UC San Diego
UC San Diego Previously Published Works

Title

Synthesis of the cobalt–alkyne complex (η5-C5H5)(PPh3)Co{η2-(Me3Si)CC(CO2Et)} and structural characterization of trimethylsilyl substituted cobaltacyclopentadiene complexes derived therefrom

Permalink

https://escholarship.org/uc/item/1p6184kv

Authors

Bunker, Kevin D
Rheingold, Arnold L
Moore, Curtis E
et al.

Peer reviewed

CrossMark

Synthesis of the cobalt–alkyne complex $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\eta^2\text{-}(Me_3Si)C\equiv C(CO_2Et)\}$ and structural characterization of trimethylsilyl substituted cobaltacyclopentadiene complexes derived therefrom

Kevin D. Bunker, Arnold L. Rheingold, Curtis E. Moore, Marissa Aubrey, Joseph M. O'Connor*

Department of Chemistry and Biochemistry (0358), University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0358, USA

ARTICLE INFO

ABSTRACT

The reaction of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ with $TMSC\equiv C(CO_2Et)$ leads to the formation of the cobalt–alkyne complex $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\eta^2\text{-}(Me_3Si)C\equiv C(CO_2Et)\}$ (**6**). In benzene-d_6 solution containing PPh_3, **6** undergoes slow conversion to the cobaltacyclopentadiene complex $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\kappa^2\text{-}(TMS)C=C(CO_2Et)C(TMS)=C(CO_2Et)\}$ (**7**, TMS = $SiMe_3$). Alternatively, reaction of **6** and $PhC\equiv CPh$ forms the metallacyclopentadiene regioisomers $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\kappa^2\text{-}(R^1)C=C(R^2)C(Ph)=C(Ph)\}$ [**9**-major, $R^1 = SiMe_3$, $R^2 = CO_2Et$; **9**-minor, $R^1 = CO_2Et$, $R^2 = SiMe_3$). The metallacycle substitution pattern in **9**-major and **9**-minor is readily deduced from the ^1H NMR spectral resonances of the diastereotopic ethoxycarbonyl hydrogens. When the diastereotopic hydrogens of the ethoxycarbonyl have similar chemical shifts the ester is situated on the β-carbon of the metallacycle. When the methylene hydrogens give rise to well-separated resonances the ethoxycarbonyl is situated on the α-carbon of the metallacycle. The solid state structures of **7** and **9**-major were determined by X-ray crystallography.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Trimethylsilyl substituted alkynes play a key role in many reactions that proceed via cobaltacycle intermediates [1–5]. Vollhardt pioneered the use of trimethylsilyl alkynes for regio- and chemoselective reactions involving metallacyclopentadiene intermediates [1,2], as highlighted by the cyclization of **1** and (TMS)C≡C(R) to give 2,3-dihydro-5(1H)-indolizinone derivatives **2** (Scheme 1) [5]. In the cobaltacyclobutene area, we previously found that alkyne complex **3** undergoes regio- and diastereoselective cyclization to cobaltacyclobutene **4** [4a,b], which in turn undergoes regioselective coupling reactions with diazo compounds [4c], alkenes [4d], and alkynes [4e], as well as oxidation to trisubstituted furan **5** [4f] (Scheme 1).

The trimethylsilyl alkyne substituent plays an important role in the high degree of selectivity observed in the **1** to **2** and **3** to **5** cyclizations. In the course of our studies on the conversion of cobalt–alkyne complexes to cobaltacycles, we were surprised to find that there have been no previous examples of structurally
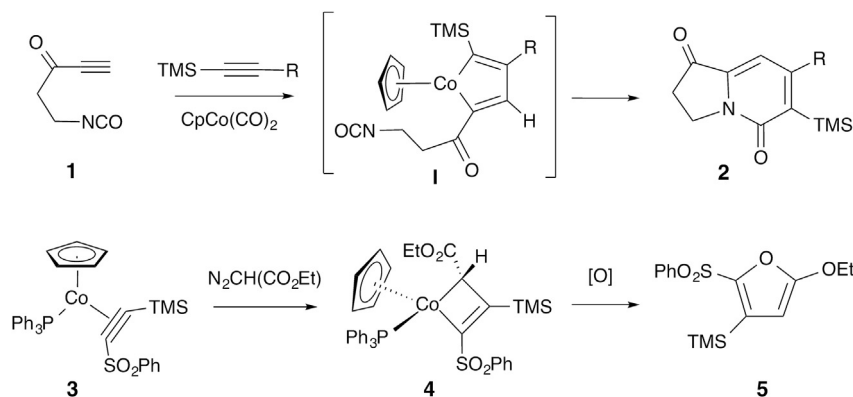
characterized cobaltacyclopentadienes bearing trimethylsilyl ring substituents. Here we report the synthesis of the cobalt–alkyne complex, $(\eta^5\text{-}C_5H_5)(PPh_3)Co[\eta^2\text{-}(Me_3Si)C\equiv C(CO_2Et)]$ (**6**), and its conversion to the first trimethylsilyl-substituted cobaltacyclopentadiene complexes to be characterized by X-ray crystallography. The substitution pattern in chiral cobaltacyclopentadienes bearing an ethoxycarbonyl ring substituent is readily deduced from the ^1H NMR resonances of the ester ring substituent. When the diastereotopic hydrogens of the ethoxycarbonyl have similar chemical shifts the ester is situated on the β-carbon of the metallacycle. When the methylene hydrogens give rise to well-separated resonances the ethoxycarbonyl is situated on the α-carbon of the metallacycle.

