Synthesis and reactivity of bis-alkynyl appended metallocenes of Ti, Fe, and Co

Preeti Chadha, Jason L. Dutton, and Paul J. Ragogna

Abstract: (Dimethyl)(phenylethynyl)silyl-substituted cyclopentadiene $C_5H_5SiMe_2C_2Ph$ (1) was synthesized by the reaction of in situ generated $C_5H_5SiMe_2Cl$ with LiC₂Ph. Metallation of 1 with "BuLi or KN(SiMe₃)₂ gave the corresponding Li (2) and K (3) salts. Transmetallation of 2 with transition metal halides MCl₂ (M = TiCl₂, Fe, and Co) generated the corresponding early and late transition metal metallocenes (4, 5, and 6) with pendant alkynyl substituents. Compounds 4 and 6 are the first examples of bis alkyne appended Ti and Co metallocenes. Complexes 5 and 6 undergo alkyne dimerization in the presence of CpCo(CO)₂ generating metallocenophanes 7 and 8 incorporating two metal atoms. Compounds 3, 4Cl₂, 6, and [8][OTf] have been characterized by single crystal X-ray structure analysis.

Key words: cyclopentadiene, alkyne, titanium, cobalt, heterometallic, metallocenophane.

Résumé : On a réalisé la synthèse du (diméthyl)(phényléthynyl)silylcyclopentadiène, $C_5H_5SiMe_2C_2Ph$ (1) par réaction du chlorure de (diméthyl)(phényléthynyl)silyle, $C_5H_5SiMe_2Cl$ avec le LiC₂Ph. La métallation du produit 1 avec "BuLi ou le KN(SiMe₃)₃ conduit aux sels correspondants du lithium (2) ou du potassium (3). La transmétallation du produit 2 avec des halogénures de métaux de transitions, MCl₂ (M = TiCl₂, Fe et Co) conduit aux métallocènes correspondants (4, 5 et 6) de métaux de transition du début et de la fin de cette série portant des substituants alcynyles. Les composés 4 et 6 sont les premiers exemples de métallocènes du titane et du cobalt portant deux appendices bisalcyne. Les complexes 5 et 6, mis en présence de CpCo(CO)₃, donnent lieu à une dimérisation de l'alcyne qui conduit aux métallocénophanes 7 et 8 incorporant deux atomes métalliques. On a caractérisé les composés 3, 4Cl₂, 6 et [8][OTf] par diffraction des rayons-X par un cristal unique.

Mots-clés : cyclopentadiène, alcyne, titane, cobalt, hétérométallique, métallocénophane.

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Introduction

Cyclopentadienyl (Cp) ligands are one of the most common ligands used in organometallic chemistry as they form complexes with most of the transition metals. Various functional groups have been attached to the Cp ring such as phosphines,1 amines,2 and carboxylates,3 as well as directly linked hetero atoms including numerous p-block elements⁴ and transition metals.⁵ In many of these cases, the substituents are attached to the π -ligand framework early on during the ligand synthesis, prior to complexation of the central metal. The attachment of various types of alkenyl substituents continues to be of considerable interest, since it allows for the development of organic functional group chemistry at the framework of the preassembled metallocene systems. This includes addition reactions,⁶ carbon–carbon coupling reactions at the metallocene backbone resulting in the formation of ansa-metallocenes by intramolecular olefin metathesis (RCM),⁷ photochemical [2 + 2] cycloaddition reactions,⁸ or by a Mannich type reaction.⁹ However, there are few examples of metallocenes with alkyne-appended Cp ligands except for the group 8 metals, which are easily accessible owing to their high stability under various conditions.¹⁰ The bis-alkynyl substituted ferrocenes have been primarily prepared by the coupling of alkynes with diiodo ferrocene.^{11a,11b} To make these alkyne substituents more accessible for other transition metals, we have developed a preassembled alkyne-appended Cp ligand (1), which can then be attached to various metals such as Ti, Co, and Fe to generate the corresponding metallocenes.

In this context, we describe the synthesis of an alkyneappended Cp ligand where the alkyne is bridged to the Cp ring by the heteroatom silicon. Various metallocenes have been synthesized using the ligand, and dimerization of the alkyne substituent has been carried out yielding metallocenophanes 7 and 8 incorporating two metal atoms.

Results and discussion

Synthesis

Ligand synthesis

The 1:1 stoichiometric reaction of LiCp with Me_2SiCl_2 at -40 °C in THF resulted in a pale yellow solution. The reaction mixture was allowed to stir for 3-4 h, warming

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P. Chadha, J.L. Dutton, and P.J. Ragogna.¹ Department of Chemistry, The University of Western Ontario, 1151 Richmond St, London, ON N6A 5B7, Canada.

¹Corresponding author (e-mail: pragogna@uwo.ca).

Scheme 1. Synthesis and deprotonation of the ligand.

