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Authors
Buckley, Heather L
Arnold, John

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Recent developments in out-of-plane metallocorrole chemistry across the periodic table

Heather L. Buckley and John Arnold*

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This article presents a brief review of recent developments in metallocorrole chemistry, with a focus on species with significant displacement of the metal from the N_4 plane of the corrole ring. Comparisons based on X-ray crystallographic data are made between a range of early and/or heavy transition metal, lanthanide, actinide, and main group metallocorrole species.

Introduction

The field of corrole chemistry is rapidly growing, with new corrole ligands, new metallocorrole complexes, and new synthetic methodologies surrounding corroles appearing in the chemical literature on a frequent basis. For a molecule that has been synthetically readily accessible for only fifteen years, the breadth of chemistry now demonstrated is remarkable. This is well demonstrated by the changes in corrole chemistry discussed in *The Porphyrin Handbook* in 2000 [1,2] as compared to the much more extensive chemistry discussed in the 2010 edition of the *Handbook of Porphyrin Science*.[3,4]

The original preparation[5–9] and structural characterization[10] of corrole in the 1960s and 1970s was inspired at least in part by the structural similarity of corrole to the naturally occurring corrin ring in vitamin B12. Subsequent study was hampered by synthetic inaccessibility of corroles until 1999, when two new routes to the preparation of free base corrole were published by Paolesse[11] and Gross.[12,13] Over the next decade, a wealth of synthetic methodologies and variants were developed for synthesis of corroles,[14] with *meso*-substituents,[15–21] various beta-substituents,[22–26] and eventually including both charged[27,28] and chiral[29] free-base corroles. The development of these organic syntheses is beyond the scope of this review, but the range of properties imparted by these synthetic options has greatly broadened the scope of applications of corroles.

Given that it was a biological metallomacrocycle that first inspired the preparation of corrole, it is unsurprising that much of the interest in corroles lies in the preparation and application of metallocorrole complexes. Several review articles have appeared in the last five years outlining the inorganic chemistry of corroles. In particular, a 2009 review by Aviv-Harel and Gross[30] outlined some exceptional properties of corroles that led to early applications of their complexes, and a 2012 review by Palmer[31] outlined the use of many first row transition metal corrole complexes as oxo, imido, and nitrido transfer agents. The latter review also discussed in great detail the noninnocence of the corrole ligand in formally high-valent metal complexes. This topic is also discussed in the latest edition of the Handbook of Porphyrin Science,[3] and has great relevance to the applications of structurally modified species such as hangman porphyrins and pacman porphyrin-corrole dyads, which have seen application in oxygen reduction and water oxidation.[4] A review of main group corrole chemistry has also highlighted advances and applications in this field.[32] The contents of these aforementioned reviews will not be repeated here, except insofar as they serve for comparison to new corrole chemistry.

Much of the most recent progress in corrole chemistry has been towards the preparation of more air-sensitive complexes. As a result, several unexplored regions of the periodic table have recently become subjects of great interest. Alkali metals, early transition metals, lanthanides, and actinides were unknown in the corrole literature until 2012, and heavy elements including third row transition metals and heavy main group species had very limited representation. Fig. 1 shows a depiction of the periodic table with those elements that have been coordinated to corrole ligand highlighted. The preparation, structural characteristics, and preliminary reactivity of these corrole complexes will be the focus of this review.

The development of metallocorrole chemistry closely mirrors that of metalloporphyrins. Much of the early work on metallocorroles focused on Mn, Fe, Co, and Cu due to their synthetic accessibility and biological significance. Corrole complexes are often prepared by similar methods to their porphyrin analogues,[37] by combining the free-base ligand in solution or suspension with a simple metal halide or acetate salt, with or without heating. The complex is then typically isolated by column chromatography.

