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Synthesis of Neutral Mixed Sandwich CH_2-SiR_2 Bridged [2]Cobaltoarenophanes from the Dilithiation of Cb*CoCp [Co(η^4-C_4Me_4)(η^5-C_5H_5)]

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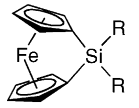
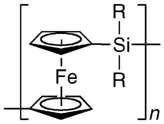
Summary: The dilithiation of [Co(η^4-C_4Me_4)(η^5-C_5H_5)] to give [Co(η^4-$C_4Me_3CH_2Li$)(η^5-C_5H_4Li)]·PMDETA and the subsequent synthesis and characterization of the CH_2-SiR_2-bridged [2]-cobaltoarenophanes is reported. This is the first development in the chemistry of neutral 18-electron metalloarenophanes featuring a group 9 transition metal.

There has been a recent surge of interest in the synthesis of strained *ansa*-metallocenes, as they exhibit unusual structure, reactivity, and bonding motifs. Furthermore, there are potential applications of these compounds as monomeric precursors for metallopolymers via ring-opening polymerization (ROP) methodologies.[1] The [1]silaferrocenophanes (**1**) have been the most extensively studied system in this class of compounds. Noteworthy is their remarkable utility in the synthesis of well-controlled, high molecular weight poly(ferrocenylsilane)s (**2**).[2] This success can be attributed to several properties that derivatives of compound **1** possess, such as their relatively straightforward synthesis, a stable 18-electron configuration, and inherent ring strain. The [1]silaferrocenophanes are normally synthesized by a two-step process involving the dilithiation of ferrocene, followed by salt metathesis using R_xECl_2, where E is the desired bridging element.[3] Similar approaches have been successfully utilized in the synthesis of other homoleptic or heteroleptic metallarenocenophanes derived from their parent metallareneocenes (e.g., [M(η^5-C_5H_5)$_2$], M = Fe, Ru, Cr; [M(η^6-C_6H_6)$_2$], M = V, Cr, Mo; [M(η^5-C_5H_5)(η^7-C_7H_7)], M = Ti, Cr, V; [Mn(η^5-C_5H_5)(η^6-C_6H_6)]).[4] In all cases, the metalloarenophanes contain early transition metals up to group 8, but there are no reported examples of neutral, late transition metal metalloarenophanes. The synthesis and isolation of a neutral cobaltoarenophane has been identified as a very desirable, key synthetic target, both from a fundamental standpoint and for the potential that such a molecule may have in materials science.[1b] The dilithiation methodology has been extended to the formation of CH_2-ER_x-bridged [2]ferrocenophanes (**3**), utilizing the mixed sandwich complex [Cp*FeCp] (Cp* = Me_5C_5; Cp = C_5H_5).[5] This presents an opportunity for a further extension of this chemistry to the isoelectronic, mixed sandwich cobaltoarenocene [Co(η^4-C_4Me_4)(η^5-C_5H_5)] ([Cb*CoCp]; **4**).[6]



1
R = alkyl, aryl



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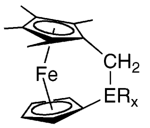
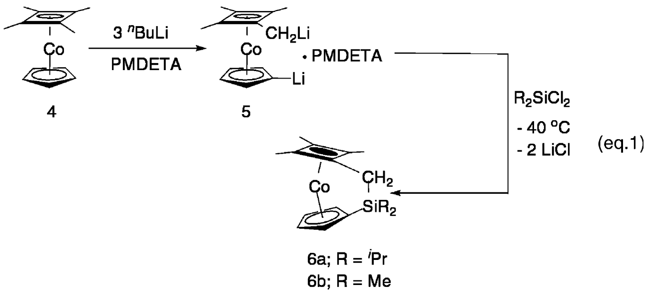


3
ER_x = $SiMe_2$, PPh,
PMes, S

In this context, we report the dilithiation of **4** (see Supporting Information) to give [Co(η^4-$C_4Me_3CH_2Li$)(η^5-C_5H_4Li)]·PMDETA (**5**; PMDETA = pentamethyldiethylenetriamine) and the subsequent synthesis and comprehensive characterization of the CH_2-SiR_2-bridged [2]cobaltoarenophanes (**6a**, R = ^{i}Pr; **6b**, R = Me; eq 1).[7] This represents the first development in the chemistry of neutral 18-electron metalloarenophanes featuring a group 9 transition metal and, furthermore, one that incorporates a cyclobutadiene ligand.