slowly to room temperature. The reaction mixture was cooled again to -40 °C and 1 stoichiometric equiv of lithium phenyl acetylide was added (Scheme 1). The solvent was removed in vacuo and the solids washed with *n*-pentane and filtered. The filtrate was concentrated resulting in the formation of a yellow-orange oil. Proton NMR spectroscopy of the crude oil revealed signals consistent with one major product; however, one broad signal was observed for the Cp protons at room temperature. Upon lowering the temperature to -20 °C, the Cp protons became resolved within the NMR spectra and the three expected isomers (1a-1c) were detected. The ratio of the three isomers 1a (84%), 1b (13%), and 1c (3%) were obtained by ¹H NMR spectroscopy at -20 °C.¹¹ The presence of the three isomers were confirmed by ²⁹Si NMR spectroscopy (¹H-²⁹Si gHMBC) and were observed at $\delta_{Si} = -18.6$ for **1a** and $\delta_{Si} = -25$ ppm for **1b** and **1c**). The intermediate CpSiMe₂Cl^{11a} generated during the initial reaction of LiCp and Me₂SiCl₂ was not isolated as it has a very low boiling point,¹² which hinders its isolation in good yields. The in situ generation of CpSiMe₂Cl in a one-pot procedure results in higher yields of **1**. In an independent recent report by Roewer and co-workers,¹³ where the CpSiMe₂Cl was isolated, the yield was 30%, whereas our approach gives a 50% yield. Reverse addition of Me₂SiCl₂ to the LiCp solution leads to the formation of other unwanted side products, namely Cp₂SiMe₂. Traces of Cp₂SiMe₂ and (PhC₂)₂SiMe₂ were identified in the crude mixture resulting from slight variations in the stoichiometry. Further purification was carried out by fractional distillation to give the ligand (1) in 50% overall yield. The ligand must be pure before attempting the subsequent deprotonation to generate the lithium salt (2) cleanly. Freshly prepared 1 was either stored at -30 °C or converted to its stable Li or K salt (2^{13} and 3, respectively) by deprotonation with either "BuLi or KN(SiMe₃)₂. Single crystals were obtained for the potassium salt (3) by slow diffusion of *n*-pentane into a THF solution of the ligand and X-ray diffraction studies confirmed the expected connectivity (Fig. 1).

Metallation of the ligand — Formation of cyclopentadienyl sandwich complexes

To probe the reactivity and utility of the ligand, metal–Cp complexes were synthesized. The general scheme for the synthesis of the $(RC_5H_4)_2M$ complexes $(M = TiCl_2, Fe, Co; R = SiMe_2C_2Ph)$ involved transmetallation of the lithium salt (2) with the corresponding transition metal halide. Reaction of 2.4 stoichiometric equiv of 2 with TiCl₄ in *n*-hexane resulted in a colour change from white to yellow and finally to red over a period of 4 h. Proton NMR spectra obtained from the yellow solution showed two sets of Cp pseudo triplets and when the reaction mixture turned red, only one set of Cp protons remained. An excess of the ligand 2 (2.4 stoi-

Scheme 2. Synthesis of compounds 4Cl₂, 4Me₂, 5, and 6.

$$2 + MCI_2 \xrightarrow{M} M \xrightarrow{Et_2O} M \xrightarrow{M} M$$

$$M = TiCI_2 (4CI_2); n-Hexane M = TiMe_2 (4Me_2)$$

$$M = Fe (5); THF M = Co (6); Et_2O/THF R = SiMe_2C_2Ph$$

chiometric equiv instead of 2) was used to ensure complete conversion. The red solution was filtered, cooled to -30 °C for complete precipitation of LiCl, filtered again, then concentrated and left at -30 °C allowing red crystals of $4Cl_2$ to form. X-ray quality crystals of $4Cl_2$ were obtained from a concentrated *n*-hexane solution (see X-ray crystallography, see Fig. 2). Compound $4Cl_2$ was treated with 3 stoichiometric equiv of MeMgCl in an Et₂O/*n*-hexane mixture resulting in a colour change from red to yellow-orange (Scheme 2). The ¹H NMR spectrum of an aliquot of the reaction mixture showed a significant shift of the Cp protons ($\Delta \delta = 0.59$ in $4Cl_2$ to $\Delta \delta = 0.09$ in $4Me_2$) and an upfield shift of 0.3 ppm in the methyl groups attached to the silicon atom (Table 1). An upfield shift of ~6 ppm is observed in the ²⁹Si NMR spectrum of $4Cl_2$ and $4Me_2$ when compared with the free ligand (1).

Treatment of 2 with 0.5 stoichiometric equiv of anhydrous FeCl₂ or CoCl₂ in THF at room temperature resulted in the formation of a yellow-orange or red solution, respectively, over a period of 3-4 h (Scheme 2). The solvent was removed in vacuo, the residue washed with n-pentane, and centrifuged. The *n*-pentane was then removed to give orange or red-maroon solids, respectively. The orange solid was identified as compound 5 by comparison with the literature.¹⁴ However, the literature procedure involves the reaction between dilithio-ferrocene and chloro(dimethyl)(phenylethynyl) silane, which is not readily accessible. Compound 5 was further purified by sublimation or recrystallization from *n*-hexane. The ¹H NMR spectrum of the redissolved red-maroon powder showed a singlet at 3.62 ppm integrating to six protons (SiMe₂), a doublet and two triplets in the aryl region integrating in a 2:2:1 ratio. The Cp protons were not observed owing to the paramagnetic nature of compound 6. Single crystals were obtained from a concentrated Et₂O solution of the red-maroon powder and X-ray diffraction studies showed the expected connectivity (Fig. 3).

Compound **6** was purified by recrystallization from Et_2O/n -pentane and was then oxidized with AgOTf to form compound **[6][OTf]**, allowing full NMR spectroscopic characterization.

Fig. 1. Extended solid-state structure of **3**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are removed for clarity. The THF molecule is disordered with the four carbon atoms occupying two different positions of 50% occupancy each. Only one set of carbon atoms is shown for THF.



Fig. 2. Solid-state structure of $(RC_5H_4)_2TiCl_2$ (**4Cl**₂), R = Si-Me₂C₂Ph. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are removed for clarity.



Cyclization of the alkyne moiety

Compounds 5, 6, and [6][OTf] were photolyzed with $CpCo(CO)_2$ to study if the alkynes undergo inter- or intramolecular cyclization. The reactions were performed in benzene- d_6 and monitored by ¹H NMR spectroscopy. The reaction proceeded to completion over a period of 40 h (Scheme 3). Some decomposition was observed, resulting in the formation of a brown solid, which was filtered off, the volatiles removed, and the residue washed with *n*-pentane to give orange (7) and brown solids (8 and [8][OTf]), respectively. The ¹H NMR spectra of the solids revealed a lowering of symmetry resulting in four different signals for the cyclopentadienyl rings and two different methyl signals in 7 and [8][OTf] for the silicon-bound methyl groups.