University of California, Berkeley, USA. E-mail: arnold@berkeley.edu

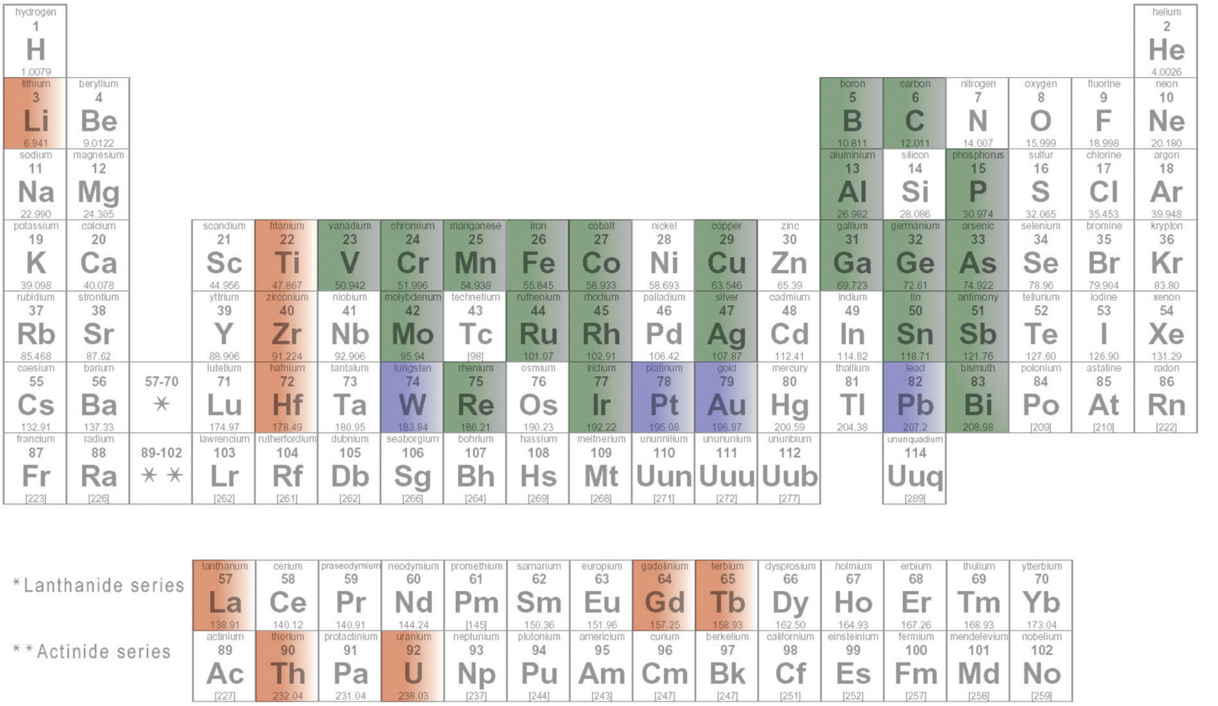


Fig. 1 Periodic table of corroles. Green denotes metals with some corrole species known as of 2009. Blue denotes three new metals coordinated to corrole by other scientists: tungsten,[33] platinum,[34] gold,[35] and lead.[36] Red denotes metals coordinated to corrole as a result of recent work in the Arnold group.

The relatively late development of early transition metal, lanthanide, and actinide chemistry in both fields is largely due to the limitations of these methods in the face of air sensitive compounds. The sensitivity of these molecules is twofold. For one, the early transition metals, lanthanides, and actinides are all strongly oxophilic. Compounding this is the fact that, due to their larger radii as compared to their late transition metal counterparts, all of these metals are forced to sit significantly out of the plane of the macrocycle ring. This leaves the metal more sterically exposed, and strains the metal–nitrogen bonds, making these bonds more prone to hydrolysis to reform the free-base ligand. The oxophilicity may serve to explain why many of the species reviewed here and many examples of heavier metal porphyrin complexes are metal-oxo compounds.

