), 149.5 (C^q), 150.1 (C^q).

2-methoxy-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole ***3.11***.

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Methanol (5 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 min). All volatiles are removed under vacuum yielding a light-orange oil. 47 mg (0.111 mmol, yield = 96 %) are obtained. **^{1}H (500 MHz, $CDCl_3$) δ** 1.07 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.27-1.32 (m, 2H), 1.33-1.41 (m, 4H), 2.49 (sept, *J* = 7.0 Hz, 1H), 2.61-2.72 (m, 4H), 3.23 (sept, *J* = 7.0 Hz, 1H), 3.26 (s, 3H), 3.30 (sept, *J* = 7.0 Hz, 1H), 5.42 (s, 1H), 6.84 (s, 1H), 6.87 (s, 1H). **^{13}C (125 MHz, $CDCl_3$) δ** 24.6 ($CH(CH_3)_2$), 25.2 (CH_2), 25.3 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 25.5 ($CH(CH_3)_2$), 26.4 (CH_2), 31.3 ($CH(CH_3)_2$), 35.2 ($CH(CH_3)_2$), 51.1 (NCH_2), 53.1 (OCH_3), 112.6 (*C*H), 121.6 (CH_{ar}), 128.9 (C^q), 129.8 (C^q), 134.6 (C^q), 149.4 (C^q), 149.5 (C^q), 150.1 (C^q).

2-N-diethylamine-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole ***3.12***.

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Diethylamine (13 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction complete after 4 hours). All volatiles are removed under vacuum yielding an orange oil. 46 mg (0.124 mmol, yield = 78 %) are obtained. **^{1}H (300 MHz, $CDCl_3$) δ** 1.25 (t, *J* = 6.8 Hz, 6H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.36-1.47 (m, 6H), 1.52 (d, *J* = 6.8 Hz, 6H), 1.57-1.72 (m, 6H), 2.90 (sept, *J* = 6.8 Hz, 1H), 3.05-3.27 (m, 8H), 3.69 (sept, *J* = 6.8 Hz, 1H), 3.79 (sept, *J* = 6.8 Hz, 1H), 5.84 (s, 1H), 7.24 (s, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 15.4 (NCH_2CH_3), 24.6 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 25.5 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 25.9 (CH_2), 26.7 (CH_2), 31.3 ($CH(CH_3)_2$), 31.4 ($CH(CH_3)_2$), 35.2 ($CH(CH_3)_2$), 46.4 (NCH_2), 50.8 (NCH_2), 113.2 (*C*H), 121.6 (CH_{ar}), 127.3 (C^q), 129.1 (C^q), 130.2 (C^q), 149.2 (C^q), 149.3 (C^q), 149.8 (C^q).

2-P-diethylphosphine-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole ***3.13***.

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Diethylphosphine (11.7 mg, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 hours). All volatiles are removed under vacuum yielding a brown oil. 35 mg (0.072 mmol, yield = 56 %) are obtained. **^{1}H (300 MHz, C_6D_6) δ** 1.05-1.93 (m, 32H), 2.10-2.24 (m, 2H), 2.89 (sept, *J* = 6.8 Hz, 1H), 3.21-3.57 (m, 4H), 3.62 (sept, *J* = 6.8 Hz, 1H), 3.72 (sept, *J* = 6.8 Hz, 1H), 5.69 (s, 1H), 7.21 (s, 1H), 7.22 (s, 1H). **^{13}C (75 MHz, C_6D_6) δ** 11.5 (PCH_2CH_3), 11.8 (PCH_2CH_3), 21.2 (d, $^1J_{PC}$ = 16.0 Hz, PCH_2CH_3), 21.4 (d, $^1J_{PC}$ = 16.0 Hz, PCH_2CH_3), 24.6 ($CH(CH_3)_2$), 25.3 (CH_2), 25.9 ($CH(CH_3)_2$), 26.7 (CH_2), 31.3 ($CH(CH_3)_2$), 31.4 ($CH(CH_3)_2$), 35.1 ($CH(CH_3)_2$), 49.8 (NCH_2), 50.0 (NCH_2), 102.5 (d, $^1J_{PC}$ = 27.0 Hz, SSNPC^q), 114.7 (C=CH), 121.6 (CH_{ar}), 121.7 (CH_{ar}), 122.9 (C^q), 131.3 (C^q), 149.0 (C^q), 149.7 (C^q), 150.0 (C^q). **^{31}P{^{1}H} (121 MHz, C_6D_6) δ** 6.50 (s).

*2-(phenylethynyl)-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.14**.*

In a Schlenk tube is loaded a solution of dithiolium salt tetrafluoroborate (100 mg, 0.210 mmol) in 10 mL of THF. A solution of lithium phenylacetylide in THF (0.5 M, 0.420 mL) is added at room temperature. The reaction is stirred 30 min. Solvent is evaporated under vacuum and the residue is extracted with 20 mL of pentane. All volatiles are removed under vacuum yielding a yellow oil. 93 mg (0.190 mmol, yield = 90 %) are obtained. **^{1}H (300 MHz, C_6D_6) δ** 1.30 (d, *J* = 6.8 Hz, 6H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.44-1.53 (m, 8H), 1.60-1.72 (m, 4H), 2.80-2.89 (m, 1H), 3.27 (br s, 4H), 3.79 (sept, *J* = 6.8 Hz, 1H), 4.17 (sept, *J* = 6.8 Hz, 1H), 5.77 (s, 1H), 6.98 (m, 2H), 7.20-7.29 (m, 3H), 7.38 (s, 1H), 7.40 (s, 1H). **^{13}C (75 MHz, C_6D_6) δ** 23.6 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 24.5 (CH_2), 24.6 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 25.9 (CH_2), 30.5 ($CH(CH_3)_2$), 30.8 ($CH(CH_3)_2$), 34.5 ($CH(CH_3)_2$), 48.4 (NCH_2), 87.8 (C^q), 89.9 (C^q), 91.3 (C^q), 113.1 (CH), 121.0 (CH_{Tipp}), 121.4 (CH_{Tipp}), 122.4 (C^q), 128.2 (CH_{ar}), 128.5 (CH_{ar}), 130.0 (C^q), 131.6 (CH_{ar}), 148.5 (C^q), 149.6 (C^q), 149.7 (C^q), 152.2 (C^q).

*2-(1-methylhydrazin-1-yl)-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.16**.*

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Methylhydrazine (7 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 2 hours). All volatiles are removed under vacuum yielding a brown powder. 46 mg (0.106 mmol, yield = 82 %) are obtained. Single crystals are obtained from a saturated solution in pentane at −20°C (Figure S.3). **m.p.** 72 °C (dec). **^{1}H (400 MHz, C_6D_6) δ** 1.12 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.21-1.38 (m, 2H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.36-1.44 (m, 4H), 2.61 (s, 3H), 2.71 (sept, *J* = 6.8 Hz, 1H), 2.92 (m, 4H), 3.32 (sept, *J* = 6.8 Hz, 1H), 3.46 (sept, *J* = 6.8 Hz, 1H), 3.61 (br s, 2H), 5.53 (s, 1H), 7.02 (s, 1H), 7.05 (s, 1H). **^{13}C (75 MHz, C_6D_6) δ** 24.0 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 25.2 (CH_2), 26.0 (CH_2), 30.7 ($CH(CH_3)_2$), 31.0 ($CH(CH_3)_2$), 34.5

(*C*H(CH_3)$_2$), 40.9 (N*C*H_3), 50.9 (N*C*H_2), 112.2 (*C*H), 121.0 (*C*H_{ar}), 128.5 (*C*^{q}), 129.0 (*C*^{q}), 132.6 (*C*^{q}), 148.6 (*C*^{q}), 149.5 (*C*^{q}).

*1-(4-(2,4,6-triisopropylphenyl)-1,3-dithiol-2-yl)piperidine **3.18**.*

In a sealed Young NMR tube is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Ammonia-Borane (4 mg, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 5 min). All volatiles are removed under vacuum yielding an light brown oil. 49 mg (0.126 mmol, yield = 98 %) are obtained. **^{1}H (300 MHz, C_6D_6) δ** 1.33 (d, *J* = 6.8 Hz, 9H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.45-1.60 (m, 6H), 1.50 (d, *J* = 6.8 Hz, 3H), 2.60-2.72 (m, 4H), 2.89 (sept, *J* = 6.8 Hz, 1H), 3.55 (sept, *J* = 6.8 Hz, 1H), 3.75 (sept, *J* = 6.8 Hz, 1H), 5.79 (s, 1H), 6.47 (s, 1H), 7.23 (s, 1H), 7.25 (s, 1H). **^{13}C (75 MHz, C_6D_6) δ** 24.6 (CH(*C*H_3)$_2$), 24.9 (*C*H_2), 25.3 (CH(*C*H_3)$_2$), 25.7 (CH(*C*H_3)$_2$), 26.2 (*C*H_2), 31.1 (*C*H(CH_3)$_2$), 31.4 (*C*H(CH_3)$_2$), 35.1 (*C*H(CH_3)$_2$), 48.4 (N*C*H_2), 83.8 (SSN*C*H), 114.0 (C=*C*H), 121.5 (*C*H_{ar}), 121.9 (*C*H_{ar}), 128.9 (*C*^{q}), 131.2 (*C*^{q}), 148.8 (*C*^{q}), 150.0 (*C*^{q}), 150.1 (*C*^{q}).

*2-(trichloromethyl)-2-(piperidin-1-yl)-4-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.19**.*

In a sealed Young NMR tube is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Chloroform (10 µL, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 30 min). All volatiles are removed under vacuum yielding an light brown oil. 47 mg (0.126 mmol, yield = 72 %) are obtained. **^{1}H (500 MHz, C_6D_6) δ** 1.09 (d, *J* = 7.0 Hz, 6H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.34-1.41 (m, 6H), 2.66 (sept, *J* = 7.0 Hz, 1H), 2.94-3.04 (m, 4H), 3.45 (sept, *J* = 7.0 Hz, 1H), 3.59 (sept, *J* = 7.0 Hz, 1H), 5.34 (s, 1H), 6.99 (d, *J* = 1.5 Hz, 1H), 7.00 (d, *J* = 1.5 Hz, 1H). **^{13}C (125 MHz, C_6D_6) δ** 24.5 (CH(*C*H_3)$_2$), 24.7 (*C*H_2), 25.0 (CH(*C*H_3)$_2$), 25.3 (CH(*C*H_3)$_2$), 25.4 (CH(*C*H_3)$_2$), 25.5 (CH(*C*H_3)$_2$), 27.2 (*C*H_2), 31.1 (*C*H(CH_3)$_2$), 31.3 (*C*H(CH_3)$_2$), 35.2 (*C*H(CH_3)$_2$), 53.4 (N*C*H_2), 109.2 (*C*^{q}), 113.2 (C=*C*H), 114.0 (*C*^{q}), 121.6 (*C*H_{ar}), 121.8 (*C*H_{ar}), 127.6 (*C*^{q}), 130.2 (*C*^{q}), 149.4 (*C*^{q}), 150.3 (*C*^{q}), 150.6 (*C*^{q}).