Carbon-13 NMR spectra of 7 and **[8]**[**OTf**] revealed an upfield shift in the alkyne carbon signals ($\delta = 93$ and 106 ppm in 5 to $\delta = 66$ and 88 ppm in 7; see Table 1), which is typical of CbCoCp complexes¹⁵, giving evidence for the formation of a cyclobutadiene ring. A similar effect was observed for **[8]**[**OTf**]. Silicon-29 NMR spectrum showed a downfield shift of about 12 ppm in both 7 and **[8]**[**OTf**].

Compound [8][OTf] can be prepared either by the alkyne cyclization of [6][OTf] or by the cyclization of 6 first to form 8 and then oxidation of 8 with AgOTf to yield [8][OTf] (Scheme 3).



Scheme 3. Synthesis of compounds 7–8.



X-ray crystallography

The solid-state structure of the potassium salt of the ligand (3) shows that the K atom is sandwiched between two Cp rings and is coordinated by a THF molecule. The interaction between the K and the Cp rings gives rise to extended zigzag chain structure (Fig. 1), reminiscent of group 1 metallocenes.^{1a,16,17} The K–Cp_{centroid} distances are 2.81 Å and 2.82 Å; the Cp_{centriod}–K–Cp_{centroid} angle is 138.0°; the K–K– K angle is 138.5°; and the K–Cp_{centroid}–K angle is 173.2°, which are indicative of a formal coordination number of 8 for each K atom.¹⁷ This suggests an interaction with the alkyne filling the eighth coordination site (K–C8 = 3.406(3) Å). Similar interaction was observed for an appended alkene moiety; however, the interaction was slightly weaker (3.58(3) Å).¹⁷

The molecular structure of $4Cl_2$ reveals the anticipated connectivity (Fig. 2).¹⁸ Selected bond lengths and angles are given in Table 2. The alkyne fragments are oriented away from each other and away from the metal centre, and there is no interaction observed between the metal and the alkyne.

In the solid-state structure of 6 (Fig. 3), the two alkynes are oriented away from each other in a trans fashion, the two Cp rings being completely staggered, with the alkynes bent towards the metal centre as opposed to 4Cl₂. However, for the cyclization to take place, the alkynes are forced to rotate to obtain a cis geometry. As reported earlier for various [2 + 2] cyclization reactions at the cobalt centre,¹⁹ initial complexation of one of the alkynes with the cobalt centre, probably drives the formation of the cyclized products 7, 8, and [8][OTf]. In this case, the formation of only one isomer (cis isomer) was observed where the two phenyl groups are cis to each other, as seen from the solid-state structure of [8][OTf] (Fig. 4) and from NMR spectroscopy. There is no indication of intermolecular cyclization. The change from sp to sp² hybridization is clearly evident on comparison of the C-Calkyne bond lengths in 8 and [10][OTf], which changes from 1.20 Å (avg.) in 6 to 1.48 Å (avg.) in [8][OTf], typical of other CbCoCp compounds (Table 2). The Si-CC_{alkvne}

	Spectral data							
			¹ H NMR shifts (ppm)					
Compound	²⁹ Si (ppm)	¹³ C (Si–CC–Ph) (ppm)	Ср	$\Delta \delta_{Cp}$	SiMe ₂			
1			6.59, 6.67	0.08	0.10			
4Cl ₂	-25.0	93.51, 107.96	6.20, 6.79	0.59	0.65			
4Me ₂	-25.8	93.29, 107.57	6.35, 6.44	0.09	0.35, 0.39			
5	-21.5	93.40, 106.00	4.35, 4.51	0.16	0.52			
7	-9.3	66.42, 88.11 (Cb)	4.16, 4.27, 4.46		0.40, 0.60			
[6][OTf]	-22.5	92.71, 109.34	5.73, 5.93	0.20	0.47			
[8][OTf]	-9.8	61.35, 88.77 (Cb)	4.96, 5.78, 6.09, 6.48		0.08, 0.41			

Table 1. Selected spectral data for compounds 1-8.

Fig. 3. Solid-state structure of compound **6**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are removed for clarity.



bond length is slightly elongated in **[8]**[**OTf**] (1.858(5) and 1.856(6) Å) compared with that in **6** (1.848(3) Å). The Cb–Co–Cp angle remains almost linear (179.6°), indicating that the structure is not strained and is in accordance to what is expected for a [4]cobaltocenophane.²⁰ However, there are no other known structures of [4]cobaltocenophanes. The crystallographic data for **3**, **4Cl**₂, **6**, and **[8]**[**OTf**] are found in Table 3.

Similar [2 + 2] cyclization reactions of the appended alkynes in compound **4Me**₂ were, however, unsuccessful and lead to the formation of multiple products as seen from the ¹H NMR spectrum of the crude sample.

Conclusion

Early and late transition metal metallocenes ($4Cl_2$, $4Me_2$, 6, and 7) with a cyclopentadienyl ligand bearing an appended alkyne moiety have been synthesized following a general metathesis route with the preassembled ligand system. Compounds 4 and 6 are the first examples of bis(alkyne)appended Ti and Co metallocenes. This shows the potential of this ligand to form complexes with a wide variety of transition metals. Alkyne dimerization of the appended alkynes gave rise to metallocenophanes 7 and 8 incorporating two metal atoms. Compound 8 is the first example of a [4]cobaltocenophane with a single Si₂C₂ bridge.

Experimental section

Manipulations were performed in an N2-filled MBraun

Labmaster 130 glovebox in 4 dram vials (1 dram = 3.552 cm^3) affixed with Teflon-lined screw caps or using standard Schlenk techniques. Dichloromethane, THF, MeCN, Et₂O, *n*-pentane, and *n*-hexane were obtained from Caledon Laboratories and dried using the MBraun solvent purification system that utilizes appropriate drying agents. The dried solvents were stored in Straus flasks under a N₂ atmosphere or over 4 Å molecular sieves in the glovebox. Solvents for NMR spectroscopy (CDCl₃, C₆D₆, CD₃CN, and C₅D₅N) were purchased from Cambridge Isotope Laboratories and dried by stirring overnight over CaH₂, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves.