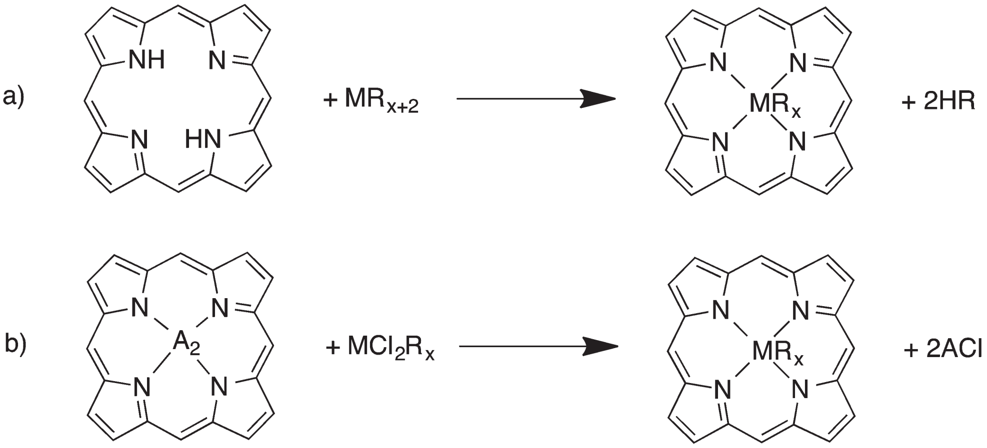
To prepare and isolate air-sensitive metalloporphyin complexes, a new set of methodologies was developed.[38,39] The first involves reacting the free base porphyrin with a metal alkyl or silyl amide complex to generate the metal complex (Scheme 1a). This reaction is driven thermodynamically by the formation of a strong C–H or C–N bond to produce metal porphyrins such as (OEP)Y[CH(SiMe$_3$)$_2$] (OEP = β-octaethylporphyrin).[40,41]

The second method for the preparation of air sensitive metalloporphyrin complexes was made possible by the isolation of alkali metal porphyrins, Li$_2$(porphyrin), Na$_2$(porphyrin) and K$_2$(porphyrin).[42–45] Salt metathesis of one of these with a metal halide X$_2$MR$_n$ leads to the formation of R$_n$M(porphyrin) complexes (Scheme 1b). Examples include (OEP)ZrCl$_2$,[46] (OEP)ScCl,[47,48] (OEP)ZrCl$_2$ and (OEP)Zr(CH$_2$SiMe$_3$)$_2$,[46,49] (TPP)SnPh$_2$,[50] and the sandwich complexes [Ta(OEP)$_2$][TaCl$_6$],[51] Zr(OEP)$_2$ and Hf(OEP)$_2$.[52] Beyond the initial preparation of these complexes, several formally lower valent species were synthesized, facilitated by the redox active nature of the porphyrin ligand.[53,54] This type of reactivity has not yet been achieved with early transition metal corrole chemistry. However, the similar redox-active nature of corrole, as demonstrated by catalytic multi-electron chemistry with first row transition metal complexes,[4,55] suggests that reduction chemistry of some of the complexes presented here should be possible.

Just as the two major synthetic routes discussed above led to the development of a wide range of previously inaccessible porphyrin compounds, so have analogous developments facilitated the preparation of new classes of metallocorrole complexes. In the sections that follow, these recent developments of alkali metal, early transition metal, lanthanide, actinide, and heavy transition metal and main-group corrole complexes are highlighted. The review then concludes with a comparison of some basic structural properties of known metallocorrole species, and a prospectus on the next frontiers of air-sensitive chemistry of metal corrole complexes.

Alkali metal corroles

While metalloporphyrin salts of Li, Na, and K have all been isolated and fully structurally characterized,[43] alkali metal corrole complexes have proven considerably more elusive. The only structurally characterized compound in this group is a



Scheme 1 General scheme for preparation of early transition metal porphyrin complexes by (a) C–H bond formation and (b) salt metathesis (M = metal, R = alkyl substituent, *x* = any integer, A = alkali metal). Substituents on porphyrins are not shown.