2. Results and discussion

In order to prepare an analog of cobalt–alkyne **3**, we employed the room temperature reaction of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ and 1-(ethoxycarbonyl)-2-(trimethylsilyl)acetylene in dry tetrahydrofuran. The resultant air stable cobalt–alkyne complex, $(\eta^5\text{-}C_5H_5)(PPh_3)Co[\eta^2\text{-}(Me_3Si)C\equiv C(CO_2Et)]$ (**6**), was isolated as orange–brown crystals in 83% yield (Scheme 2). In the IR spectrum (neat, NaCl) of **6**, $\nu(C\equiv C)$ is observed at 1797 cm^{-1}; a 385 cm^{-1}

* Corresponding author.
  E-mail address: jmoconnor@ucsd.edu (J.M. O'Connor).

Scheme 1. Regioselective cyclizations of TMS substituted alkynes.

shift to lower wavenumber relative to the corresponding value for the free alkyne (2182 cm^{-1}). In the ^{13}C NMR (C$_6$D$_6$) spectrum of **6**, the alkyne "sp" hybridized carbon resonances are observed at δ 106.5 (J_{PC} = 10.7 Hz) and 105.1 (J_{PC} $\approx$ 0 Hz); 11–13 ppm downfield of the corresponding carbon resonances for the free alkyne. For comparison, the alkyne "sp" carbons in (η^5-C$_5$H$_5$)(PPh$_3$)Co[η^2-(Ph)C≡C(Ph)] are observed at essentially the same chemical shift (δ 90.4) as those in diphenylacetylene [6]. The similar chemical shift values for the two alkyne carbons in **6** may be contrasted to those observed for more polar cobalt–alkyne complex **3** which are observed at δ 105.5 (d, J_{PC} = 3.5 Hz) and 118.1 (d, J_{PC} = 11.6 Hz) [4a]. In the case of **3**, it is the carbon bearing the electron-withdrawing sulfone substituent that exhibits the larger carbon–phosphorus coupling constant, leading us to tentatively assign the δ 106.5 resonance in **6** to the alkyne carbon bearing the electron-withdrawing ester substituent.
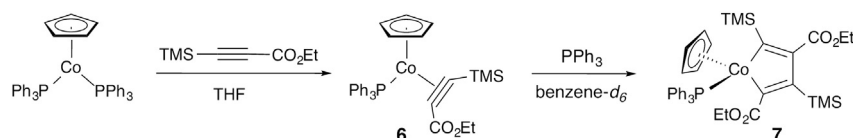
In examining the solution behavior of **6**, we observed the formation of a bis(trimethylsilyl) substituted cobaltacyclopentadiene complex (Scheme 2). Thus, when a benzene-d_6 solution of **6**, containing triphenylphosphine (0.2 equiv), was monitored by ^{1}H NMR spectroscopy at room temperature, complex **7** was observed to form over the course of 11 days, as indicated by the appearance of a new C$_5$H$_5$ resonance at δ 4.97. In addition to the C$_5$H$_5$ resonance for **7**, a singlet at δ 5.04 indicated that a minor cyclopentadienyl cobalt product had formed in <3% yield.

In the ^{1}H NMR spectrum (C$_6$D$_6$) of isolated **7**, resonances at δ 7.04 (m, 9H) and 7.70 (m, 6H) were indicative of a PPh$_3$ ligand on cobalt, and two singlets at δ 0.13 (9H, SiMe$_3$) and 0.21 (9H, SiMe$_3$) indicated that **7** had formed from a head-to-tail coupling of two alkynes. The methylene hydrogens for one of the ethoxycarbonyl substituents are observed as a two-proton multiplet at δ 4.22 whereas the other ethoxycarbonyl exhibits two methylene hydrogen resonances at 3.86 (m, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 11 Hz, 1H) and 4.03 (m, 1H) (Fig. 1). The δ 3.86 and 4.03 resonances are assigned to the diastereotopic hydrogens of the ethoxycarbonyl substituent on the α-carbon of the metallacycle ring, and the 4.22 multiplet is assigned to the ethoxycarbonyl substituent on the β-carbon. The larger chemical shift difference observed for the two diastereotopic hydrogens of the α-ethoxycarbonyl group is attributed to its the closer proximity to the stereogenic metal center.

In the ^{13}C NMR spectrum (C$_6$D$_6$) of **7**, six downfield resonances between 150 and 182 ppm are attributed to the four metallacycle ring carbons and the two ester carbonyl carbons. Resonances at δ 179.5 (J_{PC} = 29.0 Hz) and 181.5 (J_{PC} = 26.7 Hz) are readily assigned to the α-carbons of the metallacycle based on the magnitude of the carbon-phosphorus coupling constants. The β-carbons of the metallacycle are tentatively assigned to doublets at δ 167.3 (J_{PC} = 5.3 Hz) and 167.7 (J_{PC} = 3.0 Hz), and resonances at 163.4 (s) and 176.2 (s) are assigned to the ester carbonyl carbons. For comparison, one of the few cobaltacyclopentadiene analogs of **7** for which ^{13}C NMR data have been reported, (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-(Ph)C=C(Ph)C(Ph)=C(Ph)], exhibits metallacycle α- and β-carbon resonances at δ 167.7 (J_{PC} = 28 Hz) and 158.5 (J_{PC} = 2 Hz), respectively [6,7].