Dicyclopentadiene and phenyl acetylene were purchased from Sigma-Aldrich and distilled prior to use. Lithium cyclopentadienide^{21a} and lithium phenylacetylide^{21b} were prepared using literature methods. ^{*n*}BuLi (1.6 mol/L solution in *n*-hexane), MeMgCl (2 mol/L solution in THF), KN(SiMe₃)₂, and PPh₃ were purchased from Sigma-Aldrich and used as received. Cobalt chloride, FeCl₂, and CpCo(CO)₂ were purchased from Strem Chemicals. Dichlorodimethylsilane was purchased from the Fluka Chemical Company, dried over CaH₂, distilled prior to use, and stored in the glovebox. Titanium tetrachloride (TiCl₄) and AgOTf were purchased from Alfa Aesar and used as received (OTf = triflate; trifluoromethanesulphonate).

NMR spectra were recorded using a Varian INOVA 400 MHz spectrometer (${}^{31}P$ = 161.83 MHz, ${}^{29}Si$ = 19.86 MHz, and ${}^{13}C$ = 100.52 MHz). Phosphorus-31 NMR spectra was externally referenced to 85% H₃PO₄ (δ = 0.00 ppm). Proton and ¹³C{¹H} NMR spectra were referenced relative to Me₄Si using the NMR solvent (¹H–CHCl₃, δ = 7.26 ppm; C₆HD₅, δ = 7.16 ppm; CHD₂CN, δ = 1.96 ppm; C₅HD₄N, δ = 8.74, 7.58, or 7.22 ppm; ¹³C{¹H}- $CDCl_3, \delta = 77.2 \text{ ppm}; C_6D_6, \delta = 128.4 \text{ ppm}; CD_3CN, \delta =$ 1.3 or 118.3 ppm; C_5D_5N , $\delta = 150.2$, 135.9, or 123.9 ppm). Fluorine-19 NMR spectra were referenced relative to CFCl₃ $(\delta = 0.00 \text{ ppm})$ using neat Ph–CF₃ ($\delta = -63.7 \text{ ppm}$) as an external standard. Silicon-29 NMR chemical shifts were determined by gradient heteronuclear multiple bond coherence (gHMBC) experiments. FT-IR spectra were collected on samples as thin films on KBr plates or as a KBr disk using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm⁻¹. Decomposition and (or) melting points were recorded in flame-sealed capillary tubes using a Gallenkamp variable heater. Suitable single crystals for X-ray diffraction studies were individually selected under Paratone-N oil and

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	Compound					
	3	4Cl ₂	6	[8][OTf]		
Bond length (Å)						
M—Cp _{centroid}	2.81(±0.01)	2.06(±0.01)	1.72(±0.01)	1.64(±0.01)		
C-Calkyne	1.200(4)	1.200(4), 1.203(4)	1.207(3)	1.475(7), 1.477(7), 1.488(7), 1.506(7) (Cb)		
Bond angles (°)						
Cpcentroid-M-Cpcentroid	138(±1)	132(±1)	180(±1)	179(±1)		
(Cp)C-Si-Calkyne	107.5(1)	107.0(1), 101.6(1)	111.2(1)	109.3(2), 109.4(3)		
Si-C-C _{alkyne}	173.0(3)	168.3(3), 176.5(3)	175.1(2)	_		
Ph-C-Calkyne	179.4(3)	175.0(4), 177.6(4)	177.8(3)			

Table 2. Selected bond lengths and angles for compounds 3, 4Cl₂, 6, and [8][OTf].

Fig. 4. Solid-state structure of compound **[8][OTf]**. Thermal ellipsoids are drawn to the 50% probability level and hydrogen atoms are removed for clarity. The triflate anion is disordered and has been removed for clarity.



mounted on nylon loops and immediately placed in a cold stream of N₂ (150 K). Data were collected on a Bruker Nonius Kappa CCD X-ray diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å). The solution and subsequent refinement of the data were performed using the SHELXTL suite of programs. Elemental analyses were performed by Columbia Analytical Services, Tucson, Arizona. Mass spectra were recorded using an electron ion-

ization Finnigan MAT 8200 mass spectrometer. Photolysis experiments were performed using an Ace Glass medium pressure 450 Watt mercury vapour lamp.

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Elemental analysis was performed on compounds 7 and 8, but the results obtained were not satisfactory. HRMS data is provided for samples that do not decompose in the mass spectrometer. Proton NMR data is provided in the supporting information as a proof of purity of the samples.

Synthesis of ligand (1a–1c)