lithium corrole, $Mes_2(p\text{-}OMePh)corroleLi_3\cdot 6THF$ reported by our group in 2012.[56] This complex was structurally characterized as the $[Li(DME)_{2.5}]^+[Mes_2(p\text{-}OMePh)corroleLi_2(DME)_{1.5}]^-$ salt with one lithium coordinated by solvent and two lithiums coordinated by all four nitrogen atoms of the corrole, sitting above and below the plane of the ring. This is different from both reported lithium porphyrin species: dilithium octaethylporphyrin and dilithium mesotetrakis(3,4,5-tri-methoxypheny1)porphyrin ($Li_2(OEP)$ and $Li_2(TMPP)$) both are observed as ion pairs with a single lithium in the plane of the porphyrin ring and the second lithium coordinated only by solvent.[43] The structure of the lithium corrole complex more closely resembles that of sodium and potassium porphyrinates, in which one metal ion is coordinated above and the other below the plane of the porphyrin.[43] However, the single lithium peak observed in the ^{7}Li NMR spectrum of the lithium corrole suggests rapid exchange between the lithium atoms, and unpublished data from our group suggest that the solution-phase coordination environment of lithium in this species may be solvent-dependent.

The only other mention of lithium corroles in the literature is a metal organic framework (MOF) impregnated with corrole and doped with lithium.[57] The locations of the lithium atoms are determined computationally and are not consistent with those of the structurally characterized lithium salt.

Group 4 and 5 metallocorroles

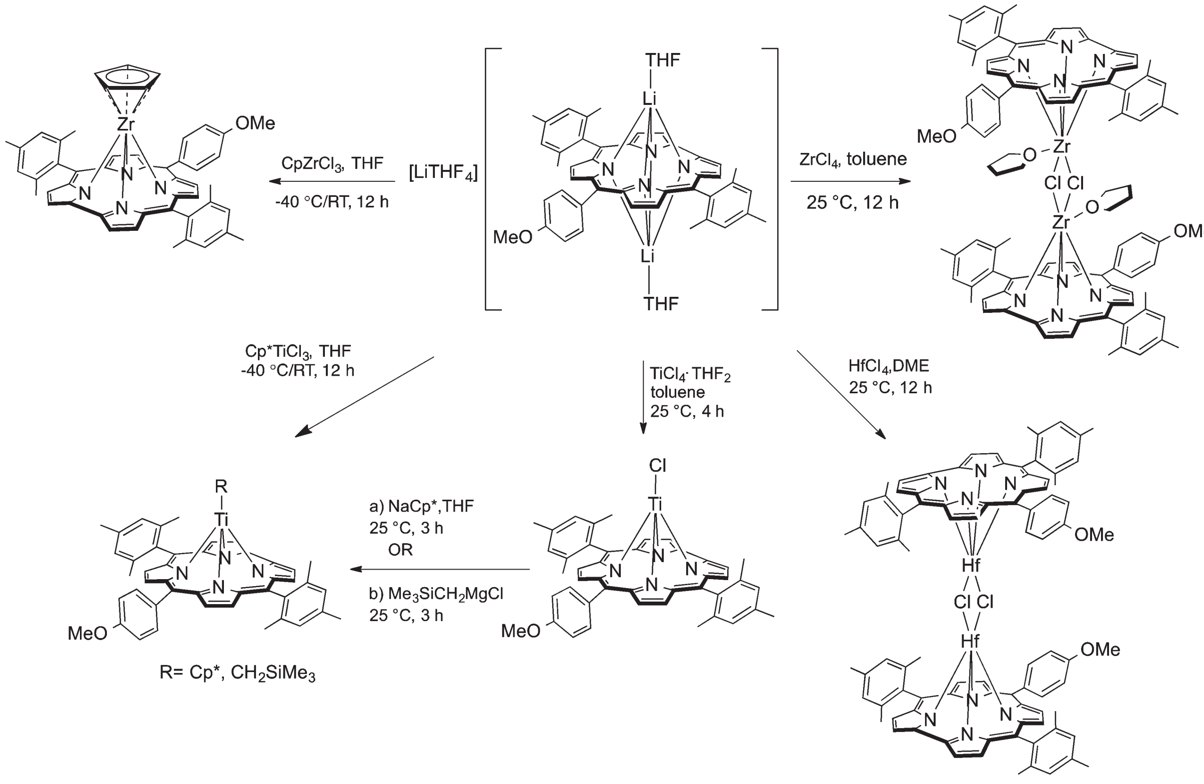
The first group 4 and 5 corrole complexes to be isolated were oxotitanium(IV) and oxovandium(IV) species identified spectroscopically by Licoccia *et al.* in 1995.[58] These compounds are both reported as doubly deprotonated [MO(corroleH)] species, and ^{1}H NMR spectroscopy and IR spectroscopy of the Ti complex appear to confirm the characterization of the extra proton as being associated with the corrole, rather than a more typical configuration with corrole as a trianionic ligand and a terminal hydroxo. The vanadium complex is believed not to form a metal(V) species due to the small ionic radius of high-valent vanadium.