The minor product observed in the conversion of **6** to **7** exhibits a TMS resonance at δ 0.26 (18H) in addition to the C$_5$H$_5$ resonance at 5.04 (5H). Thus the minor product has incorporated two equivalents of TMSC≡CCO$_2$Et into a symmetric structure. Precedent for conversion of trimethylsilyl alkynes to cyclobutadiene complexes is found in the reaction of (Cp)Co(PPh$_3$)$_2$ and TMSC≡CC$_6$H$_4$C$_6$H$_4$C≡TMS to give η^4-cyclobutadiene complexes (**8**, Scheme 3) [8]. The first example of an isolated cobaltacyclopentadiene complex bearing trimethylsilyl substituents (**9**) was also formed from (Cp)Co(PPh$_3$)$_2$ and a diyne [8]. Because the minor product observed in the conversion of **6** to **7** was not successfully isolated it is not possible to distinguish between κ^2-cobaltacyclopentadiene and η^4-cyclobutadiene structures.

The solid state structure of **7** was determined by X-ray crystallographic analysis of an orange–brown single crystal (Fig. 2, Tables 1 and 2). A comparison of the structure for **7** to that of the parent cobaltacyclopentadiene, (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-CH=CHCH=CH] (**8** [3o]) reveals a number of significant perturbations in the bond distance and angle metrics that are due to the large size of the TMS substituent (cone angle = 118° [9], cyclohexane A-value 2.5 kcal/mol [10]). The Co–P and Co–C(1) bond distances in **7** are 0.051 and 0.048 Å longer than in **8** and the Co–C(1)–Si(1) angle in **7** is 3.3° larger than the Co–C(1)–H angle in **8**. These differences are presumably a consequence of steric congestion between the TMS substituent and the cyclopentadienyl/phosphine ligands. The observation that the Co–C(4)–C(11) angle in **7** is 3.6° smaller than

Scheme 2. Synthesis of bis(TMS)-substituted cobaltacyclopentadiene complex **7**.
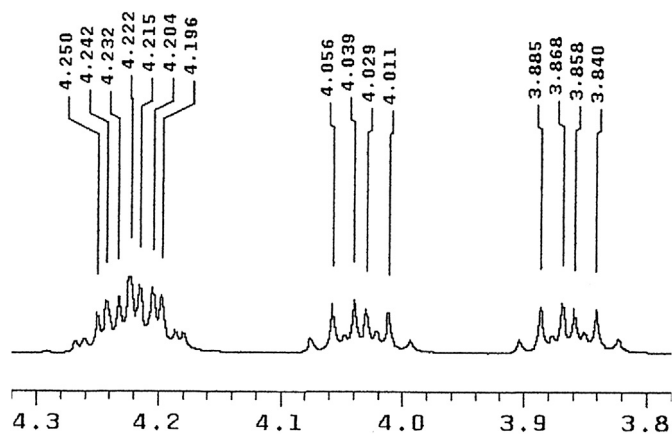
Fig. 1. ^{1}H NMR resonances for the diastereotopic methylene hydrogens of the ethoxycarbonyl substituents in **7**.

the Co–C1–H angle of **8** points to greater steric congestion between the C(4) ester and the C(3) trimethylsilyl substituents than between the C(4) ester and the cyclopentadienyl/phosphine ligands. In **7**, the trimethylsilyl group on C(3) is displaced 0.201 Å above the Co–C(1)–C(2)–C(3)–C(4) mean plane whereas the trimethylsilyl group on C(1) is displaced by only 0.030 Å. The larger displacement of Si(2) is presumably due to relief of steric congestion between the TMS and the flanking ethoxycarbonyls on C(2) and C(4).

In order to determine if ethoxycarbonyl ^{1}H NMR resonances may prove more generally useful in facilitating the assignment of regiochemistry in $(C_5H_5)Co(PPh_3)(\kappa^2$-butadiendiyl) complexes, we next examined the reaction of **6** with the symmetrically substituted alkyne, PhC≡CPh. A "one-pot" procedure was carried out in which $(\eta^5$-$C_5H_5)Co(PPh_3)_2$ was treated with an equimolar amount of ethyl 3-(trimethylsilyl) propionate, followed by the addition of excess diphenylacetylene at room temperature (Scheme 4). This procedure led to the isolation of two metallacyclopentadiene complexes, **9**-major (56%) and **9**-minor (12%). The regiochemistry for **9**-major
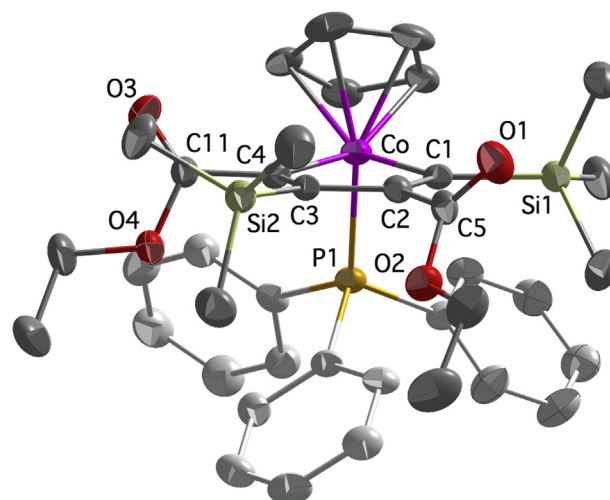