A solution of LiCp (6.25 g, 87 mmol; 100 mL THF) was added to a solution of Me₂SiCl₂ (10.5 mL, 87 mmol; 30 mL THF) at -40 °C, at which time the solution turned yellow. The reaction mixture was allowed to slowly warm to 0 °C, then the cold bath was removed and the reaction mixture was stirred for a further 3-4 h at room temperature (RT). The flask was then cooled to -40 °C and PhC₂Li (9.39 g, 87 mmol; 40 mL THF) was added, generating an orange solution. The reaction mixture was stirred for 15 h. The volatiles were removed under vacuum, and the resulting mixture taken up in *n*-hexane or *n*-pentane, filtered to remove LiCl, and the volatiles removed in vacuo to yield a yellow-orange liquid. The liquid was then distilled under vacuum (0.1 Torr; 1 Torr = 133.3224 Pa) and the required fraction was obtained at 100 °C. Yield: 9.74 g, 50%. ¹H NMR (CDCl₃, -20 °C) δ: major isomer 1a (84%): 0.10 (s, 6H, Me), 3.59 (m, 1H, Cp), 6.59 (m, 2H, Cp), 6.67 (m, 2H, Cp), 7.32 (m, 3H, Ph), 7.49 (m, 2H, Ph); isomer 1b (13%): 0.40 (s, 6H, Me), 3.16 (m, 2H, Cp), 6.74 (m, 2H, Cp), 7.01 (m, 1H, Cp); isomer 1c (3%): 0.41 (s, 6H, Me), 3.09 (m, 2H, Cp), 6.63 (m, 2H, Cp, overlapped with other Cp from isomer 1b), 6.89 (m, 1H, Cp). All phenyls are overlapped. ¹³C{¹H} NMR (CDCl₃) δ : major isomer 1a: -2.9 (Me), 51.1 (Cp, CHSiMe₂), 92.5 (CC-SiMe₂), 105.8 (CC-Ph), 122.9 (Ph), 128.3 (Ph), 132.1 (Ph), 133.1 (Ph), 138.8 (Cp), 143.6 (Cp); isomer 1b: -0.5 (Me), 45.3 (Cp, CH₂), 92.9 (CC-SiMe₂), 105.9 (CC-Ph), 123.2 (Ph), 128.6 (Ph), 128.8 (Ph), 131.2 (Ph) 135.1 (Cp), 144.1 (Cp), 144.6 (Cp). ²⁹Si NMR (CDCl₃) δ: -18.6 ppm (major isomer 1a), -28 ppm (isomers 1b and 1c). FT-IR (cm⁻¹) (ranked intensity): 434 (12), 536 (13), 690 (2), 732 (9), 756 (3), 801 (5), 819 (10), 846 (1), 981 (7), 950 (11), 1066 (14), 1250 (6), 1488 (8), 2159 (4), 2960 (15). ESI-MS (m/z): M⁺ (224, 26%), M⁺ – Me (209, 10%), M⁺ – Cp (159, 100%).

Synthesis of LiC₅H₄SiMe₂C₂Ph (2)

ⁿBuLi (10.5 mL of a 1.6 mol/L solution in *n*-hexane) was

	3	4Cl ₂	6	[8][OTf]		
Empirical formula	C ₁₉ H ₂₃ KOSi	C ₃₀ H ₃₀ Cl ₂ Si ₂ Ti	C ₃₀ H ₃₀ CoSi ₂	C37H37Cl2C02F3O3SSi2		
Formula weight	334.56	565.52	505.65	863.67		
Colour, form	Colourless, block	Red, plate	Red, plate	Red, plate		
Crystal size (mm)	$0.15 \times 0.1 \times 0.1$	$0.25 \times 0.2 \times 0.04$	$0.58 \times 0.25 \times 0.18$	0.33×0.18×0.12		
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic		
Space group	P2(1)/c	P2(1)/c	P2(1)/n	P2(1)/c		
a (Å)	8.921(2)	6.532(1)	9.870(2)	18.210(4)		
<i>b</i> (Å)	21.330(4)	35.024(7)	5.875(1)	10.181(2)		
<i>c</i> (Å)	10.523(2)	12.645(3)	22.102(4)	20.404(4)		
β (°)	107.55(3)	95.00(3)	93.38(3)	96.53(3)		
$V(Å^3)$	1909.1(7)	2881.9(1)	1279.4(4)	3758.2(1)		
Ζ	4	4	2	4		
$D_c (Mg m^{-3})$	1.164	1.303	1.313	1.526		
$\mu \text{ (mm}^{-1})$	0.341	0.583	0.781	1.195		
Absorption correction	Semi-empirical from equivalents					
<i>F</i> (000)	712	1176	530	1768		
θ range (°)	2.04-27.48	2.04-27.48	1-27.48	1-27.48		
Observed reflections	7802	12061	4854	15206		
Independent reflections	4360	6618	2885	8557		
Data-restraints-parameters	4360-193-238	6618-0-320	2885-0-151	8557-2-418		
Temp (K)	150(2)	150(2)	150(2)	150(2)		
<i>R</i> indices $(I > 2\sigma(I))^{a,b}$	$0.058, wR_2 = 0.132$	$0.059, wR_2 = 0.150$	$0.043, wR_2 = 0.097$	$0.077, wR_2 = 0.208$		
R indices (all data) ^{a,b}	$0.122, wR_2 = 0.161$	$0.096, wR_2 = 0.173$	$0.071, wR_2 = 0.108$	$0.132, wR_2 = 0.250$		
Goodness-of-fit (S) ^a	1.059	1.071	1.088	1.061		
Largest diff. peak and hole (e $Å^{-3}$)	0.29 and -0.42	0.53 and -0.73	0.52 and -0.43	1.20 and -1.21		

Table 3. Crystal data for compounds 3, 4Cl₂, 6, and [8][OTf].

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|; wR(F^{2}) = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}]^{1/2}; S = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/(n-p)]^{1/2} (n = \text{No. of data}; p = \text{No. of parameters varied}.$ ${}^{b}w = 1/[\sigma^{2}(F_{o}^{2}) + (aP^{2}) + bP]), \text{ where } P = (F_{o}^{2} + 2Fc^{2})/3 \text{ and } a \text{ and } b \text{ are constants suggested by the refinement program.}$

added to purified 1 (3.72 g, 16.60 mmol; 100 mL n-hexane) at -30 °C. The reaction mixture was allowed to slowly warm over a period of 8 h over which time a white solid precipitated. The suspension was filtered under nitrogen, and the solids were collected, washed twice with n-hexane or *n*-pentane (30 mL), and dried under vacuum. Yield: 3.44 g, 90%; dp 55 °C. Note: Without the extended stirring, the yield will be low (2.29 g, 60%, 4 h. ¹H NMR (C₅ND₅) δ : 0.79 (s, 6H, Me), 6.64 (b, 2H, Cp), 6.79 (b, 2H, Cp), 7.34 (b, 3H, Ph), 7.62 (b, 2H, Ph). ${}^{13}C{}^{1}H{}$ NMR (C₅ND₅) δ : 1.6 (Me), 98.8 (Cp), 104.3 (CC), 106.1 (CC), 108.5 (Cp), 113.2 (Cp), 124.6 (Ph), 128.3 (Ph), 128.6 (Ph), 132.0 (Ph). ²⁹Si NMR (C₅ND₅) δ : -29.9 ppm. FT-IR (cm⁻¹) (ranked intensity): 434 (10), 536 (12), 689 (4), 768 (2), 805 (6), 847 (1), 980 (13), 1039 (8), 1177 (9), 1220 (14), 1248 (3), 1440 (15), 1489 (7), 2159 (5), 2959 (11). ESI-MS (m/z): M⁺ – Li (224, 19%), $M^+ - (Me + Li)$ (209, 11%), $M^+ - (Cp + Li)$ (159) 100%).