More recently, a number of group 4 corrole complexes have been isolated and structurally characterized using the salt metathesis methodology outlined above (Scheme 2). Titanium(IV) and zirconium(IV) cyclopentadienyl species were prepared from metal trichloride cyclopentadienyl starting materials, providing lopsided "sandwich" complexes of the two metals.[56] Subsequent to this, reactions of titanium, zirconium, and hafnium tetrachloride with $Mes_2(p\text{-}OMePh)corroleLi_3\cdot 6THF$ provided the metal(IV) chloride corrole complexes of all three group 4 metals.[59] Interestingly, the Zr and Hf corrole chlorides exist as dimers both in solution and in solid-state structure, but the Ti corrole chloride exists as a monomer. The preference of the Ti corrole complex for a monomeric structure may be attributed to the smaller ionic radius of Ti as compared to its heavier congeners. The Ti corrole chloride has been reacted with both NaCp* and Me_3SiCH_2MgCl to produce the corresponding organometallic species in a preliminary demonstration of possible reactivity of these systems.

Group 6 metallocorroles

High valent chromium[60] and molybdenum[61] oxo corrole complexes have been known for over 30 years, and their chemistry is extensively covered in the aforementioned review by Palmer.[31] Lower valent corrole complexes are considerably less common in general and in the early metals in particular, although an interesting $[((C_6F_5)_3corroleMo)O]_2Mg(THF)_4$ species, initially formed with adventitious magnesium residual from starting material synthesis, was recently reported and is an example of a structurally characterized molybdenum(IV) corrole.[62] This structural characterization supports the spectroscopic identification of two other related molybdenum(IV) corrole species.

The first example of a tungsten corrole species, and indeed the first 5d early transition metal corrole complex, was also



Scheme 2 Preparation of group 4 corrole complexes from lithium corrole.[59]

reported recently.[33] The compound is binuclear, with two tungsten(VI) corrole units bridged by three oxygen atoms. This structure is similar to those known for a number of early transition metal porphyrins, with hafnium[63–65] being one of the closest in structural analogy both to this species and to the chloride-bridged hafnium corrole mentioned above. Similar to other heavy metal-macrocycle complexes, the tungsten is large enough that it sits considerably out of the plane of the corrole despite its high oxidation state.