*2,4-bis-S-(phenylthio)-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.20**.*

In an NMR tube fitted with a J. Young-type teflon valve is dissolved ethylnylcarbamodithioate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Diphenyldisulfide (28 mg, 0.129 mmol) is added. Reaction completion is monitored by ^{1}H NMR spectroscopy at room temperature (reaction is complete after 15 min). All volatiles are removed under vacuum yielding a yellow solid. 71 mg (0.117 mmol, yield = 91 %) are obtained. Single crystals are obtained from a saturated solution in pentane at −20°C (Figure S.4). **m.p.** 68 °C (dec).**^{1}H (300 MHz, $CDCl_3$) δ** 1.26 (d, *J* = 6.8 Hz, 9H), 1.40 (d, d, *J* = 6.8 Hz, 3H), 1.45-1.56 (m, 15H), 2.85 (sept, *J* = 6.8 Hz, 1H), 3.30 (br s, 4H), 3.62 (sept, *J* = 6.8 Hz, 1H), 3.79 (sept, *J* = 6.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 7.05-7.28 (m, 7H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H). **^{13}C (75 MHz, $CDCl_3$) δ** 24.5 (CH(*C*H_3)$_2$), 24.8 (CH(*C*H_3)$_2$), 24.9 (*C*H_2), 25.3 (CH(*C*H_3)$_2$), 26.1 (CH(*C*H_3)$_2$), 26.3 (CH(*C*H_3)$_2$), 26.6 (*C*H_2), 31.3 (*C*H(CH_3)$_2$), 31.6 (*C*H(CH_3)$_2$), 35.1 (*C*H(CH_3)$_2$), 51.3

(N*C*H$_2$), 107.3 (*C*^{q}), 117.7 (*C*^{q}), 121.9 (*C*H$_{Tipp}$), 122.2 (*C*H$_{Tipp}$), 126.6 (*C*H$_{ar}$), 126.8 (*C*^{q}), 128.9 (*C*H$_{ar}$), 129.1 (*C*H$_{ar}$), 129.2 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 129.7 (*C*H$_{ar}$), 134.1 (*C*^{q}), 136.6 (*C*H$_{ar}$), 136.7 (*C*^{q}), 137.7 (*C*^{q}), 149.1 (*C*^{q}), 149.5 (*C*^{q}), 150.6 (*C*^{q}).

*2-fluoro-2-(piperidin-1-yl)-4-(benzoyl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.22***.

In an NMR tube fitted with a J. Young-type teflon valve was dissolved ethynyl dithiocarbamate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Benzoyl fluoride (14 µL, 0.129 mmol) was added. The reaction completion was monitored by ^{1}H NMR spectroscopy at room temperature (the reaction is complete after 6 hours). All volatiles were removed under vacuum yielding a yellow foam. 64 mg (97 % yield). **^{1}H (300 MHz, C_6D_6) δ** 0.92-1.00 (m, 2H), 0.98 (d, *J* = 7.0 Hz, 6H), 1.03-1.12 (m, 2H), 1.19 (br s, 6H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.32-1.39 (m, 2H), 2.56 (sept, *J* = 7.0 Hz, 1H), 2.67 (br s, 4H), 3.39 (br s, 1H), 3.61 (br s, 1H), 6.77-6.94 (m, 3H), 6.92 (s, 1H), 6.95 (s, 1H), 7.75-7.82 (m, 2H); **^{13}C (125 MHz, C_6D_6) δ** 24.3 (CH(*C*H$_3$)$_2$), 24.4 (*C*H$_2$), 25.8 (*C*H$_2$), 26.3 (CH(*C*H$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 31.8 (*C*H(CH$_3$)$_2$), 35.0 (*C*H(CH$_3$)$_2$), 51.9 (N*C*H$_2$), 121.6 (*C*H$_{Tipp}$), 122.0 (*C*H$_{Tipp}$), 128.7 (*C*H$_{ar}$), 129.8 (*C*H$_{ar}$), 133.1 (*C*H$_{ar}$), 135.7 (d, $^1J_{C\text{-}F}$ = 274 Hz, *C*FSSN), 148.5 (*C*^{q}), 149.6 (*C*^{q}), 150.7 (*C*^{q}), 187.3 (*C*=O); **^{19}F{^{1}H} (282 MHz, C_6D_6) δ** −33.3.

*2-fluoro-2-(piperidin-1-yl)-4-(2,3,5,6-tetrafluoropyridin-4-yl))-5-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.22***.

In an NMR tube fitted with a J. Young-type teflon valve was dissolved ethynyl dithiocarbamate **3.1** (50 mg, 0.129 mmol) in C_6D_6 (1 mL). Pentafluoropyridine (14 µL, 0.129 mmol) was added. The reaction completion was monitored by ^{1}H NMR spectroscopy at room temperature (the reaction is complete after 18 hours). All volatiles were removed under vacuum yielding a yellow foam. 71 mg (99 % yield). **m.p.** 62 °C (dec); **^{1}H (300 MHz, C_6D_6) δ** 1.12 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18-1.30 (m, 6H, C*H*$_2$), 1.30 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.35 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.51 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 2.70 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.94 (br s, 4H, NC*H*$_2$), 3.49 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.75 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 7.10 (s, 1H, C*H*$_{ar}$), 7.15 (s, 1H, C*H*$_{ar}$); **^{13}C (125 MHz, C_6D_6) δ** 23.1 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 23.9 (*C*H$_2$), 25.4 (*C*H$_2$), 26.9 (CH(*C*H$_3$)$_2$), 27.1 (CH(*C*H$_3$)$_2$), 30.9 (*C*H(CH$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 34.5 (*C*H(CH$_3$)$_2$), 51.6 (N*C*H$_2$), 109.1 (*C*^{q}), 121.6 (*C*H$_{ar}$), 122.3 (*C*H$_{ar}$), 124.5 (*C*^{q}), 126.5 (t, $^2J_{C\text{-}F}$ = 17 Hz, *C*^{q}), 134.0 (*C*^{q}), 136.4 (d, $^1J_{C\text{-}F}$ = 274 Hz, *C*FSSN), 140.0 (dd, $^1J_{C\text{-}F}$ = 259 Hz, $^2J_{C\text{-}F}$ = 34 Hz, *C*F$_{ar}$), 143.6 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *C*F$_{ar}$), 148.7 (*C*^{q}), 150.0 (*C*^{q}), 151.3 (*C*^{q}); **^{19}F{^{1}H} (282 MHz, C_6D_6) δ** −140.4-−140.1 (m, 2F), −91.7-−91.4 (m, 2F), −36.9 (s, 1F). **HRMS:** m/z calculated for $C_{28}H_{34}F_5N_2S_2^+$ (M+H$^+$) 557.2078, found 557.2071.

*2-fluoro-2-(piperidin-1-yl)-4-(1-trifluoromethyl-2,3,5,6-tetrafluorophenyl))-5-(2,4,6-triisopropylphenyl)-1,3-dithiole **3.23***.

In an NMR tube fitted with a J. Young-type teflon valve was dissolved ethynyl dithiocarbamate **3.1** (70 mg, 0.181 mmol) in 1,4-dioxane (1 mL). Octafluorotoluene (26 µL, 0.181 mmol) was added. The reaction completion was monitored by ^{1}H NMR

spectroscopy at room temperature (the reaction is complete after 36 hours, the reaction completion time can be lowered to 5 hours by heating at 45 °C). The product is precipitated with pentane at −30 °C and the supernatant is removed by filtration. A yellow powder is obtained. 100 mg (89 % yield). Single crystals suitable for X-Ray diffraction studies were obtained from a saturated solution of **3.23** in dioxane at −30 °C. **m.p.** 73 °C; **^{1}H (300 MHz, THF-d_8) δ** 1.17 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.20-1.26 (m, 9H, CH(C*H*$_3$)$_2$), 1.27-1.33 (m, 6H, CH(C*H*$_3$)$_2$), 1.54-1.61 (m, 2H, C*H*$_2$), 1.71-1.77 (m, 4H, C*H*$_2$), 2.87 (sept, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 2.91-3.02 (m, 4H, NC*H*$_2$), 3.22 (sept, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 3.38 (sept, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 7.03 (s, 1H, C*H*$_{ar}$), 7.06 (s, 1H, C*H*$_{ar}$); **^{13}C (125 MHz, THF-d_8) δ** 23.0 (*C*H$_2$), 23.2 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 26.0 (*C*H$_2$), 26.6 (CH(*C*H$_3$)$_2$), 26.8 (CH(*C*H$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 34.8 (*C*H(CH$_3$)$_2$), 51.9 (N*C*H$_2$), 109.3 (*C*^{q}), 118.2 (t, $^{2}J_{C\text{-}F}$ = 17 Hz, *C*^{q}), 121.0 (q, $^{2}J_{C\text{-}F}$ = 30 Hz, *C*CF$_3$), 121.6 (q, $^{1}J_{C\text{-}F}$ = 274 Hz, *C*F$_3$), 121.9 (*C*H$_{ar}$), 122.3 (*C*H$_{ar}$), 124.7 (*C*^{q}), 133.6 (*C*^{q}), 136.2 (d, $^{1}J_{C\text{-}F}$ = 272 Hz, *C*FSSN), 144.8 (dd, $^{1}J_{C\text{-}F}$ = 257 Hz, $^{2}J_{C\text{-}F}$ = 15 Hz, *C*F$_{ar}$), 145.4 (dd, $^{1}J_{C\text{-}F}$ = 250 Hz, $^{2}J_{C\text{-}F}$ = 12 Hz, *C*F$_{ar}$), 149.0 (*C*^{q}), 149.9 (*C*^{q}), 151.1 (*C*^{q}); **^{19}F{^{1}H} (282 MHz, THF-d_8) δ** −144.0-−143.9 (m, 2F), −137.7-−138.1 (m, 2F), −59.1-−58.8 (m, 3F), −38.3 (s, 1F). **HRMS:** m/z calculated for $C_{30}H_{34}F_8NS_2^+$ (M+H$^+$) 624.1999, found 624.2007.

3) Crystallographic Data

Crystal data and structure refinement for 3.4.

Identification code	Br2 adduct	
Empirical formula	C26 H39 Br2 Cl6 N S2	
Formula weight	802.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.255(3) Å	α= 90°
	b = 18.1365(17) Å	β= 99.5430(10)°
	c = 14.9446(14) Å	γ = 90°
Volume	7017.7(11) Å^3	
Z	8	
Density (calculated)	1.519 Mg/m^3	
Absorption coefficient	2.904 mm^{-1}	
F(000)	3248	
Crystal size	0.32 x 0.17 x 0.10 mm^3	
Theta range for data collection	1.85 to 29.24°	
Index ranges	-35<=h<=35, -24<=k<=23, -20<=l<=19	
Reflections collected	28847	
Independent reflections	8841 [R(int) = 0.0.0279]	
Completeness to theta = 38.23°	92.7 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9807 and 0.9401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8841 / 0 / 334	
Goodness-of-fit on F^2	1.696	
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.2155	

R indices (all data)	R1 = 0.0704, wR2 = 0.2230
Largest diff. peak and hole	0.966 and -1.609 e.Å^{-3}

Crystal data and structure refinement for 3.6.

Identification code	CO2 adduct	
Empirical formula	$C_{24}H_{33}NO_2S_2$	
Formula weight	431.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.6468(10) Å	α= 90°
	b = 10.2043(13) Å	β= 92.593(6)°
	c = 33.579(4) Å	γ = 90°
Volume	2959.8(6) Å^3	
Z	4	
Density (calculated)	0.969 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	928	
Crystal size	0.32 x 0.17 x 0.10 mm^3	
Theta range for data collection	2.09 to 38.23°	
Index ranges	-13<=h<=14, -14<=k<=16, -43<=l<=52	
Reflections collected	47801	
Independent reflections	13728 [R(int) = 0.0327]	
Completeness to theta = 38.23°	83.9 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9807 and 0.9401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13728 / 0 / 268	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1864	
R indices (all data)	R1 = 0.0813, wR2 = 0.1961	
Largest diff. peak and hole	0.712 and -0.481 e.Å^{-3}	

Crystal data and structure refinement for 3.7.