Synthesis of KC₅H₄SiMe₂C₂Ph (3)

Potassium bis(trimethylsilyl)amide (0.089 g, 0.446 mmol; 5 mL Et₂O) was added to **1** (0.1 g, 0.446 mmol; 20 mL *n*-hexane) at -30 °C. The reaction mixture was stirred for 3.5 h after which a white precipitate was filtered, washed twice with *n*-pentane (8 mL), and then dried in vacuo. Yield: 0.11 g, 93%. X-ray quality crystals were obtained by a slow diffusion of *n*-pentane into a THF solution of **3** at RT; dp 60 °C. ¹H NMR (C₅ND₅) δ : 0.73 (s, 6H, Me), 6.67 (b, 2H, Cp), 6.82 (b, 2H, Cp), 7.21 (overlapped with Py-d₅,

3H, Ph), 7.50 (d, 2H, Ph). ${}^{13}C{}^{1}H}$ NMR (C₅ND₅) δ : 2.0 (Me), 110.3 (Cp), 114.5 (Cp), 128.7 (Ph), 129.0 (Ph), 132.5 (Ph) (quaternary carbons not observed owing to low solubility and stability of the compound in C₅ND₅). ${}^{29}Si$ NMR (C₅ND₅) δ : -30.5 ppm. FT-IR (cm⁻¹) (ranked intensity): 443 (7), 656 (13), 674 (5), 690 (8), 740 (1), 778 (4), 826 (2), 1038 (3), 1185 (6), 1246 (9), 1346 (15), 1438 (11), 1487 (12), 2147 (10), 3052 (14).

Synthesis of (C₅H₄SiMe₂C₂Ph)₂TiCl₂ (4Cl₂)

A slurry of LiC₅H₄SiMe₂C₂Ph (0.91 g, 3.30 mmol; 50 mL *n*-hexane) was cooled to -35 °C and TiCl₄ (0.15 mL, 1.37 mmol; 2 mL *n*-hexane) was added to the slurry when the colour of the reaction mixture turned from white to yellow and finally to red. The cold bath was removed when the temperature reached -5 °C and the reaction mixture was allowed to warm up to room temperature over 4 h, at which time stirring was stopped and the solids settled, the reaction mixture was filtered, and the filtrate was cooled to -30 °C, filtered a second time, concentrated, and then left in a -30 °C freezer overnight. Red crystals were formed that were collected and dried. Yield: 0.54 g, 70%; mp 107 °C. ¹H NMR $(C_6D_6) \delta$: 0.65 (s, 6H, Me), 6.20 (pt, 4H, Cp), 6.79(pt, 4H, Cp), 6.90–6.92 (m, 6H, Ph), 7.45–7.47 (m, 4H, Ph). ¹³C{¹H} NMR (C₆D₆) δ : 0.7 (Me), 93.5 (SiCC), 108.0 (CCPh), 120.3 (Cp), 123.7 (Ph), 127.2 (Cp_{ipso}), 128.9 (Ph), 129.3 (Ph), 131.3 (Cp), 132.6 (Ph). ²⁹Si NMR (C₆D₆) δ: -25 ppm. FT-IR (cm⁻¹) (ranked intensity): 537 (9), 690 (5), 756 (3), 805 (2), 847 (1), 898 (10), 1026 (12), 1043 (8),

1069 (11), 1220 (14), 1251 (7), 1442 (15), 1488 (6), 2158 (4), 2960 (13). ESI-MS (m/z): M⁺ – Cl (529). Elemental anal. calcd: C, 63.72; H, 5.35; Found: C, 64.10; H, 5.49.

Synthesis of (C₅H₄SiMe₂C₂Ph)₂TiMe₂ (4Me₂)

 $(C_5H_4SiMe_2C_2Ph)_2TiCl_2$ (4Cl₂) (0.20 g, 0.35 mmol; 40 mL Et_2O/n -hexane (1:1.5) was treated with 3 stoichiometric equiv of MeMgCl (0.35 mL, 1.05 mmol; 3 mol/L solution in THF) at -15 °C. The reaction mixture was stirred for 4 h during which time it warmed to room temperature and the colour changed from red to yellow-orange. The LiCl was filtered off and the yellow-orange solution was concentrated to give orange oil. Yield: 0.15 g, 80%. ¹H NMR (C₆D₆) δ: 0.40 (s, 6H, Me), 0.42 (s, 12H, Me), 6.38 (pt, 4H, Cp), 6.47 (pt, 4H, Cp), 6.90-6.91 (m, 6H, Ph), 7.47–7.49 (m, 4H, Ph). ${}^{13}C{}^{1}H{}NMR$ (C₆D₆) δ : 0.9 (Me), 48.3 (Me), 93.3 (SiCC), 107.57 (CCPh), 116.8 (Cp_{ipso}), 118.7 (Cp), 121.9 (Cp), 123.7 (Ph), 128.9 (Ph), 129.3 (Ph), 132.5 (Ph). ²⁹Si NMR (C₆D₆) δ : –25.8 ppm. FT-IR (cm⁻¹) (ranked intensity): 442 (13), 537 (11), 689 (4), 756 (3), 823 (1), 905 (10), 1027 (14), 1047 (7), 1070 (15), 1186 (9), 1251 (5), 1488 (8), 2159 (2), 2888 (12), 2958 (6). ESI-MS (m/z): M⁺ – Me (507). Elemental anal. calcd: C, 73.26; H 6.92. Found: C, 72.54; H, 6.23.