Fig. 2. ORTEP drawing of $(\eta^5$-$C_5H_5)(PPh_3)Co[\kappa^2$-(Me$_3$Si)C=C(CO$_2$Et)C(TMS)=C(CO$_2$Et)] (**7**). Hydrogen atoms are omitted and phenyl carbons are shown in lighter color for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
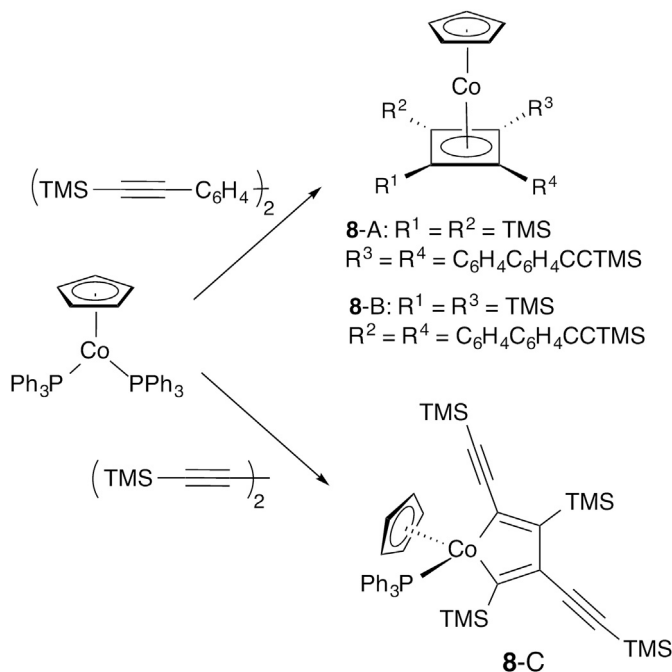
and **9**-minor is once again readily deduced from the ^{1}H NMR resonances of the ethoxycarbonyl methylene hydrogens. In the ^{1}H NMR spectrum (CDCl$_3$) of **9**-major the methylene hydrogens appear as a multiplet at δ 3.77 (2H), whereas for **9**-minor the methylene hydrogens are observed as two multiplets at 3.24 (1H) and 3.73 (1H). On this basis alone we tentatively assigned the structure of **9**-major as having the ethoxycarbonyl on the β-carbon of the metallacycle, and **9**-minor as the isomer with the ethoxycarbonyl on the α-carbon of the metallacycle. This assignment was confirmed by an X-ray crystallographic analysis of **9**-major (Fig. 3, Tables 1 and 2).

The regioselectivity observed in the formation of **9** may be compared to that previously reported for the conversion of $(\eta^5$-$C_5H_5)(PPh_3)Co[\eta^2$-(Ph)C≡C(CO$_2$Me)] (**10**) and diphenylacetylene to a 5:1 ratio of cobaltacyclopentadienes **11**-major and **11**-minor (Scheme 5) [3n,11]. The regioselectivity observed for the formation of **11** was explained as the result of a competition between steric and electronic effects, with the electronic effect favoring the electron-withdrawing methoxycarbonyl at the α-carbon, and the steric effect favoring the larger phenyl at the α-carbon. The steric effect was thought to dominate over the electron effect thereby resulting in the observed product distribution. The TMS and phenyl groups are both large substituents, with cone angles of 118° (TMS

Scheme 3. TMS-substituted cyclobutadiene and cobaltacyclopentadiene complexes [7].

Table 1
Selected bond distances (Å) and angles (°) for **7**, $(C_5H_5)(PPh_3)Co(CH=CHCH=CH)$ (**8**) [3o] and **9**-major.

Cmpd	**7**	**9**-Major	**8** [3o]
Co–C(1)	1.991(7)	1.96(1)	1.943(6)
Co–P	2.195(3)	2.157(3)	2.144(2)
Co–C(4)	1.937(7)	1.956(7)	1.947(6)
C(1)–C(2)	1.365(9)	1.31(1)	1.337(9)
C(2)–C(3)	1.471(9)	1.44(1)	1.45(1)
C(3)–C(4)	1.360(9)	1.34(1)	1.35(1)
C(1)–Si(1)	1.899(7)	1.873(9)	–
C(2)–C(5)	1.49(1)	1.50(1)	–
C(3)–Si(2)	1.891(7)	–	–
C(1)–Co–P	95.3(2)	93.4(3)	91.2(2)
C(4)–Co–P	92.4(2)	92.9(2)	90.5(2)
C(1)–Co–C(4)	82.9(3)	83.7(4)	83.2(2)
Co–C(1)–C(2)	110.0(4)	110.2(7)	112.8(5)
Co–C(4)–C(3)	117.5(5)	113.1(6)	113.7(5)
C(1)–C(2)–C(3)	119.5(6)	119.9(8)	115.2(6)
C(2)–C(3)–C(4)	109.6(5)	112.8(7)	114.8(6)

Table 2
Crystallographic data and experimental details for complexes **7** and **9**-major.