Identification code	Sulfur adduct	
Empirical formula	$C_{46}H_{66}N_2S_6$	
Formula weight	839.37	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2(1)22(1)	
Unit cell dimensions	a = 14.1663(7) Å	α= 90°
	b = 28.6522(15) Å	β= 90°
	c = 11.2420(6) Å	γ = 90°
Volume	4563.1(4) Å^3	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.333 mm^{-1}	
F(000)	1808	
Crystal size	0.28 x 0.14 x 0.10 mm^3	

Theta range for data collection	1.81 to 29.35°
Index ranges	-17<=h<=18, -37<=k<=38, -15<=l<=15
Reflections collected	41017
Independent reflections	11644 [R(int) = 0.0218]
Completeness to theta = 29.35°	95.0 %
Absorption correction	Sadabs
Max. and min. transmission	0.9668 and 0.9139
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11644 / 0 / 499
Goodness-of-fit on F^2	1.210
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0920
R indices (all data)	R1 = 0.0416, wR2 = 0.1084
Absolute structure parameter	0.55(5)
Extinction coefficient	0.0090(6)
Largest diff. peak and hole	0.981 and -0.570 e.$Å^{-3}$

Crystal data and structure refinement for 3.16.

Identification code	Hydrazine adduct	
Empirical formula	$C_{24}H_{39}N_3S_2$	
Formula weight	433.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.183(4) Å	α= 110.355(5)°
	b = 11.096(4) Å	β= 102.649(5)°
	c = 13.140(5) Å	γ = 106.782(5)°
Volume	1245.5(8) $Å^3$	
Z	2	
Density (calculated)	1.156 Mg/m^3	
Absorption coefficient	0.229 mm^{-1}	
F(000)	472	
Crystal size	0.32 x 0.17 x 0.10 mm^3	
Theta range for data collection	2.13 to 28.16°.	
Index ranges	-13<=h<=13, -14<=k<=10, -17<=l<=17	
Reflections collected	9450	
Independent reflections	5697 [R(int) = 0.0221]	
Completeness to theta = 28.16°	93.0 %	
Max. and min. transmission	0.9775 and 0.9305	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5697 / 0 / 381	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1140	
R indices (all data)	R1 = 0.0588, wR2 = 0.1380	
Extinction coefficient	0.022(4)	
Largest diff. peak and hole	0.524 and -0.396 e.$Å^{-3}$	

Crystal data and structure refinement for 3.20.

Identification code	PhSSPh adduct
Empirical formula	$C_{35}H_{43}NS_4$

Formula weight	605.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8860(14) Å	α= 99.683(2)°.
	b = 11.8697(19) Å	β= 97.095(2)°.
	c = 16.810(3) Å	γ = 107.841(2)°.
Volume	1634.5(4) $Å^3$	
Z	2	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.315 mm^{-1}	
F(000)	648	
Theta range for data collection	2.50 to 21.04°	
Index ranges	-8<=h<=8, -11<=k<=11, -16<=l<=16	
Reflections collected	5822	
Independent reflections	2897 [R(int) = 0.0446]	
Completeness to theta = 21.04°	82.7 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2897 / 96 / 367	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0781, wR2 = 0.2488	
R indices (all data)	R1 = 0.0955, wR2 = 0.2587	
Largest diff. peak and hole	0.597 and -0.682 e.$Å^{-3}$	

Crystal data and structure refinement for 3.23.

Identification code	octafluorotoluene adduct	
Empirical formula	$C_{34}H_{41}F_8NO_2S_2$	
Formula weight	711.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.620(4) Å	α= 78.662(7)°
	b = 11.274(5) Å	β= 81.249(7)°
	c = 16.599(10) Å	γ = 72.397(5)°
Volume	1674.2(14) $Å^3$	
Z	2	
Density (calculated)	1.412 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	744	
Crystal size	0.26 x 0.13 x 0.10 mm^3	
Theta range for data collection	1.92 to 23.29°	
Index ranges	-10<=h<=10, -12<=k<=12, 0<=l<=18	
Reflections collected	4733	
Independent reflections	4733 [R(int) = 0.066]	
Completeness to theta = 23.29°	97.9 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9768 and 0.9411	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4733 / 0 / 431	

Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1282
R indices (all data)	R1 = 0.1174, wR2 = 0.1608
Extinction coefficient	0.002(2)
Largest diff. peak and hole	0.483 and -0.389 e.Å^{-3}

B) Chemistry of the adducts.

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Varian Inova 500, Jeol 500 or Bruker 300 spectrometer at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

2) General procedure for fluorine transfer reactions

In a Schlenk tube, the corresponding reagent was added to a solution of **2a** (0.26 mmol) in 1,4-dioxane (4 mL) containing 5 mol% of fluorobenzene (internal standard). The reaction advancement was monitored by ^{19}F NMR. The reaction was stopped when the signal at −37 ppm disappeared completely. The reaction mixture was allowed to decant, and the supernatant was filtered.

Isolation of the desired fluorinated product could be done by:

1) Evaporation of the solvent.

2) Distillation of the product.

3) Distillation of the solvent.

Yields are given as an average of 3 independent runs.

3) Synthesis and characterization

Bis-(2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium-4-thiolyl)methane ***3.24***.

Betaine **3.7** (50 mg, 119 mmol) was dissolved in dichloromethane (5 mL). The reaction was heated at 55 °C for 3 hours. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. xx mg (xx % yield). **^{1}H (300 MHz, CD_3CN) δ** 1.18 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.20 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.27 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.80 (br s, 4H, CH_2), 1.89 (br s, 4H, CH_2), 1.96 (br s, 4H, CH_2), 2.85-3.00 (m, 6H, C*H*(CH$_3$)$_2$), 3.83 (t, *J* = 5.4 Hz, 4H, NCH_2), 3.90 (t, *J* = 5.4 Hz, 4H, NCH_2),

4.59 (s, 2H, SCH_2S), 7.23 (s, 4H, CH_{Tipp}); **^{13}C (75 MHz, CD_3CN) δ** 21.3 (*C*H_2), 23.1 (CH(*C*H_3)$_2$), 23.4 (CH(*C*H_3)$_2$), 24.5 (CH(*C*H_3)$_2$), 24.6 (*C*H_2), 24.7 (*C*H_2), 30.8 (*C*H(CH$_3$)$_2$), 34.2 (*C*H(CH$_3$)$_2$), 42.9 (S*C*H$_2$S), 57.0 (N*C*H$_2$), 57.1 (N*C*H$_2$), 120.9 (*C*^{q}), 122.3 (*C*H$_{ar}$), 125.2 (*C*^{q}), 139.0 (*C*^{q}), 149.3 (*C*^{q}), 152.7 (*C*^{q}), 184.1 (*C*^{q}).

4-benzoylthio-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.25***.

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). Benzoyl chloride was added (125 mmol). The reaction was stirred for 1 hour. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 62 mg (93 % yield). **^{1}H (300 MHz, CD_3CN) δ** 1.15 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.73-1.86 (m, 2H, C*H*$_2$), 1.87-2.02 (m, 4H, C*H*$_2$), 2.82-3.02 (m, 3H, C*H*(CH$_3$)$_2$), 3.83 (t, *J* = 5.4 Hz, 2H, NC*H*$_2$), 3.89 (t, *J* = 5.4 Hz, 2H, NC*H*$_2$), 7.23 (s, 2H, C*H*$_{Tipp}$), 7.55 (t, *J* = 7.5 Hz, 2H, C*H*$_{meta}$), 7.74 (t, *J* = 7.5 Hz, 1H, C*H*$_{para}$), 7.88 (d, *J* = 7.5 Hz, 2H, C*H*$_{ortho}$); **^{13}C (75 MHz, CD_3CN) δ** 21.1 (*C*H$_2$), 23.0 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 24.4 (*C*H$_2$), 24.5 (*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 34.1 (*C*H(CH$_3$)$_2$), 56.8 (N*C*H$_2$), 57.0 (N*C*H$_2$), 120.0 (*C*^{q}), 120.6 (*C*^{q}), 122.3 (*C*H$_{ar}$), 127.7 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 134.2 (*C*^{q}), 135.6 (*C*H$_{ar}$), 143.0 (*C*^{q}), 149.2 (*C*^{q}), 152.9 (*C*^{q}), 185.0 (*C*^{q}), 186.7 (*C*^{q}).

4-benzhydrylthio-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.26***.

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). Diphenylmethyl chloride was added (125 mmol). The reaction was stirred for 1 hour. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 72 mg (97 % yield). **^{1}H (300 MHz, CD_3CN) δ** 1.20 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.74 (m, 2H, C*H*$_2$), 1.83 (m, 4H, C*H*$_2$), 2.86 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.97 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.61 (br s, 2H, NC*H*$_2$), 3.74 (br s, 2H, NC*H*$_2$), 5.68 (s, 1H, SC*H*Ph$_2$), 7.24 (s, 2H, C*H*$_{Tipp}$), 7.28-7.41 (m, 5H, C*H*$_{ar}$), 7.48-7.53 (m, 5H, C*H*$_{ar}$); **^{13}C (75 MHz, CD_3CN) δ** 21.1 (*C*H$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 24.4 (*C*H$_2$), 24.5 (CH(*C*H$_3$)$_2$), 30.9 (*C*H(CH$_3$)$_2$), 34.2 (*C*H(CH$_3$)$_2$), 56.5 (N*C*H$_2$), 56.7 (N*C*H$_2$), 58.2 (S*C*HPh$_2$), 121.2 (*C*^{q}), 122.2 (*C*H$_{ar}$), 127.1 (*C*^{q}), 128.1 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 129.2 (*C*H$_{ar}$), 136.4 (*C*^{q}), 139.4 (*C*^{q}), 149.2 (*C*^{q}), 152.6 (*C*^{q}), 184.3 (*C*^{q}).

4-((2-methylallyl)thio)-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.27***.

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). 2-methylallyl chloride was added (125 mmol). The reaction was stirred for 1 hour. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 60 mg (99 % yield). **^{1}H (300 MHz, CD_3CN) δ** 1.19 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 6.8 Hz, 6H,

CH(CH_3)$_2$), 1.27 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.74-1.93 (m, 6H, CH_2), 1.80 (s, 3H, CH_3), 2.86 (sept, *J* = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 2.95 (sept, *J* = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.55 (s, 2H, SCH_2), 3.79 (t, *J* = 5.4 Hz, 2H, NCH_2), 3.85 (t, *J* = 5.4 Hz, 2H, NCH_2), 5.01 (s, 1H, =CH_2), 5.07 (s, 1H, =CH_2), 7.23 (s, 2H, CH_{Tipp}); **^{13}C (75 MHz, CD$_3$CN) δ** 20.1 (*C*H$_3$), 21.2 (*C*H$_2$), 23.0 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.5 (*C*H$_2$), 24.6 (*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 34.2 (*C*H(CH$_3$)$_2$), 43.4 (S*C*H$_2$), 56.6 (N*C*H$_2$), 56.7 (N*C*H$_2$), 116.0 (=*C*H$_2$), 121.1 (*C*^{q}), 122.2 (*C*H$_{ar}$), 128.0 (*C*^{q}), 136.0 (*C*^{q}), 140.3 (*C*^{q}), 149.3 (*C*^{q}), 152.6 (*C*^{q}), 184.1 (*C*^{q}).