Synthesis of $(C_5H_4SiMe_2C_2Ph)_2Fe$ (5)

A solution of $LiC_5H_4SiMe_2C_2Ph$ (2) (0.36 g, 1.58 mmol; 3 mL THF) was added to a solution of anhydrous FeCl₂ (0.1 g, 0.79 mmol; 5 mL THF) at room temperature. The reaction mixture was stirred for 4 h, during which time the colour turned dark yellow. The volatiles were then removed, the residue redissolved in *n*-pentane, and filtered to remove LiCl. The filtrate was then concentrated to give an orange solid. Yield: 0.317 g, 80%; mp 75 °C. The orange solid was then sublimed at 140 °C onto a cold finger at -18 °C. ¹H NMR (C₆D₆) δ: 0.52 (s, 12H, Me), 4.35 (pt, 4H, Cp), 4.51 (pt, 4H, Cp), 6.91-6.95 (m, 6H, Ph), 7.49-7.53 (m, 4H, Ph). $^{13}C{^{1}H}NMR (C_6D_6) \delta: 0.6 (Me), 69.4 (Cp), 73.1 (Cp), 74.5$ (Cp), 94.2 (SiCC), 106.8 (CCPh), 124.1 (Ph), 128.9 (Ph), 129.1 (Ph), 132.6 (Ph). ²⁹Si NMR (C₆D₆) δ: -21.5 ppm. FT-IR (cm⁻¹) (ranked intensity): 690 (7), 776 (2), 802 (4), 846 (1), 897 (14), 1036 (8), 1166 (3), 1220 (11), 1249 (6), 1383 (15), 1421 (13), 1442 (12), 1488 (9), 2158 (5), 2960 (10). ESI-MS (*m*/*z*): M⁺ (502.2, 100%).¹⁴ λ_{max} = 312 and 348 nm.

Synthesis of (C₅H₄SiMe₂C₂Ph)₂Co (6)

LiC₅H₄SiMe₂C₂Ph (**2**) (0.17 g, 0.77 mmol) was added to a solution of anhydrous CoCl₂ (0.05 g, 0.38 mmol; 5 mL Et₂O), followed by the addition of 1 mL THF at room temperature. The reaction mixture was stirred for 3–4 h, during which time the colour turned dark red. The reaction mixture was then filtered to remove the LiCl and the clear solution was pumped down to give a sticky solid mass, which was then washed twice with *n*-pentane and dried to yield a dark maroon solid. Yield: 0.175 g, 90%; mp 80 °C. X-ray quality crystals were obtained from concentrated Et₂O solution at –30 °C. ¹H NMR (C₆D₆) δ : 3.62 (b, 12H, Me), 6.81 (t, 2H, Ph), 7.07 (t, 4H, Ph), 7.46 (d, 4H, Ph); Cp protons were not observed within the range of –2 to 14 ppm. FT-IR (cm⁻¹) (ranked intensity): 536 (13), 599 (14), 676 (8), 688 (7), 756 (2), 774 (4), 802 (1), 822 (3), 840 (5), 1034 (6),

1158 (11), 1250 (9), 1346 (15), 1486 (10), 2146 (12). ESI-MS (*m*/*z*): M⁺ – 268 (237.1, 100%). Elemental anal. calcd: C, 71.26; H, 5.98. Found: C, 71.49; H, 5.99. $\lambda_{max} = 335$ and 429 nm.

Synthesis of 7

 $CpCo(CO)_2$ (0.04 g, 0.23 mmol) was added to a C_6D_6 solution of 5 (0.118 g, 0.335 mmol) in an NMR tube. The solution was then photolyzed with broad wavelength UV light for 40–50 h. The reaction was monitored for completion by ¹H NMR spectroscopy, after which the reaction mixture was filtered, the solvent was removed in vacuo to give an orange solid, which was washed with 0.5 mL n-pentane and dried again. Yield: 0.136 g, 65%; mp 180 °C. ¹H NMR (C_6D_6) δ : 0.40 (s, 6H, Me), 0.60 (s, 6H, Me), 4.16 (b, 2H, Cp), 4.27 (b, 4H, Cp), 4.46 (b, 2H, Cp), 4.76 (s, 5H, Cp), 7.04–7.16 (m, 6H, Ph), 7.55 (d, 4H, Ph). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆) δ : 2.4 (Me), 4.1 (Me), 66.4 (SiC(Cb)), 69.3 (Cp_{ipso}), 71.9 (Cp), 72.6 (Cp), 74.5 (Cp), 75.2 (Cp), 82.8 (CpCo), 88.1 (CPh(Cb)), 126.9 (Ph), 128.5 (Ph), 129.7 (Ph), 138.4 (Ph). ²⁹Si NMR (C₆D₆) δ : -9.3 ppm. FT-IR (cm⁻¹) (ranked intensity): 666 (7), 696 (2), 765 (3), 813 (1), 898 (11), 1036 (6), 1110 (12), 1165 (5), 1245 (4), 1384 (8), 1439 (9), 1599 (10). EI-MS (*m/z*): M⁺ (625.9, 100%). HRMS (EI) for C₃₅H₃₅Si₂FeCo (calcd: 626.09; found: 626.09. Elemental anal. calcd: C, 71.69: H, 6.02. Found: C, 66.20; H, 5.50. $\lambda_{\text{max}} = 357 \text{ and } 423 \text{ nm.}$

Synthesis of [(C₅H₄SiMe₂C₂Ph)₂Co(III)][OTf] ([6][OTf])