	7	9-Major
Empirical formula	$C_{39}H_{48}CoO_4PSi_2$	$C_{45}H_{44}CoO_2PSi$
Formula weight	726.85	734.79
Temperature	293(2) K	205(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Tetragonal
Space group	P2(1)/c	I-4
Unit cell dimensions	$a = 10.673(13)$ Å	$a = 25.444(10)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$b = 9.828(13)$ Å	$b = 25.444(10)$ Å
	$\beta = 94.20(10)°$	$\beta = 90°$
	$c = 38.74(4)$ Å	$c = 12.541(6)$ Å
	$\gamma = 90°$	$\gamma = 90°$
Volume	4053(8) Å^3	8119(6) Å^3
Z	4	8
Density (calculated)	1.191 mg/m^3	1.202 mg/m^3
Absorption coefficient	0.557 mm^{-1}	0.526 mm^{-1}
F(000)	1536	3088
Crystal size	0.40 × 0.40 × 0.40 mm^3	0.5 × 0.2 × 0.1 mm^3
Theta range for data collection	1.91–22.50°	2.42–23.73°
Index ranges	$0 \le h \le 11, 0 \le k \le 10,$ $-41 \le l \le 41$	$-28 \le h \le 28, -28 \le k \le 28,$ $-14 \le l \le 12$
Reflections collected	5602	20,891
Independent reflections	5287 [R(int) = 0.0483]	6030 [R(int) = 0.0881]
Completeness to theta	23.73°, 99.5%	23.73°, 97.7%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5287/0/480	6030/0/495
Goodness-of-fit on F^2	1.066	0.999
Final R indices [I > 2sigma(I)]	R1 = 0.0641, wR2 = 0.1693	R1 = 0.0677, wR2 = 0.1565
R indices (all data)	R1 = 0.0926, wR2 = 0.1928	R1 = 0.0848, wR2 = 0.1663
Absolute structure parameter	–	0.06(2)
Largest diff. peak and hole	0.467 and −0.461 e.Å^{-3}	0.616 and −0.443 e.Å^{-3}

Fig. 3. ORTEP structure of (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-(Me$_3$Si)C≡C(CO$_2$Et)C(Ph)=C(Ph)] (**9**-major). Hydrogen atoms are omitted and phenyl carbons are shown in lighter color for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
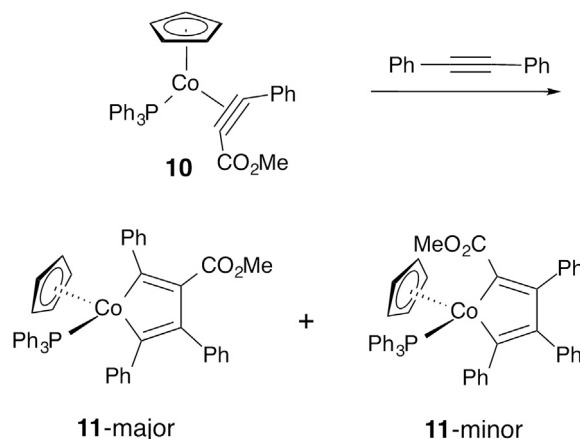
3. Experimental

3.1. General

[9]) and 105° (Ph [12]), and cyclohexane A values of 2.5 kcal/mol (TMS [10]) and 2.87 kcal/mol (Ph [13]). However the TMS substituent is a much stronger sigma donor than phenyl ($\sigma_p = -0.07$ and $\sigma_m = -0.04$ for TMS and $\sigma_p = -0.01$ and $\sigma_m = 0.06$ for Ph) [14]. The observation that the **9**-major:**9**-minor ratio is very similar to the **11**-major:**11**-minor ratio may be rationalized if TMS is larger than Ph in the context of cobaltacyclopentadiene substituent steric interactions and the steric effect is compensated for by the stronger electron-donor properties of TMS.

3.2. Preparation of (η^5-C$_5$H$_5$)(PPh$_3$)Co[η^2-(Me$_3$Si)C≡C(CO$_2$Et)] (**6**)

(η^5-C$_5$H$_5$)Co(PPh$_3$)$_2$ (0.356 g, 0.549 mmol) [3c] was dissolved in dry THF (25 mL) and 1-(ethoxycarbonyl)-2-(trimethylsilyl)

Scheme 4. Synthesis of trimethylsilyl substituted cobaltacyclopentadiene complexes **9**.

Scheme 5. Synthesis of tris(phenyl) substituted cobaltacyclopentadiene complexes **11** [10].

acetylene (106.6 μL, 0.549 mmol) was added via syringe. After stirring for 5 min the solvent was removed under vacuum and the residue was recrystallized from dry hexanes (3 mL) to give **6** (0.252 g, 83%) as air-sensitive dark orange–brown crystals. mp: 103–105 °C. IR (NaCl): 1797 (C≡C), 1677 (C=O) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (s, 9H, TMS), 1.02 (t, 3H, J = 7.2 Hz, CH$_3$), 4.09 (m, 2H, OCH$_2$), 4.64 (s, 5H, C$_5$H$_5$), 7.01 (m, 9H, m,p-PPh$_3$), 7.70 (m, 6H, o-PPh$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 0.5 (TMS), 14.8 (CH$_3$), 60.3 (OCH$_2$), 83.0 (d, J_{PC} = 3.1 Hz, C$_5$H$_5$), 105.1 (C≡C), 106.5 (d, J_{PC} = 10.7 Hz, C≡C), 127.8 (d, J_{PC} = 6.8 Hz, C$_m$, PPh$_3$), 129.2 (d, J_{PC} = 2.3 Hz, C$_p$, PPh$_3$), 134.4 (d, J_{PC} = 10.0 Hz, C$_o$, PPh$_3$), 135.7 (d, J_{PC} = 37.3 Hz, C$_i$, PPh$_3$), 163.8 (C=O). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 56.5. HRMS (FAB) Calculated for C$_{31}$H$_{34}$CoO$_2$PSi: 556.1398; Found: 556.1413.