4-butylthio-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.28****.*

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). Butyl chloride was added (xx mL, xx mmol). The reaction was stirred for 3 hours at 55 °C. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 60 mg (98 % yield). **^{1}H (300 MHz, CD$_3$CN) δ** 0.91 (t, *J* = 7.3 Hz, 3H, CH_3), 1.20 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.26 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.39 (sext, *J* = 7.3 Hz, 2H, CH_2CH$_3$), 1.65 (qi, *J* = 7.3 Hz, 2H, SCH$_2$CH_2), 2.80-3.01 (m, 5H), 3.81 (t, *J* = 5.4 Hz, 2H, NCH_2), 3.88 (t, *J* = 5.4 Hz, 2H, NCH_2), 7.23 (s, 2H); **^{13}C (75 MHz, CD$_3$CN) δ** 12.8 (*C*H$_3$), 21.2 (*C*H$_2$), 21.4 (*C*H$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.6 (*C*H$_2$), 24.7 (*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 31.7 (*C*H$_2$), 34.2 (*C*H(CH$_3$)$_2$), 36.2 (S*C*H$_2$), 56.7 (N*C*H$_2$), 56.8 (N*C*H$_2$), 121.2 (*C*^{q}), 122.2 (*C*H$_{ar}$), 128.5 (*C*^{q}), 134.7 (*C*^{q}), 149.3 (*C*^{q}), 152.5 (*C*^{q}), 184.2 (*C*^{q}).

4-ethylthio-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.29****.*

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). Ethyl chloride was added (125 mmol). The reaction was stirred for 2 hours at 55 °C. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 52 mg (90 % yield). **^{1}H (300 MHz, CD$_3$CN) δ** 1.20 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.34 (t, *J* = 7.3 Hz, 3H, CH_3), 1.73-1.84 (m, 2H, CH_2), 1.84-2.01 (m, 4H, CH_2), 2.90 (sept, *J* = 6.8 Hz, 3H, CH(CH$_3$)$_2$), 2.98 (q, *J* = 7.3 Hz, 2H, SCH_2), 3.82 (t, *J* = 5.5 Hz, 2H, NCH_2), 3.89 (t, *J* = 5.5 Hz, 2H, NCH_2), 7.23 (s, 2H, CH_{Tipp}); **^{13}C (75 MHz, CD$_3$CN) δ** 14.6 (*C*H$_3$), 21.2 (*C*H$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.5 (*C*H$_2$), 24.6 (*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 34.2 (*C*H(CH$_3$)$_2$), 56.7 (N*C*H$_2$), 56.9 (N*C*H$_2$), 121.2 (*C*^{q}), 122.2 (*C*H$_{ar}$), 128.2 (*C*^{q}), 134.9 (*C*^{q}), 149.3 (*C*^{q}), 152.5 (*C*^{q}), 184.3 (*C*^{q}).

4-isopropylthio-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride ***3.30****.*

Betaine **3.7** (50 mg, 119 mmol) was dissolved in acetonitrile (5 mL). Isopropyl chloride was added (125 mmol). The reaction was stirred for 4 hours at 55 °C. All volatiles were removed under vacuum and the residue was washed with ether, then pentane and dried under vacuum. The title product was obtained as a yellow powder. 57 mg (96 % yield). **^{1}H (300 MHz, CD$_3$CN) δ** 1.19 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, *J* = 6.8 Hz, 6H,

CH(CH_3)$_2$), 1.28 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.35 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.78-1.99 (m, 6H, CH_2), 2.89 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.97 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.51 (sept, *J* = 6.8 Hz, 1H, SC*H*(CH$_3$)$_2$), 3.81 (t, *J* = 5.5 Hz, 2H, NCH_2), 3.88 (t, *J* = 5.5 Hz, 2H, NCH_2), 7.23 (s, 2H, CH_{Tipp}); **^{13}C (75 MHz, CD$_3$CN) δ** 21.2 (*C*H$_2$), 22.6 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.6 (*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 34.2 (*C*H(CH$_3$)$_2$), 41.7 (S*C*H(CH$_3$)$_2$), 56.7 (N*C*H$_2$), 56.8 (N*C*H$_2$), 121.1 (*C*^{q}), 122.2 (*C*H$_{ar}$), 127.9 (*C*^{q}), 135.1 (*C*^{q}), 149.3 (*C*^{q}), 152.5 (*C*^{q}), 184.3 (*C*^{q}).

*4-ethylthio-2-methoxy-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride **3.31***.

Dithiolium salt **3.29** (50 mg, 103 mmol) and sodium methoxide (6.0 mg, 110 mmol) were dissolved in THF (5 mL). The reaction was stirred for 1 hour. All volatiles were removed under vacuum and the residue was extracted with hexanes and dried under vacuum. The title product was obtained as a yellow powder. 43 mg (88 % yield). **^{1}H (300 MHz, CD$_3$CN) δ** 1.16 (t, *J* = 7.3 Hz, 3H, CH_3), 1.29 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.34 (br s, 2H, CH_2), 1.52 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.54 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.59 (br s, 4H, CH_2), 2.58-2.69 (m, 2H, SCH_2), 2.88 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.10 (br s, 4H, NCH_2), 3.54 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.58 (sept, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.67 (s, 3H, OCH_3), 7.27 (s, 1H), 7.28 (s, 1H); **^{13}C (75 MHz, CD$_3$CN) δ** 15.0 (*C*H$_3$), 23.9 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.7 (*C*H$_2$), 25.5 (CH(*C*H$_3$)$_2$), 25.7(CH(*C*H$_3$)$_2$), 25.8 (*C*H$_2$), 29.4 (S*C*H$_2$), 30.9 (*C*H(CH$_3$)$_2$), 31.0(*C*H(CH$_3$)$_2$), 34.4 (*C*H(CH$_3$)$_2$), 50.4 (N*C*H$_2$), 52.3 (O*C*H$_3$), 67.6 (*C*^{q}), 118.2 (*C*^{q}), 121.3 (*C*H$_{ar}$), 125.4 (*C*^{q}), 129.0 (*C*^{q}), 148.3 (*C*^{q}), 148.6 (*C*^{q}), 149.6 (*C*^{q}).

*4-(2,3,5,6-tetrafluoropyridin-4-yl)-2-(piperidin-1-yl)-5-(2,4,6-triisopropylphenyl)-1,3-dithiolium chloride **3.32***.

In a Schlenk tube, trimethylchlorosilane (33 µL, 0.26 mmol) was added to a solution of **3.22** (145 mg, 0.26 mmol) in 1,4-dioxane (5 mL). A white precipitate immediately appeared. The mixture was stirred for 5 min and then allowed to decant. The supernatant was removed by filtration and the white residue was dried under vacuum. 149 mg (quantitative yield). Single crystals suitable for X-Ray diffraction studies were obtained by layering pentane on top of a saturated chloroform solution. **m.p.** 198 °C (dec); **^{1}H (500 MHz, CDCl$_3$) δ** 1.07 (d, *J* = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.16 (d, *J* = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.18 (d, *J* = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.84-2.05 (m, 6H, CH_2), 2.76-2.89 (m, 3H, C*H*(CH$_3$)$_2$), 4.18 (br s, 2H, NCH_2), 4.34 (br s, 2H, NCH_2), 6.96 (s, 2H, CH_{ar}); **^{13}C (125 MHz, CDCl$_3$) δ** 21.2 (*C*H$_2$), 23.1 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 25.6 (*C*H$_2$), 26.8 (CH(*C*H$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 34.4 (*C*H(CH$_3$)$_2$), 58.2 (N*C*H$_2$), 58.3 (N*C*H$_2$), 117.4 (*C*^{q}), 118.7 (*C*^{q}), 121.8 (t, $^2J_{C\text{-}F}$ = 16 Hz, *C*^{q}), 122.6 (*C*H$_{ar}$), 139.9 (dd, $^1J_{C\text{-}F}$ = 264 Hz, $^2J_{C\text{-}F}$ = 35 Hz, *C*F$_{ar}$), 141.3 (*C*^{q}), 143.6 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *C*F$_{ar}$), 149.3 (*C*^{q}), 153.3 (*C*^{q}), 182.8 (*C*^{q}); **^{19}F{^{1}H} (282 MHz, CDCl$_3$) δ** −138.5-−138.1 (m, 2F), −89.0-−88.8 (m, 2F); **HRMS:** m/z calculated for $C_{28}H_{33}F_4N_2S_2^+$ (M^+) 537.2016, found 537.2012.

4) Fluorine transfer reactions

Benzoyl fluoride

The "General procedure for fluorine transfer reactions" was followed using benzoyl chloride as reagent. The product was obtained by distillation. Run 1: 26 mg (83 % yield), Run 2: 28 mg (89 % yield), Run 3: 28 mg (89 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 7.43 (t, J = 7.8 Hz, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.94 (d, J = 7.8, 2H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** 17.1.

Propionyl fluoride

The "General procedure for fluorine transfer reactions" was followed using propionyl chloride as reagent. The product was obtained by distillation. Run 1: 17 mg (84 % yield), Run 2: 16 mg (81 % yield), Run 3: 17 mg (84 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 2.70-2.52 (m, 2H), 1.32 (t, J = 7.8 Hz, 3H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** 39.1.

para-toluenesulfonyl fluoride

The "General procedure for fluorine transfer reactions" was followed using *para*-toluenesulfonyl chloride as reagent. The product was obtained by evaporation of the solvent. Run 1: 46 mg (quantitative yield), Run 2: 44 mg (98 % yield), Run 3: 40 mg (87 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.43 (d, J = 7.8 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** 64.7.

2,4-dinitrofluorobenzene

The "General procedure for fluorine transfer reactions" was followed using *para*-toluenesulfonyl chloride as reagent. The product was obtained by evaporation of the solvent. Run 1: 46 mg (95 % yield), Run 2: 42 mg (88 % yield), Run 3: 44 mg (92 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 7.60-7.67 (m, 1H), 8.53-8.59 (m, 1H), 8.84 (s, 1H) **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** −107.4.

Benzyl fluoride

The "General procedure for fluorine transfer reactions" was followed using benzyl bromide or benzyl tosylate as reagents. The product was obtained by distillation.

Benzyl bromide: Run 1: 20 mg (67 % yield), Run 2: 22 mg (76 % yield), Run 3: 22 mg (76 % yield).

Benzyl tosylate: Run 1: 26 mg (92 % yield), Run 2: 22 mg (76 % yield), Run 3: 25 mg (88 % yield).

Benzyl mesylate: Run 1: 26 mg (92 % yield), Run 2: 22 mg (77 % yield), Run 3: 25 mg (88 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 5.33 (d, $^{2}J_{HF}$ = 48.0 Hz, 2H), 7.29-7.40 (m, 5H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** −206.7.

2-fluoropropane

The "General procedure for fluorine transfer reactions" was followed using isopropyl iodide or isopropyl triflate as reagents. The product yield was determined by ^{19}F NMR spectroscopy.

Isopropyl iodide: Run 1: 72 % yield, Run 2: 76 % yield, Run 3: 74 % yield.

Isopropyl triflate: Run 1: 63 % yield, Run 2: 60 % yield, Run 3: 68 % yield.

^{1}H (300 MHz, $CDCl_3$) δ 1.4 (d, *J* = 7.0 Hz, 6H), 4.75-4.90 (m, 1H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** −150.8.

1-fluorobutane

The "General procedure for fluorine transfer reactions" was followed using benzoyl chloride as reagent. The product was obtained by distilling the solvent away. In order to obtain accurate yields, the reactions were conducted at double the usual scale (0.52 mmol). Run 1: 16 mg (42 % yield), Run 2: 24 mg (60 % yield), Run 3: 24 mg (60 % yield).

^{1}H (300 MHz, $CDCl_3$) δ 0.91-0.96 (m, 3H), 1.69-1.77 (m, 4H), 4.39-4.50 (m, 2H); **^{19}F{^{1}H} (282 MHz, $CDCl_3$) δ** −220.1.