Addition of a solution of 8 (0.20 g, 0.40 mmol; 1 mL of CH₃CN or C₆H₆) to 1 equiv of AgOTf (0.11 g, 0.40 mmol) resulted in the instantaneous formation of [6][OTf]. The yield was quantitative by ¹H NMR spectroscopy, but the product could not be obtained as a solid. Removing the solvent always resulted in a sticky mass, which was 90% pure by ¹H NMR spectrum. Yield: 0.233 g, 90%. ¹H NMR (C₆D₆) δ: 0.47 (s, 12H, Me), 5.73 (b, 4H, Cp), 5.93 (b, 4H, Cp), 7.05–7.09 (m, 6H, Ph), 7.61 (d, 4H, Ph). ¹H NMR (CD₃CN) δ: 0.56 (s, 12H, Me), 5.81 (pt, 4H, Cp), 5.92 (pt, 4H, Cp), 7.42–7.45 (m, 6H, Ph), 7.58 (d, 4H, Ph). ¹³C{¹H} NMR (CD₃CN) δ: -0.5 (Me), 89.2 (Cp), 90.6 (Cp), 91.0 (Cp), 92.7 (SiCC), 109.3 (CCPh), 122.9 (Ph), 130.0 (Ph), 130.9 (Ph), 133.2 (Ph). ¹⁹F NMR (CD₃CN) δ: -78.9 ppm. ²⁹Si NMR (C_6D_6) δ : -22.5 ppm. FT-IR (cm⁻¹) (ranked intensity): 691 (9), 737 (14), 759 (7), 805 (6), 825 (8), 851 (2), 1043 (3), 1117 (12), 1164 (4), 1230 (10), 1255 (1), 1385 (15), 1489 (11), 2159 (5), 2973 (13). ESI-MS (m/z): M⁺ -OTf (505.1, 100%), M⁺ + [M – OTf]⁺ (1159.3).

Synthesis of 8

CpCo(CO)₂ (0.03 g, 0.18 mmol) was added to a C₆D₆ solution of **6** (0.09 g, 0.18 mmol) in an NMR tube. The solution was then photolyzed with broad wavelength UV light for 40–50 h. The reaction was monitored for completion by ¹H NMR spectroscopy, after which the solution was filtered, the solvent was removed in vacuo to give a brown solid, which was washed with 0.5 mL of *n*-pentane four times and dried again. Yield: 0.086 g, 75%. ¹H NMR (C₆D₆) δ : 3.77 (b, 12H, Me), 4.91 (b, 5H, Cp), 7.05 (b, 2H, Ph), 7.11 (b, 4H, Ph), 7.69 (b, 4H, Ph); other Cp protons were not observed within the range of -2 to 14 ppm. FT-IR (cm⁻¹)

(ranked intensity): 664 (13), 696 (4), 770 (2), 805 (1), 1008 (8), 1035 (7), 1156 (9), 1247 (3), 1441 (11), 1488 (14), 1070 (15), 1597 (10), 1955 (6), 2017 (5), 2955 (12). HRMS (EI) for $C_{35}H_{35}Si_2Co_2$ calcd: 629.094; found: 629.096.

Synthesis of [8][OTf]

Method I: Addition of a solution of 8 (0.40 g, 0.64 mmol; 2 mL of CH₃CN or C_6H_6) to 1 equiv of AgOTf (0.16 g, 0.64 mmol) resulted in the instantaneous formation of [8][OTf]. The reaction mixture was then filtered to remove Ag, washed with *n*-pentane and Et_2O , and the solvent was removed in vacuo to give an orange solid. Yield: 0.32 g, 65%. Method II: CpCo(CO)₂ (0.03 g, 0.18 mmol) was added to a C_6D_6 or CD_3CN solution of [6][OTf] (0.12 g, 0.18 mmol) in an NMR tube. The solution was then photolyzed with broad wavelength UV light for 20-25 h. The reaction was monitored for completion by ¹H NMR spectroscopy, after which the solution was filtered, the solvent was removed in vacuo to give an orange solid, which was washed with 0.5 mL *n*-pentane and 0.5 mL Et₂O and dried again. Yield: 0.09 g, 65%; mp 200 °C. X-ray quality crystals were obtained by the slow diffusion of *n*-pentane into a DCM solution of the compound at RT. ¹H NMR (C₆D₆) δ: 0.08 (s, 6H, Me), 0.41 (s, 6H, Me), 4.61 (s, 5H, Cp), 4.96 (b, 2H, Cp), 5.78 (b, 2H, Cp), 6.09 (b, 2H, Cp), 6.48 (b, 2H, Cp), 7.03–7.06 (m, 6H, Ph), 7.32–7.35 (m, 4H, Ph). ${}^{13}C{}^{1}H}$ NMR (C₆D₆) δ : 1.0 (Me), 2.7 (Me), 61.3 (Cb), 82.7 (Cp), 88.8 (Cb), 89.5 (Cp), 89.7 (Cp), 90.0 (Cp), 90.4 (Cp), 91.2 (Cp), 127.5 (Ph), 128.9 (Ph), 129.5 (Ph), 137.0 (Ph); triflate was not observed. ¹⁹F NMR (C_6D_6) δ: -78.9 ppm. ²⁹Si NMR (C_6D_6) δ: -9.8 ppm. FT-IR (cm⁻¹) (ranked intensity): 444 (10), 516 (13), 636 (3), 671 (11), 700 (7), 775 (6), 820 (4), 894 (15), 1009 (9), 1030 (2), 1136 (5), 1223 (8), 1266 (1), 1386 (14), 1441 (12). ESI-MS (m/z): $M^+ - OTf (629, 100\%), M^+ + 629 (1407.2), [(RC_5H_4)_2Co]^+$ (505, 25%). HRMS (EI) for C₃₅H₃₅Si₂Co₂ calcd: 629.094; found: 629.091. $\lambda_{max} = 316$ and 427 nm.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca). CCDC 768012–768015 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc. cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc. cam.ac.uk). Proton NMR spectra for the samples have been provided.

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