3.3. Preparation of (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-(Me$_3$Si)C=C(CO$_2$Et)C(TMS)=C(CO$_2$Et)] (**7**)

In a sealed NMR tube, complex **6** (16.5 mg, 0.023 mmol, 0.071 M), PPh$_3$ (1.19 mg, 0.004 mmol, 0.011 M) and toluene (internal standard) were dissolved in benzene-d_6 (0.42 mL) under an atmosphere of nitrogen and the tube maintained at rt for 11 h, after which time a ^{1}H NMR spectrum of the sample indicated a 7% yield of (η^5-C$_5$H$_5$)Co(PPh$_3$)$_2$ and a 5% yield of **7**. Complex **7** was isolated by chromatography (silica gel, 3% ethyl acetate/benzene) of the reaction mixture to give **7** as an air-stable orange–brown crystalline powder. mp: 149–151 °C. IR (neat, NaCl): 1714 (C=O), 1690 (C=O) cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 0.13 (s, 9H, TMS), 0.21 (s, 9H, TMS), 1.07 (t, 3H, J = 7.2 Hz, CH$_3$), 1.11 (t, 3H, J = 7.2 Hz, CH$_3$), 3.86 (m, 1H, OCH*H*), 4.03 (m, 1H, OCH*H*), 4.22 (m, 2H, OCH$_2$), 4.97 (s, 5H, C$_5$H$_5$), 7.04 (m, 9H, m,p-PPh$_3$), 7.54 (m, 6H, o-PPh$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 1.98, 4.59, 14.5, 14.8, 59.98, 60.2, 88.3 (d, J_{PC} = 1.5 Hz), 127.9, 128.5, 129.8 (d, J_{PC} = 2.3 Hz), 134.5 (d, J_{PC} = 10.0 Hz), 163.5, 167.3 (d, J_{PC} = 5.3 Hz), 167.7 (d, J_{PC} = 3.0 Hz), 176.2, 179.5 (d, J_{PC} = 29.0 Hz), 181.5 (d, J_{PC} = 26.7 Hz). ^{31}P NMR (C$_6$D$_6$): δ 56.5. HRMS (FAB) Calculated for C$_{39}$H$_{48}$O$_4$Si$_2$PCo: 726.2161; Found: 726.2160.

3.4. Preparation of (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-(Me$_3$Si)C=C(CO$_2$Et)C(Ph)=C(Ph)] (**9**-major) and (η^5-C$_5$H$_5$)(PPh$_3$)Co[κ^2-(EtO$_2$C)C=C(TMS)C(Ph)=C(Ph)] (**9**-minor)

In the dry box, ethyl 3-(trimethylsilyl) propionate (295 μL, 0.258 g, 1.52 mmol) was added via syringe to a benzene solution (40 mL) of (η^5-C$_5$H$_5$)Co(PPh$_3$)$_2$ (0.985 g, 1.52 mmol) at rt. The solution was allowed to stir for 5 min followed by addition of diphenylacetylene (0.406 g, 2.28 mmol). The reaction mixture was stirred at rt for 17 h. Evaporation of the volatiles and chromatography (silica gel, 5% ethyl acetate/hexanes) in the air gave **9**-major as an orange powder in 56% yield (0.626 g), and **9**-minor as a yellowish-orange crystalline powder in 12% yield (0.131 g).

9-major: mp: 160–162. IR (NaCl, neat): 1704, 1435, 1237, 1187 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −0.06 (s, 9H, TMS), 0.78 (t, 3H, J = 7.2 Hz, CH$_3$), 3.77 (m, 2H, OCH$_2$), 4.89 (s, 5H, C$_5$H$_5$), 6.39 (br s, 2H, o-Ph), 6.53 (br s, 2H, o-Ph), 6.77 (m, 3H, m,p-Ph), 6.87 (m, 3H, m,p-Ph), 7.20–7.74 (m, 15H, PPh$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 3.2 (TMS), 13.8 (CH$_3$), 59.5 (OCH$_2$), 88.6 (d, J_{PC} = 1.5 Hz, C$_5$H$_5$), 123.7, 124.2, 126.3, 126.6, 127.8 (d, J_{PC} = 9.5 Hz, C$_m$, PPh$_3$), 128.0 (C$_p$, PPh$_3$), 128.9, 129.81, 129.83, 133.9 (br s, C$_o$, PPh$_3$), 141.3 (d, J_{PC} = 2.9 Hz, C$_i$, PPh$_3$), 153.6, 157.3 (d, J_{PC} = 3.4 Hz), 164.8, 167.3 (d, J_{PC} = 5.3 Hz), 172.5 (d, J_{PC} = 26.9 Hz), 172.8 (d, J_{PC} = 31.8 Hz). Anal. Calcd. for C$_{45}$H$_{44}$O$_2$PSiCo: C, 73.55; H, 6.04; Found: C, 73.33; H, 6.40.