5) Crystallographic Data

Crystal data and structure refinement for 3.32.

Identification code	TFP salt	
Empirical formula	$C_{28}H_{35}Cl_{1.50}F_4N_2OS_2$	
Formula weight	608.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.998(10) Å	α= 90°
	b = 7.920(3) Å	β= 93.537(4)°
	c = 23.973(8) Å	γ = 90°
Volume	5685(3) Å^3	
Z	8	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	0.380 mm^{-1}	
F(000)	2548	
Crystal size	0.32 x 0.13 x 0.10 mm^3	

Theta range for data collection	1.70 to 24.04°
Index ranges	-34<=h<=25, -9<=k<=8, -27<=l<=27
Reflections collected	13093
Independent reflections	4431 [R(int) = 0.0346]
Completeness to theta = 24.04°	99.0 %
Absorption correction	None
Max. and min. transmission	0.9630 and 0.8880
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4431 / 0 / 454
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0556, wR2 = 0.1600
R indices (all data)	R1 = 0.0737, wR2 = 0.1856
Largest diff. peak and hole	0.696 and -1.088 e.Å^{-3}

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CHAPTER 4:

Towards mesoionic carbenes with larger ring size

Adapted from:

G. Ung, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 758–761

Introduction

In contrast to their N-heterocyclic carbene (NHC) cousins, which are known to exist as 4- to 8-membered rings,[1] mesoionic carbenes have been mostly limited so far to the 5-membered series. In the 6-membered series, only scarce examples of pyridin-3-ylidenes **4.B** metal complexes have been synthesized,[2] but no other aromatic scaffolds have been studied. Note that owing to the possibility of drawing resonance structures **4.A'** and **4.C'**, pyridin-2-ylidenes **4A** and pyridin-4-ylidenes **4C** (Figure **F4. 1**), which have been well studied,[3] cannot be considered as mesoionic carbenes. In addition, no examples of 7-membered or larger ring mesoionic carbene complexes exist to date.

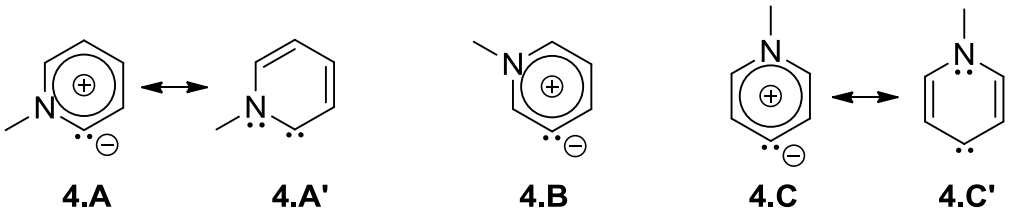


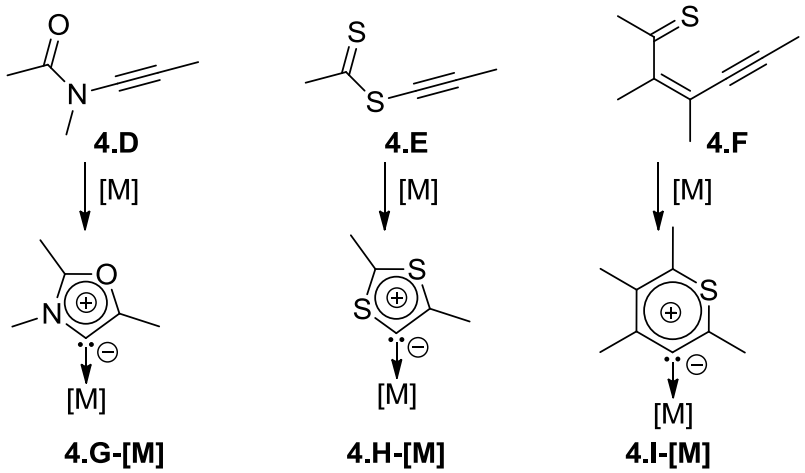
Figure F4. 1: Examples of known pyridin-n-ylidenes (n = 2,3,4).

In this chapter, we will discuss the selective preparation of a cyclic 6-membered mesoionic carbene gold complex by an unusual gold induced 6-*endo-dig* cyclization. Our attempts to synthesize a cyclic 7-membered mesoionic carbene complex will also be described.

A) 6-membered mesoionic carbene.

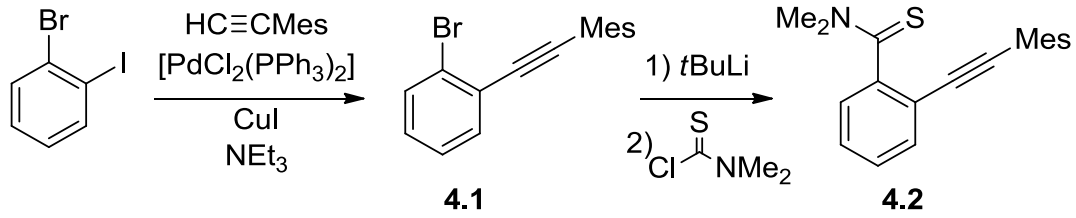
We have shown in Chapter 2 that the transition metal-induced cyclization of heteroatom-substituted alkynes **4.D** and **4.E** provides the corresponding gold complexes

4.G-[M] and **4.H-[M]**, respectively. By analogy, we envisioned that an alkyne of type **4.F** could undergo a 6-*endo-dig* cyclization, affording complex **4.I-[M]** featuring a thiopyryl-3-ylidene ligand **4.I** (Scheme **S4. 1**).



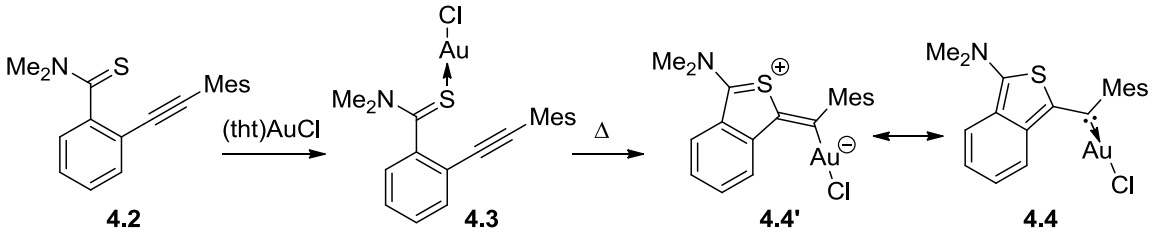
Scheme S4. 1: Transition metal induced cyclization of alkynes to the corresponding mesoionic carbene complexes.

To force a *cis* geometry between the alkyne and the thione of **4.F**, we chose a benzene fused system. 2-bromoiodobenzene was cross-coupled with mesitylacetylene, giving alkyne **4.1**. Treatment of **4.1** with *tert*-butyllithium and subsequent addition of dimethylcarbamothioyl chloride afforded the desired alkynyl benzothioamide **4.2** (Scheme **S4. 2**).



Scheme S4. 2: Synthesis of alkynyl benzothiamide **4.2**.

Compound **4.2** was first reacted with (tht)AuCl. The reaction proceeded cleanly in CH_2Cl_2; however, the $^{13}C\{^1H\}$ NMR spectrum of the product showed peaks at δ = 92.9 and 93.1 ppm, indicating that the alkyne moiety was still present and, consequently, that the expected cyclization did not occur. Nevertheless, slight but notable shifts in the $^{13}C\{^1H\}$ NMR spectrum indicated that the coordination of **4.2** to gold did take place. Single crystals were grown from a dichloromethane solution, and an X-ray diffraction study revealed that **4.2** displaced the tetrahydrothiophene ligand yielding complex **4.3**, in which the sulfur atom is coordinated to the metal (Figure **F4. 2**, left; Scheme **S4. 3**).



Scheme S4. 3: Cyclization of **4.2** with (tht)AuCl.

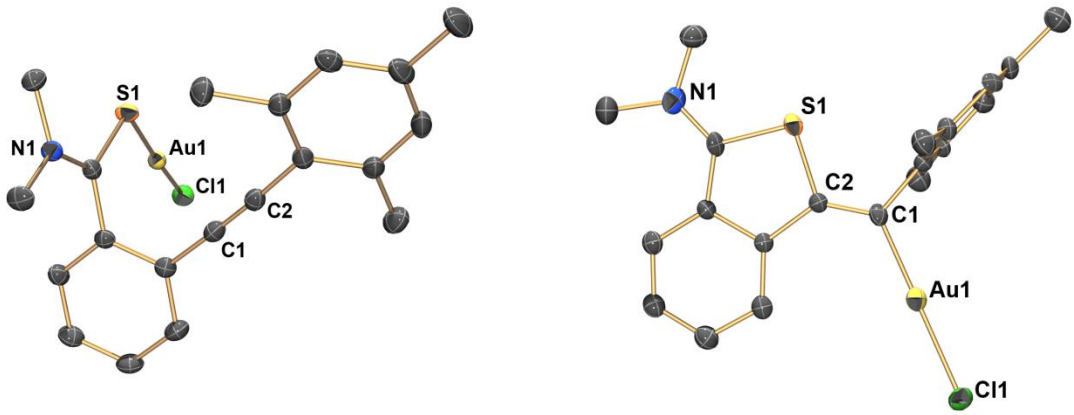
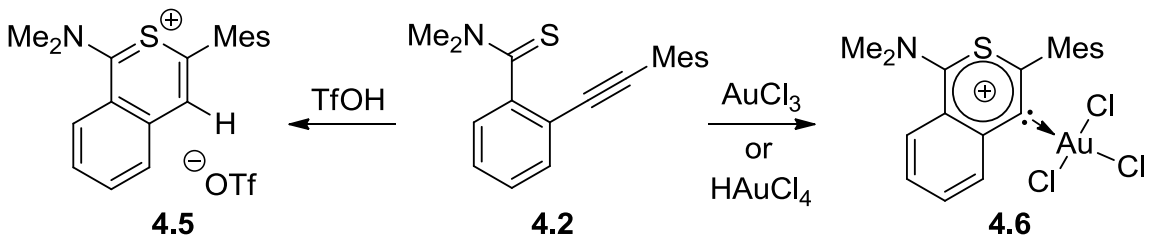


Figure F4. 2: Structure of **4.3** (left) and **4.4·(thf)** (right) in the solid state, hydrogen atoms and co-crystallized solvent molecules are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

Despite the aurophilicity of sulfur, we reasoned that the desired 6-membered mesoionic carbene-gold complex would be thermodynamically favored over a thioamide-gold complex. After heating **4.3** at 40 °C for 16 h, we observed the quantitative conversion into a new product. No alkyne carbon signals were detected in the $^{13}C\{^{1}H\}$ NMR spectrum, and the CS signal shifted drastically upfield, indicating that a cyclization process occurred. A single-crystal X-ray diffraction study showed that it was complex **4.4**, resulting from the usually encountered 5-*exo*-*dig* cyclization (Figure **F4. 2**, right). However, in contrast to previously reported studies on gold-mediated cyclization,[45] this complex is better described as the (aryl)(heteroaryl)carbene complex **4.4** rather than the zwitterionic vinyl gold complex **4.4'** (Scheme 3). The Au1–C1 bond (1.990(11) Å) is shorter than in vinyl gold complexes (2.04–2.06 Å),[5,6] and in the range observed for N-heterocyclic carbenes (NHCs) and mesoionic carbenes gold complexes (1.94–2.01 Å). Complex **4.4** is a very rare example of a non-heteroatom-substituted carbene-coinage metal complex.[7]

In order to favor a 6-*endo*-*dig* cyclization, we reasoned that the initial complexation of the metal had to occur at the triple bond instead of the sulfur atom. To test our hypothesis, we reacted alkyne **4.2** with a very alkynophilic proton source. Addition of trifluoromethanesulfonic acid to a solution of alkyne **4.2** in benzene induced an immediate precipitation of isothiochromenylium salt **4.5** (Scheme **S4. 4**). Recently, Hashmi, Nolan and co-workers reported an interesting switch of selectivity between 5-*exo*-*dig* and 6-*endo*-*dig* cyclization using two different NHC–Au complexes.[8] Both results prompted us to test other gold precursors, and we chose a more electrophilic gold

complex. A clean reaction was observed when $AuCl_3$ was added to **4.2**, and alkyne carbon signals were absent in the $^{13}C\{^1H\}$ NMR spectrum, indicating that a cyclization process had occurred. Indeed, when single crystals were obtained from a saturated acetone solution, an X-ray diffraction study proved that the desired 6-*endo-dig* cyclization took place, yielding the mesoionic carbene complex **4.6** (Figure **F4. 3**; Scheme **S4. 4**).