Lanthanide and actinide metallocorroles

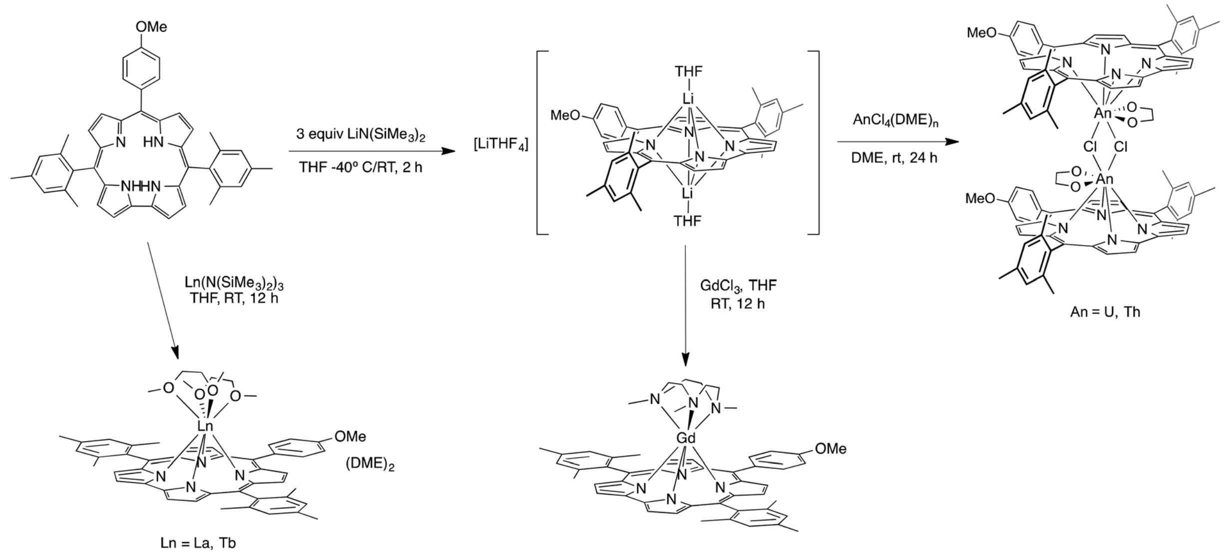
Interest in the use of conjugated macrocycles as "antennae" for luminescence sensitization of lanthanides led to the preparation some years ago of lanthanide porphyrin complexes.[66] However, the preparation of corrole complexes to the same end has been achieved only recently. In early 2013, Gross and coworkers published molecules dubbed lanthanide–corrole conjugates, where the periphery of the corrole molecule was extended to include chelating groups that supported Nd, Er, Yb, and Lu ions.[67] These metals were not directly coordinated by the corrole, but luminescence transfer between the corrole and metal was demonstrated.

Later that same year, the first examples of corroles directly coordinating to lanthanides were published by our group.[68] These were prepared by the two methodologies described above for the preparation of air-sensitive metallocorroles: the lanthanum and terbium complexes by salt metathesis and the gadolinium through the reaction of free base corrole with gadolinium(III) silyl amide (Scheme 3).

The only two actinide corrole complexes reported in the literature[69] are bridged chloride species of thorium(IV) and uranium(IV) (Scheme 3) which very closely resemble the zirconium and hafnium(IV) corrole chlorides.[59] Differences between the cyclic voltammetry of the uranium(IV) and the thorium(IV) species indicate that the uranium(IV) centre is likely involved in the redox activity of this species; the thorium species shows only two simple reversible oxidation waves, while in the case of uranium each apparent oxidation shows multiple peaks.

Comparison of structurally characterized corrole complexes of large metals

Metals with a range of ionic radii are accommodated by macrocycles in a number of ways. Porphyrins have the ability to ruffle slightly to contract their ring size for small metals, and to expand the N_4 core slightly for metals with ionic radii slightly larger than the optimal 0.65 Å.[39] Corroles are more rigid; it has been demonstrated computationally that they cannot ruffle,[70] and the slightly contracted ring as compared to porphyrin has even less space to accommodate early transition metals and heavy metals within the plane of the ring.



Scheme 3 Preparation of lanthanide and actinide corrole complexes.