9-minor: mp 180–181. IR (NaCl, neat): 1684, 1434, 1173 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −0.24 (s, 9H, TMS), 0.95 (t, 3H, J = 7.5 Hz, CH$_3$), 3.24 (m, 1H, OCH*H*), 3.73 (m, 1H, OCH*H*), 4.96 (s, 5H, C$_5$H$_5$), 6.32 (m, 2H, o-Ph), 6.72 (m, 2H, o-Ph), 6.78–6.89 (m, 6H, m,p-Ph), 7.0–7.5 (br s, 15H, PPh$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 1.1 (TMS), 13.9 (CH$_3$), 59.5

(OCH$_2$), 89.5 (d, J_{P-C} = 1.4 Hz, C$_5$H$_5$), 123.4, 124.6, 126.2, 126.6, 127.7 (d, J_{PC} = 9.2 Hz), 128.4, 129.66 (br), 129.68 (br), 129.8, 133.6 (d, J_{PC} = 9.8 Hz), 143.9 (d, J_{PC} = 3.2 Hz), 152.9, 160.5, 168.3 (d, J_{PC} = 5.3 Hz), 172.5 (d, J_{PC} = 28.4 Hz), 173.1 (d, J_{PC} = 27.0 Hz), 175.5. HRMS (FAB) Calculated for C$_{45}$H$_{44}$O$_2$PSiCo: 734.2180; Found: 734.2143.

4. Summary

In summary, three new trimethylsilyl-substituted cobaltacyclopentadiene complexes have been prepared via reactions of the unsymmetrically substituted cobalt–alkyne complex, (η^5-C$_5$H$_5$)(PPh$_3$)Co[η^2-(Me$_3$Si)C≡C(CO$_2$Et)] (**6**) with additional alkyne. The assignment of regiochemistry in cobaltacyclopentadiene complexes bearing ethoxycarbonyl ring substituents is conveniently established from the chemical shift pattern observed for the ^{1}H NMR resonances of the diastereotopic methylene hydrogens in the ethoxycarbonyl substituents. The first solid state structures of trimethylsilyl substituted cobaltacyclopentadienes are reported.

Appendix A. Supplementary material

The supplementary crystallographic data for **7** (CCDC 952275) and **9**-major (CCDC 952276) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 23 (1984) 539;
(b) K.P.C. Vollhardt, Acc. Chem. Res. 10 (1977) 1.
[2] For representative recent examples of cobalt-mediated TMS-alkyne chemistry: (a) G.K. Windler, M.-X. Zhang, R. Zitterbart, P.F. Pagoria, K.P.C. Vollhardt, Chem. Eur. J. 18 (2012) 6588;
(b) J.A. González Gómez, J.R. Green, K.P.C. Vollhardt, Synlett 6 (2011) 805;
(c) P.I. Dosa, Z. Gu, D. Hager, W.L. Karney, K.P.C. Vollhardt, Chem. Commun. (2009) 1967;
(d) G. Roidl, V. Enkelmann, R.D. Adams, U.H.F. Bunz, J. Organomet. Chem. 578 (1999) 144;
(e) G. Roidl, V. Enkelmann, U.H.F. Bunz, Organometallics 18 (1999) 4;
(f) M. Altmann, V. Enkelmann, F. Beer, U.H.F. Bunz, Organometallics 15 (1996) 394;
(g) U.H.F. Bunz, J. Organomet. Chem. 683 (2003) 269;
(h) H.V. Nguyen, M.R. Yeamine, J. Amin, M. Motevalli, C.J. Richards, J. Organomet. Chem. 693 (2008) 3668;
(i) J. Amin, C.J. Richards, Chem. Commun. 48 (2012) 10192;
(j) D.J. Cassar, E. Nagaradja, D.C.D. Butler, D. Villemin, C.J. Richards, Org. Lett. 14 (2012) 894;
(k) P. Mandapati, N. Singh, D. Kumar, A.J. Elias, J. Organomet. Chem. 716 (2012) 208;
(l) M.S. Kumar, D. Kumar, A.J. Elias, Inorg. Chim. Acta 372 (2011) 175;
(m) H.P. Gupta, M.S. Kumar, S. Upreti, A.J. Elias, Eur. J. Inorg. Chem. (2006) 5022;
(n) P. Garcia, Y. Evanno, P. George, M. Sevrin, G. Ricci, M. Malacria, C. Aubert, V. Gandon, Chem. Eur. J. 18 (2012) 4337;
(o) P. Garcia, Y. Evanno, P. George, M. Sevrin, G. Ricci, M. Malacria, C. Aubert, V. Gandon, Org. Lett. 13 (2011) 2030;
(p) G. Bertrand, L. Tortech, D. Fichou, M. Malacria, C. Aubert, V. Gandon, Organometallics 31 (2012) 126;
(q) A. Sekiguchi, M. Tanaka, T. Matsuo, H. Watanabe, Angew. Chem. Int. Ed. 40 (2001) 1675.
[3] For representative reactions of cobalt alkyne complexes: (a) H. Yamazaki, N. Hagihara, J. Organomet. Chem. 7 (1967) P22;
(b) H. Yamazaki, N. Hagihara, J. Organomet. Chem. 21 (1970) 431;
(c) H. Yamazaki, N. Hagihara, Bull. Chem. Soc. Jpn. 44 (1971) 2260;
(d) Y. Wakatsuki, H. Yamazaki, H. Iwasaki, J. Am. Chem. Soc. 95 (1973) 5781;
(e) K. Yasufuku, H. Yamazaki, J. Organomet. Chem. 139 (1976) 405;
(f) H. Yamazaki, Y. Wakatsuki, J. Organomet. Chem. 139 (1977) 157;
(g) K. Yasufuku, H. Yamazaki, J. Organomet. Chem. 127 (1977) 197;
(h) Y. Wakatsuki, H. Yamazaki, J. Organomet. Chem. 139 (1977) 169;
(i) H. Yamazaki, Y. Wakatsuki, J. Organomet. Chem. 149 (1978) 377;
(j) P. Hong, K. Aoki, H. Yamazaki, J. Organomet. Chem. 150 (1978) 279;
(k) Y. Wakatsuki, H. Yamazaki, J. Organomet. Chem. 149 (1978) 385;