Scheme S4. 4: Reactivity of **4.2** towards very electrophilic substrates.

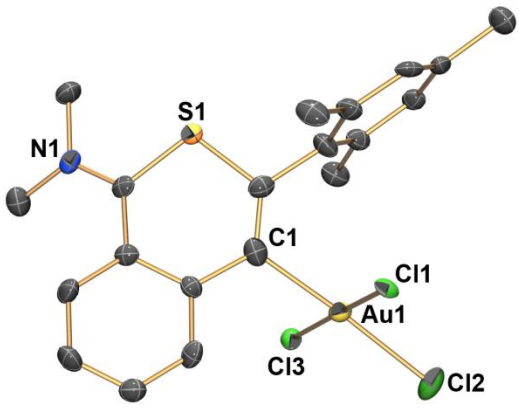


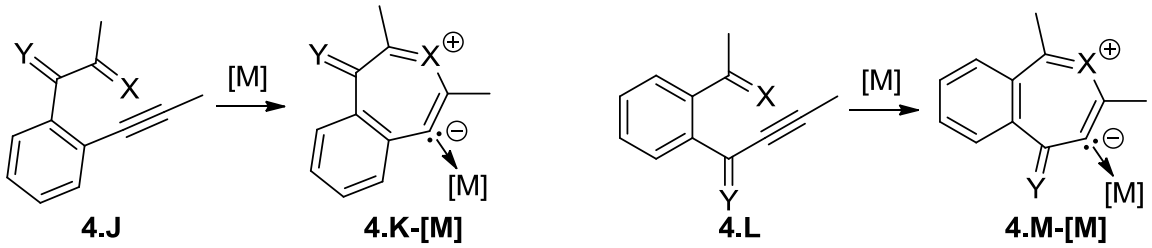
Figure F4. 3: Structure of **4.6·($CH_3C(O)CH_3$)** in the solid state, hydrogen atoms and co-crystallized solvent molecule are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

The Au1–C1 bond (2.077(7) Å) is considerably shorter than that observed for a [(vinyl)$AuCl_3$] complex (2.2743(9) Å),[9] and slightly longer than for [(NHC)$AuCl_3$]

complexes (1.98–2.01 Å).[10] The gold center features a weakly distorted square planar geometry (sum of angles = 359.98°), and the six-membered aromatic ring is only slightly twisted, which is due to the proximity of the bulky mesityl substituent with the chloride on the gold center. Although NHCs are oxidized by $AuCl_3$,[11] preventing the direct synthesis of the corresponding complexes, the formation of metallic Au was never observed in the reaction leading to **4.6**. Interestingly, the reaction of **4.2** with $HAuCl_4$ also gave rise to complex **4.6** without the loss of purity or yield. This result demonstrates the robustness of **4.6** towards protodeauration.

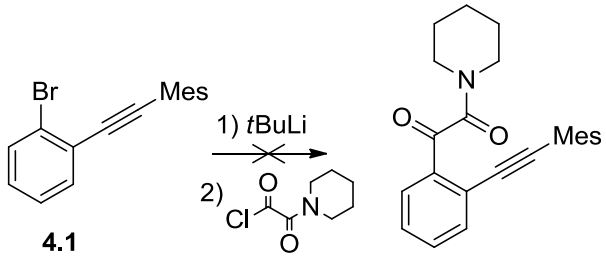
B) Towards 7-membered mesoionic carbenes.

Encouraged by our successes in the syntheses of 5-membered mesoionic carbene-metal complexes, as well as 6-membered mesoionic carbene-complexes by transition metal induced cyclization of precisely designed alkynes, we targeted the unknown 7-membered mesoionic carbene-complexes. In order to maintain a cationic aromatic system, an exocyclic double-bond has to be installed. Two synthetically viable models were designed: **4.J** and **4.L**, which would yield the carbene-complexes **4.K-[M]** and **4.M-[M]**, respectively (Scheme **S4. 5**).



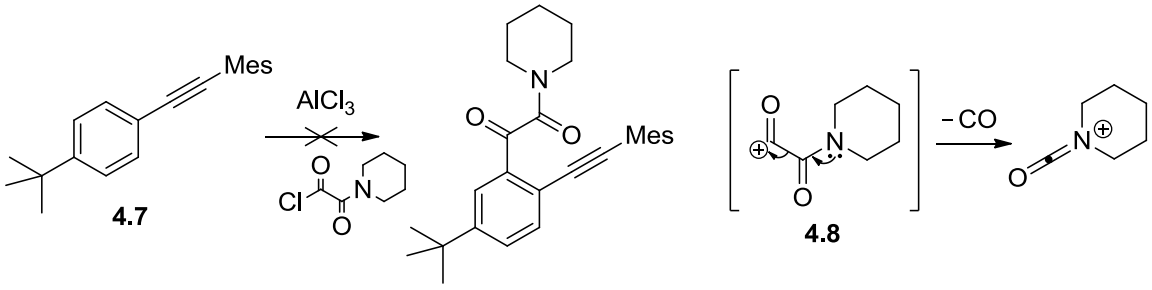
Scheme S4. 5: Design of potentially viable 7-membered mesoionic carbene ligand equivalents.

A precursor of type **4.J** was synthetically convenient since its formation would utilize the previously obtained alkyne **4.1**. However, treatment of **4.1** with tert-butyllithium and subsequent addition of 2-oxo-2-(piperidin-1-yl)acetyl chloride did not afford the desired product (Scheme **S4. 6**).



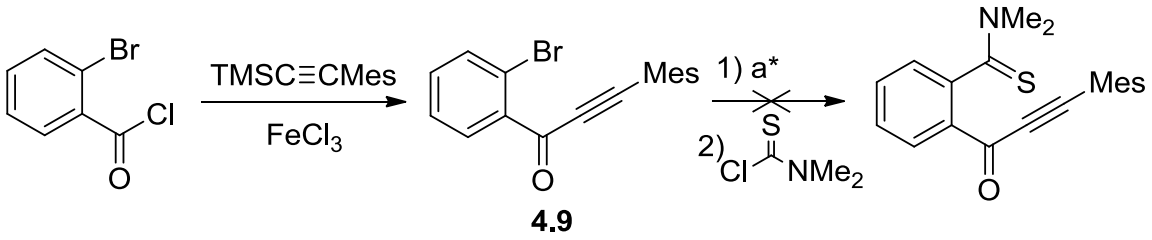
Scheme S4. 6: Attempt to synthesize a 7-membered mesoionic carbene ligand equivalent.

We envisioned another route involving a Friedel-Crafts acylation reaction. The para-protected alkyne **4.7** was synthesized by cross-coupling between 4-tertbutyliodobenzene and mesitylacetylene. Unfortunately, the acylation reaction only yielded decomposition products, most likely due to the rapid decomposition of the desired acylium cation **4.8** (Scheme **S4. 7**).



Scheme S4. 7: Attempt to synthesize a 7-membered mesoionic carbene ligand equivalent by Friedel-Crafts acylation.

To access a precursor of type **4.L**, we targeted alkynone **4.9** which was synthesized from the corresponding acyl chloride and trimethylsilylalkyne.[12] Halogen-lithium exchange of the bromine from **4.9** always yielded complex mixtures, likely due to the incompatibility between the highly basic lithium salt and the high electrophilicity of the alkynone moiety. To lessen the reactivity of the metal salt, we tried to generate the corresponding Grignard reagent. However, only starting material was recovered, even in forcing conditions (Scheme **S4. 8**).



Scheme S4. 8: Attempts to synthesize a 7-membered mesoionic carbene ligand equivalent; a*: *t*BuLi, *s*BuLi, *n*BuLi, Li, Mg.

Syntheses with carbonyl groups as additional spacers seem to lead to very reactive intermediates. To overcome these issues, an exocyclic carbon-carbon double bond could lessen the reactivity of such species; however, their syntheses are far less straightforward.

Conclusion

We have shown in this chapter, that the concept of using alkynes as mesoionic carbene ligand equivalents could be expanded to the 6-membered ring series. However, a competitive ring closure pathway was observed. Typically encountered 5-*exo-dig* cyclization occurs with a gold(I) precursor, yielding complex **4.4**, which is the first

example of a diarylcarbene–gold complex, and more generally of a diarylcarbene–metal complex obtained without using a diazo precursor[13] or an oxidative addition process.[14] In contrast, using a more electrophilic gold(III) precursor, the first metal complex featuring a non-nitrogen containing six-membered mesoionic carbene **4.6** was obtained. Unfortunately, tentative syntheses of a seven-membered mesoionic carbene ligand equivalent failed.

Chapter 4 has been adapted from materials published in G. Ung, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 758–761. The dissertation author was the primary investigator of the paper.

Appendix: Experimental section

A) 6-membered mesoionic carbene

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 500, Jeol 500 or Bruker 300 spectrometer at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

2) Synthesis and characterization

2-((2-bromophenyl)ethynyl)-1,3,5-trimethylbenzene ***4.1***.

A Schlenk tube was loaded with 1-ethynyl-2,4,6-trimethylbenzene (1.7 g, 11.8 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.021 mmol), CuI (8 mg, 0.079 mmol), 2-bromoiodobenzene (3.3 g, 11.8 mmol) and triethylamine (30 mL). The mixture was stirred for 16 hours at room temperature. All volatiles were evaporated under vacuum and the residue was dissolved in ethyl acetate. The organic layer was washed with saturated ammonium chloride and brine, dried over magnesium sulfate, filtered and concentrated to a yellow oil. The oil was purified by column chromatography on silica gel (eluent: pentane) yielding a white solid (2.2 g, 92 % yield).**m.p.** 44 °C; **^{1}H (300 MHz, $CDCl_3$) δ** 2.33 (s, 3H, C$H_{3_{para}}$), 2.55 (s, 6H, C$H_{3_{ortho}}$), 6.93 (s, 2H, CH_{ar}), 7.18 (t, *J* = 7.6 Hz, 1H, CH_{ar}), 7.31 (t, *J* = 7.6 Hz, 1H, CH_{ar}), 7.59 (d, *J* = 7.6 Hz, 1H, CH_{ar}), 7.64 (d, *J* = 7.6 Hz, 1H, CH_{ar}); **^{13}C (125 MHz, C_6D_6) δ** 21.4 (*C*H_3), 21.6 (*C*H_3), 92.3 (*C*≡C), 95.7 (C≡*C*), 127.2 (*C*H_{ar}), 127.9 (*C*H_{ar}), 128.6 (C^q), 129.1 (*C*H_{ar}), 129.6 (C^q), 132.6 (*C*H_{ar}), 133.4 (*C*H_{ar}), 138.5 (C^q), 140.5 (C^q), 140.8 (C^q); **HRMS (ESI-TOFMS):** m/z calculated for $C_{17}H_{16}Br^+$ ($M+H^+$) 299.0435 and 301.0415, found 299.0430 and 301.0409.