Table 1 Metrical parameters of selected crystallographically characterized metallocorrole complexes

Metal	*meso*-Corrole	Other ligand	M–N$_4$ plane distance (Å)	M–L distance (range) (Å)	M–N$_{\text{corrole}}$ distance range (Å)	Reference
Li	Mes$_2$(*p*-OMePh)	DME	1.030	1.934(5)–1.988(5)	2.061(5)–2.214(5)	56
Ti	Mes$_2$(*p*-OMePh)	Cp*	0.820	2.3764(19)–2.4159(18)	2.0389(15)–2.0562(14)	56
Ti	Mes$_2$(*p*-OMePh)	Cl	0.667	2.220(6)	1.985(2)–1.996(2)	59
Ti	Mes$_2$(*p*-OMePh)	CH$_2$SiMe$_3$	0.656	2.031(2)	1.978(2)–2.009(2)	59
Zr	Mes$_2$(*p*-OMePh)	Cp	0.914	2.451(3)–2.493(3)	2.094(2)–2.174(2)	56
Zr	Mes$_2$(*p*-OMePh)	μ-Cl THF	1.355	2.6852(12)–2.6897(11)	2.161(3)–2.166(3)	59
Hf	Mes$_2$(*p*-OMePh)	μ-Cl	1.184	2.121(3)–2.296(4)	2.142(4)–2.157(4)	59
Mo	(C$_6$F$_5$)$_3$	=O	0.729	1.684(2)	2.033(2)–2.039(2)	71
W	(C$_6$F$_5$)$_3$	μ-O	0.961	1.804(6)–2.217(6)	2.058(7)–2.124(7)	33
La	Mes$_2$(*p*-OMePh)	(DME)$_2$	1.469	2.661(6)–2.746(6)	2.426(6)–2.447(6)	68
Gd	Mes$_2$(*p*-OMePh)	TACNMe$_3$	1.262	2.668(5)–2.688(5)	2.294(5)–2.350(4)	68
Tb	Mes$_2$(*p*-OMePh)	(DME)$_2$	1.272	2.540(6)–2.719(8)	2.310(5)–2.325(6)	68
Th	Mes$_2$(*p*-OMePh)	μ-Cl	1.409	2.886(1)–2.932(2)	2.356(4)–2.413(7)	69
U	Mes$_2$(*p*-OMePh)	μ-Cl	1.392	2.840(1)–2.873(2)	2.293(6)–2.357(7)	69
Bi	(C$_6$F$_5$)$_3$	(None)	1.15	(N/A)	2.23(1)–2.28(1)	72

A useful metric for comparing metallocorrole structures is the distance from the N$_4$ plane to the metal. While the dataset is still too small to make broad comparisons, this information may be used to anticipate metal displacement from corrole rings in future work, which in turn should be predictive for the possibility of preparing bis-corrole or other metal sandwich complexes based on predictions of ligand-based steric interactions.

Several points of interest can be taken from Table 1. The first is in comparing three titanium corrole species, where the M–N$_4$ distance is considerably longer for the Cp* species than for either the chloride or alkyl species. This is consistent with steric interactions between the Cp* ligand and the mesityl substituents on the corrole ring. Similar steric congestion between the THF ligands and the corrole substituents may account for the fact that the M–N$_4$ distance on the zirconium μ-Cl dimer is substantially longer than for that on the equivalent hafnium species.

This extent of variation in metal corrole distances with other changes to the ligand environment suggests that great care must be taken when drawing any comparisons between corrole species. Lanthanum(III) corrole currently holds the record for the greatest distance of a metal out of an N$_4$ conjugated macrocycle plane at 1.469 Å. This seems consistent with its lower oxidation state than the actinide(IV) corroles reported and larger ionic radius than later lanthanides. However, it is clear that many factors contribute to metal–ligand interaction in corrole species, and a larger set of structurally characterized corroles will be needed before these trends can be fully elaborated.

Conclusions and future work

While coverage of the "periodic table of corroles" has increased substantially in recent years, the future of this field still poses many challenges and opportunities. Isolation of heavier alkali metal corrole salts will no doubt lead to further synthetic opportunities, as well as presenting interesting structural information themselves. While lanthanide complexes are close analogues, the smaller members of Group 3 have not yet been characterized in corrole complexes – chemistry at these valency-saturated but sterically accessible metals could be of great interest.

Across the periodic table, there is still a dearth of lower-valent metal complexes of corroles. The reactivity of such compounds could present new opportunities in small molecule activation and catalysis, particularly as the non-innocent nature of corrole as a ligand comes to be better understood.

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