(l) L.P. McDonnell Bushnell, E.R. Evitt, R.G. Bergman, J. Organomet. Chem. 157 (1978) 445;

(m) Y. Wakatsuki, K. Aoki, H. Yamazaki, J. Am. Chem. Soc. 101 (1979) 1123;

(n) Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, J. Am. Chem. Soc. 105 (1983) 1907;

(o) H. Yamazaki, Y. Wakatsuki, J. Organomet. Chem. 272 (1984) 251;

(p) Y. Wakatsuki, S. Miya, S. Ikuta, H. Yamazaki, J. Chem. Soc. Chem. Commun. (1985) 35;

(q) Y. Wakatsuki, S. Miya, H. Yamazaki, S. Ikuta, J. Chem. Soc. Dalton Trans. (1986) 1201;

(r) Y. Wakatsuki, S. Miya, H. Yamazaki, J. Chem. Soc. Dalton Trans. (1986) 1207;

(s) Y. Wakatsuki, K. Aoki, H. Yamazaki, J. Chem. Soc. Dalton Trans. (1986) 1193;

(t) Y. Wakatsuki, H. Yamazaki, Inorg. Synth. 26 (1989) 189.

[4] (a) J.M. O'Connor, K.K. Baldridge, C.L. Vélez, A.L. Rheingold, C.E. Moore, J. Am. Chem. Soc. 135 (2013) 8826;

(b) J.M. O'Connor, H. Ji, M. Iranpour, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 1586;

(c) J.M. O'Connor, M.-C. Chen, R.L. Holland, A.L. Rheingold, Organometallics 30 (2011) 369—371;

(d) R.L. Holland, K.D. Bunker, C.H. Chen, A.G. DiPasquale, K.K. Baldridge, J.M. O'Connor, J. Am. Chem. Soc. 130 (2008) 10093;

(e) J.M. O'Connor, B.S. Fong, H.-L. Ji, K. Hiibner, A.L. Rheingold, J. Am. Chem. Soc. 117 (1995) 8029;

(f) J.M. O'Connor, H. Ji, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 9846—9847;

(g) B.T. Donovan-Merkert, J. Malik, L.V. Gray, J.M. O'Connor, B.S. Fong, M.-C. Chen, Organometallics 17 (1998) 1007.

[5] R.A. Earl, K.P.C. Vollhardt, J. Am. Chem. Soc. 105 (1983) 6991.

[6] F. Hoffman, J. Wagler, G. Roewer, Z. Anorg. Allg. Chem. 634 (2008) 1133.

[7] For other cobaltacyclopentadiene complexes for which ^{13}C NMR data have been reported: (a) C.-P. Chang, R.G. Kultyshev, F.-E. Hong, J. Organomet. Chem. 691 (2006) 5831 (η^5-C$_5$H$_5$)(PPh$_3$)Co{κ^2-(PPh$_2$)C]C(H)C(H)]C(PPh$_2$)}, δ 173.4 (dd, J = 76.5, 29.5 Hz, α-carbons), 155.8 (apparent t, J = 7.4 Hz, β-carbons);

(b) R. Diercks, B.E. Eaton, S. Gürtzgen, S. Jalisatgi, A.J. Matzger, R.H. Raddle, K.P.C. Vollhardt, J. Am. Chem. Soc. 120 (1998) 8247. δ 197.4 (α-carbons) and 146.6 (β-carbons).

[8] T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, Inorg. Chim. Acta 230 (1995) 215.

[9] J.S. Panek, A. Prock, K. Eriks, W.P. Giering, Organometallics 9 (1990) 2175.

[10] W. Kitching, H.A. Olszowy, G.M. Drew, W. Adcock, J. Org. Chem. 47 (1982) 5153.

[11] See also: M.S. Kumar, S. Upreti, A.J. Elias Inorg. Chem. 45 (2006) 7835.

[12] C.A. Tolman, Chem. Rev. 77 (1977) 313.

[13] E.L. Eliel, M. Manoharan, J. Org. Chem. 46 (1981) 2085.

[14] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.