2-(mesitylethynyl)-N,N-dimethylbenzothioamide ***4.2***.

Bromoalkyne **4.1** (300 mg, 1 mmol) was dissolved in diethyl ether (10 mL) under an atmosphere of argon. The solution was cooled to −78 °C and a solution of *t*BuLi in pentane was added (1.7 M, 1.2 mL, 2 mmol). The reaction mixture was stirred at −78 °C for 15 min, then a solution of dimethylcarbamothioyl chloride (124 mg, 1 mmol) in diethyl ether (10 mL) was added. The reaction mixture was stirred for 1 hour at −78 °C, then allowed to warm up to room temperature and stirred an additional 2 hours. All volatiles were removed under vacuum and the residue was extracted with benzene via

cannula filtration. Evaporation of benzene yielded a light brown oil (300 mg, 98 % yield).**^{1}H (300 MHz, C_6D_6) δ** 2.20 (s, 3H, C$H_{3\text{para}}$), 2.55 (s, 6H, C$H_{3\text{ortho}}$), 2.66 (s, 3H, NCH_3), 3.33 (s, 3H, NCH_3), 6.82 (s, 2H, CH_{ar}), 7.04 (t, *J* = 7.4 Hz, 1H, CH_{ar}), 7.06 (t, *J* = 7.4 Hz, 1H, CH_{ar}), 7.33 (d, *J* = 7.4 Hz, 1H, CH_{ar}), 7.44 (d, *J* = 7.4 Hz, 1H, CH_{ar}); **^{13}C (75 MHz, C_6D_6) δ** 21.2 (*C*H_3), 41.8 (N*C*H_3), 42.0 (N*C*H_3), 91.3 (*C*≡C), 95.1 (C≡*C*), 119.1 (*C*^{q}), 120.1 (*C*^{q}), 126.6 (*C*H_{ar}), 127.5 (*C*H_{ar}), 127.9 (*C*H_{ar}), 128.1 (*C*H_{ar}), 128.4 (*C*H_{ar}), 131.9 (*C*H_{ar}), 138.0 (*C*^{q}), 140.2 (*C*^{q}), 145.9 (*C*^{q}), 199.0 (*C*=S); **HRMS (ESI-TOFMS):** m/z calculated for $C_{20}H_{22}NS^{+}$ ($M+H^{+}$) 308.1467, found 307.1473.

*Complex **4.3***.

CH_2Cl_2 (10 mL) was added to a Schlenk tube loaded with benzothioamide **4.2** (210 mg, 680 mmol) and (tht)AuCl (220 mg, 680 mmol), and the mixture was stirred for 14 hours. The reaction mixture was filtered and the filtrate was evaporated under vacuum. The residue was recrystallized from a saturated solution of dichloromethane. Complex **4.3** was obtained as orange crystals (240 mg, 65 % yield). **m.p.** 200 °C (dec); **^{1}H (300 MHz, $CDCl_3$) δ** 2.26 (s, 3H, C$H_{3\text{para}}$), 2.38 (s, 6H, C$H_{3\text{ortho}}$), 3.21 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 6.86 (s, 2H, CH_{ar}), 7.30-7.36 (m, 3H, CH_{ar}), 7.38-7.40 (m, 1H, CH_{ar}); **^{13}C (75 MHz, $CDCl_3$) δ** 21.2 (*C*H_3), 21.4 (*C*H_3), 44.6 (N*C*H_3), 46.1 (N*C*H_3), 92.9 (*C*≡C), 93.1 (C≡*C*), 118.9 (*C*^{q}), 119.1 (*C*^{q}), 125.9 (*C*H_{ar}), 127.8 (*C*H_{ar}), 128.8 (*C*H_{ar}), 130.1 (*C*H_{ar}), 132.5 (*C*H_{ar}), 138.8 (*C*^{q}), 140.1 (*C*^{q}), 143.2 (*C*^{q}), 197.7 (*C*=S). **HRMS (ESI-TOFMS):** m/z calculated for $C_{20}H_{21}AuNS^{+}$ ($M\text{-}Cl^{+}$) 504.1055, found 504.1048.

*Complex **4.4***.

A CH_2Cl_2 solution of **4.3** was heated at 40 °C for 16 hours. The solvent was evaporated under vacuum. The residue was recrystallized by layering pentane on top of a saturated solution of dichloromethane/THF (1:1). Complex **4.4** was obtained as yellow crystals (238 mg, quant.). **m.p.** 206 °C (dec); **^{1}H (500 MHz, dmso-d_6) δ** 2.08 (s, 6H, C$H_{3\text{ortho}}$), 2.24 (s, 3H, C$H_{3\text{para}}$), 3.41 (s, 3H, NCH_3), 3.88 (s, 3H, NCH_3), 6.86 (s, 2H, CH_{ar}), 7.67 (t, *J* = 8.0 Hz, 1H, CH_{ar}), 7.91 (t, *J* = 8.0 Hz, 1H, CH_{ar}), 8.34 (d, *J* = 8.0 Hz, 1H, CH_{ar}), 10.03 (d, *J* = 8.0 Hz, 1H, CH_{ar}); **^{13}C (125 MHz, dmso-d_6)** δ 20.0 (*C*H_3), 20.6 (*C*H_3), 46.5 (N*C*H_3), 50.1 (N*C*H_3), 127.9 (*C*H_{ar}), 128.6 (*C*H_{ar}), 131.1 (*C*H_{ar}), 135.6 (*C*H_{ar}), 144.7 (*C*^{q}), 145.4 (*C*^{q}), 166.9 (*C*^{q}), 174.2 (*C*^{q}), 179.8 (*C*^{q}). **HRMS (ESI-TOFMS):** m/z calculated for $C_{20}H_{21}AuNS^{+}$ ($M\text{-}Cl^{+}$) 504.1055, found 504.1048.

*1-(dimethylamino)-3-mesitylisothiochromenylium trifluoromethanesulfonate **4.5***.

Triflic acid was added to a solution of **4.2** (175 mg, 0.57 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 2 hours. All volatiles were removed under vacuum and the residue was solubilized in CH_2Cl_2 (10 mL) and washed with water (3 x 5 mL). The organic layer was collected, dried over $MgSO_4$, filtered and concentrated to yield a brown oil. The oil was triturated in diethyl ether, yielding a brown powder after filtration (xx mg, xx yield).

^{1}H (300 MHz, $CDCl_3$) δ 2.18 (s, 6H, CH_{3ortho}), 2.32 (s, 3H, CH_{3para}), 3.68 (br s, 3H, NCH_3), 4.04 (br s, 3H, NCH_3), 6.96 (s, 2H, CH_{ar}), 7.33 (s, 1H, C$H_{isothiochromenylium}$), 7.75-7.82 (m, 2H, CH_{ar}), 7.83-7.92 (m, 1H, CH_{ar}), 8.04 (d, *J* = 8.0 Hz, 1H, CH_{ar}); **^{13}C (75 MHz, $CDCl_3$) δ** 20.1 (*C*H_{3ortho}), 21.2 (*C*H_{3para}), 46.1 (N*C*H_3), 50.8 (N*C*H_3), 119.9 (*C*^{q}), 125.9 (*C*$H_{isothiochromenylium}$), 128.9 (*C*H_{arMes}), 129.1 (*C*H_{ar}), 129.3 (*C*H_{ar}), 130.6 (*C*H_{ar}), 134.2 (*C*^{q}), 135.9 (*C*H_{ar}), 137.9 (*C*^{q}), 138.7 (*C*^{q}), 140.5 (*C*^{q}), 177.9 (S*C*N); **^{19}F (282 MHz, $CDCl_3$) δ** −77.3; **HRMS:** m/z calculated for $C_{28}H_{34}F_5N_2S_2^+$ ($M+H^+$) 557.2078, found 557.2071.

*Complex **4.6**.*

THF (10 mL) was added at room temperature to a solid mixture of benzothioamide **4.2** (175 mg, 0.57 mmol) and gold(III) precursor ($AuCl_3$: 173 mg; $HAuCl_4$: 305 mg, 0.57 mmol) under an atmosphere of argon. The reaction mixture was stirred for 16 hours, and was allowed to decant. The supernatant was removed via cannula filtration, and the resulting yellow solid was washed with diethyl ether and dried under vacuum. The residue was recrystallized from a saturated solution of acetone. Complex **4.6** was obtained as pale yellow crystals (275 mg, 79 % yield). **m.p.** 206 °C; **^{1}H (500 MHz, dmso-*d_6*) δ** 2.33 (s, 6H, CH_{3ortho}), 2.34 (s, 3H, CH_{3para}), 3.62 (br s, 3H, NCH_3), 3.91 (br s, 3H, NCH_3), 7.04 (s, 2H, CH_{ar}), 7.85 (t, *J* = 8.0 Hz, 1H, CH_{ar}), 8.15 (t, *J* = 8.0 Hz, 1H, CH_{ar}), 8.25 (d, *J* = 8.0 Hz, 1H, CH_{ar}), 8.63 (d, *J* = 8.0 Hz, 1H, CH_{ar}); **^{13}C (125 MHz, dmso-*d_6*) δ** 20.8 (*C*H_3), 45.8 (br, N*C*H_3), 50.3 (br, N*C*H_3), 120.9 (*C*^{q}), 125.7 (*C*^{q}), 128.3 (*C*H_{ar}), 128.7 (*C*H_{ar}), 128.8 (*C*H_{ar}), 129.3 (*C*^{q}), 130.3 (*C*^{q}), 133.2 (*C*H_{ar}), 134.9 (*C*H_{ar}), 138.5 (*C*^{q}), 139.6 (*C*^{q}), 140.6 (*C*^{q}), 176.4 (*C*^{q}). **HRMS (ESI-TOFMS):** m/z calculated for $C_{20}H_{21}AuCl_2NS^+$ ($M-Cl^+$) 574.0432, found 574.0433.

3) Crystallographic Data

Crystal data and structure refinement for 4.3.

Identification code	linear	
Empirical formula	$C_{20}H_{21}AuClNS$	
Formula weight	539.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9443(6) Å	α= 78.8900(10)°
	b = 10.5397(9) Å	β= 78.9720(10)°
	c = 14.5615(13) Å	γ = 70.8740(10)°
Volume	978.58(15) Å^3	
Z	2	
Density (calculated)	1.832 Mg/m^3	
Absorption coefficient	7.761 mm^{-1}	
F(000)	520	
Crystal size	0.29 x 0.10 x 0.10 mm^3	

Theta range for data collection	2.35 to 27.10°
Index ranges	-8<=h<=8, -13<=k<=13, -17<=l<=18
Reflections collected	7611
Independent reflections	4191 [R(int) = 0.0244]
Completeness to theta = 27.10°	97.0 %
Absorption correction	Sadabs
Max. and min. transmission	0.5108 and 0.2118
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4191 / 0 / 222
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0174, wR2 = 0.0430
R indices (all data)	R1 = 0.0184, wR2 = 0.0435
Largest diff. peak and hole	0.824 and -0.871 e.Å^{-3}

Crystal data and structure refinement for 4.4.

Identification code	5MR	
Empirical formula	$C_{24}H_{28}AuClNOS$	
Formula weight	610.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.130(5) Å	α= 84.266(7)°
	b = 9.449(5) Å	β= 81.266(7)°
	c = 15.828(9) Å	γ = 71.924(6)°
Volume	1140.7(11) Å^3	
Z	2	
Density (calculated)	1.779 Mg/m^3	
Absorption coefficient	6.672 mm^{-1}	
F(000)	598	
Crystal size	0.28 x 0.16 x 0.13 mm^3	
Theta range for data collection	2.27 to 26.12°	
Index ranges	-9<=h<=10, -11<=k<=11, 0<=l<=19	
Reflections collected	4167	
Independent reflections	4167 [R(int) = 0.13]	
Completeness to theta = 26.12°	91.8 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.4775 and 0.2566	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4167 / 144 / 267	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1510	
R indices (all data)	R1 = 0.0919, wR2 = 0.1630	
Largest diff. peak and hole	3.140 and -2.849 e.Å^{-3}	

Crystal data and structure refinement for 4.6.

Identification code	6MR
Empirical formula	$C_{23}H_{27}AuCl_3NOS$

Formula weight	668.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.777(3) Å	α= 90°
	b = 11.126(2) Å	β= 107.010(2)°
	c = 16.505(3) Å	γ = 90°
Volume	2419.2(9) $Å^3$	
Z	4	
Density (calculated)	1.836 Mg/m^3	
Absorption coefficient	6.515 mm^{-1}	
F(000)	1304	
Crystal size	0.28 x 0.14 x 0.10 mm^3	
Theta range for data collection	2.24 to 26.37°	
Index ranges	-17<=h<=17, -13<=k<=13, -20<=l<=20	
Reflections collected	17145	
Independent reflections	4938 [R(int) = 0.0428]	
Completeness to theta = 26.37°	99.6 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.5619 and 0.2628	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4938 / 0 / 278	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0961	
R indices (all data)	R1 = 0.0533, wR2 = 0.1033	
Largest diff. peak and hole	2.370 and -1.317 $e.Å^{-3}$	

B) Toward 7-membered mesoionic carbenes

1) General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400, Jeol 500 or Bruker 300 spectrometer at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz.

2) Synthesis and characterization

2-oxo-2-(piperidin-1-yl)acetyl chloride.

Piperidine hydrochloride (5 g, 41 mmol) was dissolved in CCl_4, oxalyl chloride (5.2 g, 41 mmol) was added and the reaction mixture was heated to 50 °C for 24 hours. All volatiles were removed under vacuum and the residue was extracted with hexanes. Evaporation of the solvent yielded a pale yellow oil. **^1H (400 MHz, $CDCl_3$) δ** 1.65 (br s, 6H, CH_2), 3.38

(br s, 2H, NCH_2), 3.55 (br s, 2H, NCH_2); **^{13}C (100 MHz, $CDCl_3$) δ** 24.3 (*C*H_2), 25.2 (*C*H_2), 26.1 (*C*H_2), 43.0 (N*C*H_2), 47.3 (N*C*H_2), 158.1 (N*C*=O), 164.1 (Cl*C*=O).

2-((4-(tert-butyl)phenyl)ethynyl)-1,3,5-trimethylbenzene ***4.7***.

Mesityl iodide (2 g, 8.13 mmol), copper iodide (46 mg, 3 %mol), triphenylphosphane (85 mg, 4 %mol) and palladium bis-diphenylphosphane dichloride (114 mg, 2 %mol) were loaded in a Schlenk tube. Toluene (30 mL) and diisopropylamine (10 mL) were added, then 4-ethynylterbutylbenzene was added. The mixture was heated at 60 °C for 2 days. All volatiles were evaporated and the residue was passed through a pad of silica (eluent: ethyl acetate). The volatiles are removed and the residue is extracted with hexanes and dried under vacuum. A yellow powder is obtained. 1.75 g (78 % yield). **^{1}H (400 MHz, $CDCl_3$) δ** 1.34 (s, 9H, C(CH_3)$_3$), 2.30 (s, 3H, CH_3), 2.47 (s, 6H, CH_3), 6.89 (s, 2H, CH_{ar}), 7.38 (d, *J* = 8.3 Hz, 2H, CH_{ar}), 7.48 (d, *J* = 8.3 Hz, 2H, CH_{ar}); **^{13}C (75 MHz, $CDCl_3$) δ** 21.2 (*C*H_3), 21.5 (*C*H_3), 31.4 (C(*C*H_3)), 35.0 (*C*(CH_3)), 86.9 (*C*≡C), 97.4 (C≡*C*), 120.4 (*C*^{q}), 121.2 (*C*^{q}), 125.5 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 131.3 (*C*H$_{ar}$), 137.8 (*C*^{q}), 140.3 (*C*^{q}), 151.4 (*C*^{q}).

1-(2-bromophenyl)-3-mesitylprop-2-yn-1-one ***4.9***.

$FeCl_3$ (16 mg, 0.1 mmol) was dissolved in nitromethane (2 mL). The solution was cooled at −15 °C. 2-bromobenzoyl chloride (0.131 mL, 1 mmol) and TMSCCMes (325 mg, 1.5 mmol) were added. The mixture was stirred for 6 hours at −15 °C. The reaction mixture was filtered through a pad of Celite and the filtrate was concentrated under vacuum. The residue was extracted with hot hexanes and dried under vacuum. A pale yellow powder is obtained. 200 mg (70 % yield). **^{1}H (500 MHz, $CDCl_3$) δ** 2.33 (s, 3H, CH_3), 2.50 (s, 6H, CH_3), 6.93 (s, 2H, CH_{ar}), 7.50-7.35 (m, 2H, CH_{ar}), 7.71 (dd, *J* = 1.2 Hz and *J* = 7.9 Hz, 1H, CH_{ar}), 8.10 (dd, *J* = 1.2 Hz and *J* = 7.9 Hz, 1H, CH_{ar}); **^{13}C (100 MHz, $CDCl_3$) δ** 21.1 (*C*H_3), 21.6 (*C*H_3), 93.1 (*C*≡C), 95.9 (C≡*C*), 116.8 (*C*^{q}), 121.0 (*C*^{q}), 127.3 (*C*H$_{ar}$), 128.1 (*C*H$_{ar}$), 132.5 (*C*H$_{ar}$), 133.0 (*C*H$_{ar}$), 134.9 (*C*H$_{ar}$), 138.0 (*C*^{q}), 141.3 (*C*^{q}), 143.0 (*C*^{q}), 177.7 (*C*=O).

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CONCLUSION

We have demonstrated that a large variety of mesoionic carbenes and their transition metal complexes are readily accessible from simple precursors. Following the synthesis of the first imidazol-5-ylidene, a series of imidazol-5-ylidenes bearing electro active substituents were successfully obtained. Their stability and electronic properties are linked; on one hand, the presence of electron withdrawing substituents lessens the electron donating ability of the carbenes, but stabilizes them. On the other hand, electron donating substituents lead to the strongest electron donors while destabilizing the free carbenes. Owing to the decreased steric protection around the carbene center, the synthesis of free thiazol-5-ylidenes and oxazol-5-ylidenes was not achieved. Nevertheless, transition metal complexes of thiazol-5-ylidenes were synthesized by trapping the carbene at low temperature with a transition metal fragment. We also observed that mesoionic carbenes possessing a chalcogen atom in β-position were not stable and ring opened to the corresponding alkynes. Advantageously, these stable electron rich alkynes could react with transition metal fragments yielding the corresponding mesoionic carbene metal complexes. This brand new concept, *i.e.* using simple alkynes as mesoionic carbene ligand equivalents, was exploited to the synthesis of a new six-membered mesoionic carbene gold complex. Unfortunately, access to seven-membered mesoionic carbene ligand equivalent proved to be synthetically challenging.

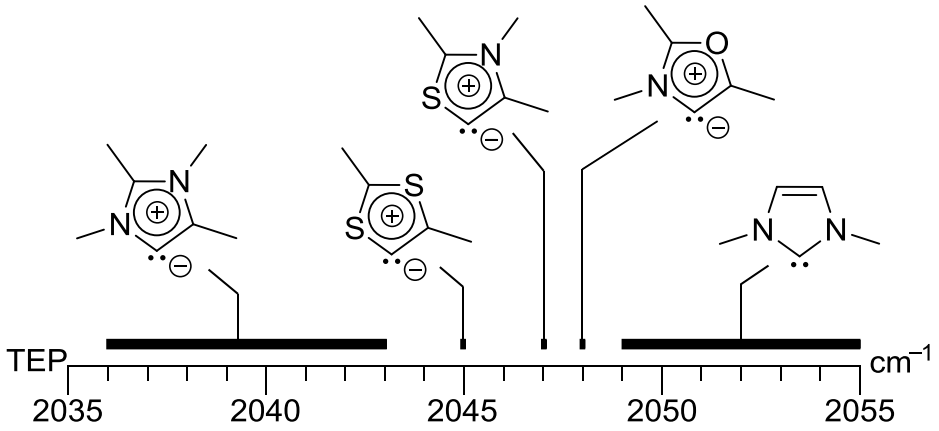

Figure C. 1: Electronic properties of all the mesoionic carbenes presented in this dissertation.

A comparison of all mesoionic carbenes synthesized is provided in Figure **C. 1**. Due to their mesoionic nature, all of them are stronger electron donors than classical imidazol-2-ylidenes. Oxazol-4-ylidenes are the weakest electron donors, which is consistent with the higher electronegativity of oxygen compared to sulfur and nitrogen. Imidazol-5-ylidenes are the stronger electron donors, and are stable as free species. These advantages have already led to some catalytic investigations.[1]

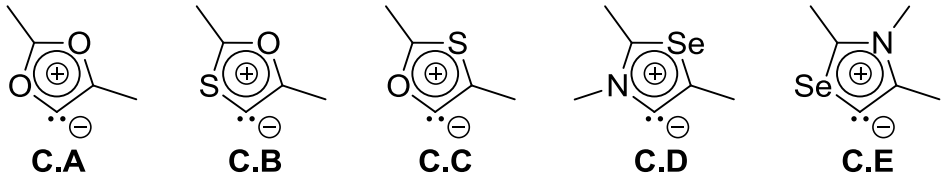

Figure C. 2: Other possible mesoionic carbenes.

In terms of design, only the dioxol-5-ylidenes **C.A**, oxathiol-4-ylidenes **C.B** and oxathiol-5-ylidenes **C.C** are left on the series. However, their synthesis is far more challenging. In contrast, heavier analogues such as selenazol-4-ylidenes **C.D** and

selenazol-5-ylidenes **C.E** can also be envisioned using methods developed in Chapters 1 and 2 using Woolins reagent to introduce the selenium atom.[2]

In addition to being a mesoionic carbene ligand equivalent, we also discovered that an apparently benign ethynyl dithiocarbamate was able to activate a large variety of enthalpically strong bonds. Polar X–H bonds such as B–H, N–H, O–H, P–H and S–H could be cleaved, as well as polarized strong C–H and C–F bonds. Small molecules such as CO_2 and elemental sulfur were also activated. These reactions proceed through an original activation mode, involving both the existence of the mesoionic carbene in equilibrium, and the cooperative effect between an electrophilic, and a nucleophilic carbon atom.

The very high activity of the ethynyl dithiocarbamate as a bond activator hindered its uses as an organocatalyst. Nevertheless, the products of C–F activation proved to be very efficient stoichiometric nucleophilic fluorination reagents. Because the synthesis of ethynyl dithiocarbamate is simple and versatile, an appropriate tuning of the steric and electronic environment could tame its reactivity and allow for catalytic reactions to take place.

References

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[2] I. P. Gray, P. Bhattacharyya, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2005**, *11*, 6221.