The addition of ^{n}BuLi to a solution of **4** and PMDETA in *n*-hexanes resulted in the slow formation of an orange-brown

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precipitate. The solids were washed with fresh *n*-hexane and *n*-pentane, then dried, resulting in an orange-brown powder (**5**) in moderate to good yields (≈65−70%). Although repeated attempts to grow single crystals have not been successful, the formulation of **5** was confirmed by the elemental analysis of the bulk material.

The dropwise addition of an *n*-hexane solution of R_2SiCl_2 (R = ^{i}Pr, Me) to a slurry of **5** at low temperature (−40 °C) slowly generated a yellow-brown solution. The reaction mixture was filtered, giving a clear yellow-brown filtrate, and upon removal of the volatiles, a yellow-brown oil remained. Proton NMR spectroscopy of the crude product revealed the expected spectrum for **6**, with two telltale pseudotriplets for the substituted Cp ring, integrating to 2 protons each (**6a**, δ = 5.06 ppm, δ = 4.98 ppm; **6b**, δ = 5.04 ppm, δ = 4.96 ppm). In addition, the methyl signals on the Cb* were now nonequivalent and a distinct methylene signal was observed (**6a**, δ = 1.67 ppm; **6b**, 1.55 ppm). Sublimation of the crude product followed by recrystallization from a concentrated *n*-pentane solution at −30 °C yielded orange single crystals of **6a**. Compound **6b** was purified by sublimation, then recrystallized by vapor diffusion (Et_2O/*n*-hexane) at −30 °C. For both derivatives, the single crystals were suitable for X-ray diffraction studies, confirming their identity as the CH_2-SiR_2-bridged [2]cobaltoarenophanes (Figure 1).

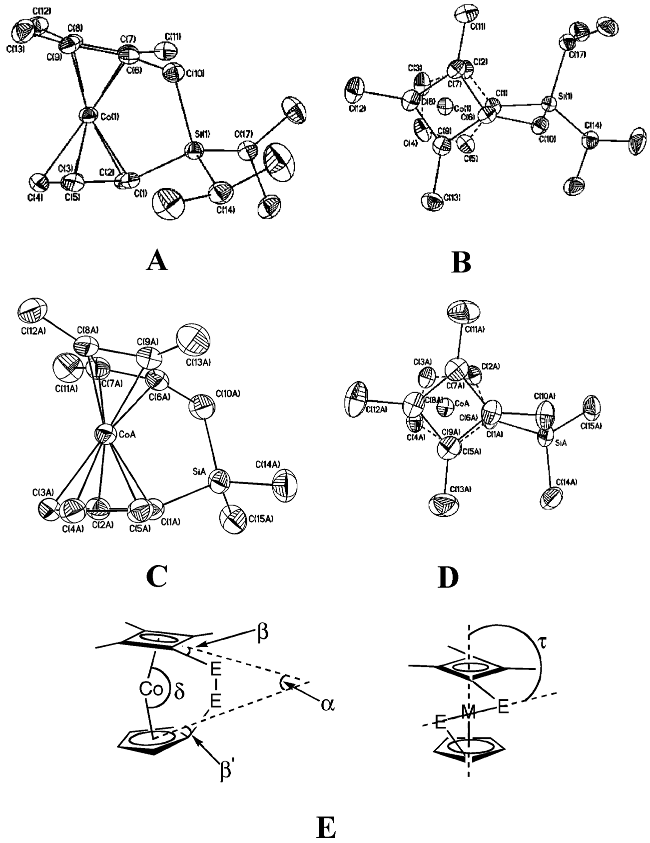

Figure 1. Two views of the solid state structure of **6a** (A, B) and **6b** (C, D). Ellipsoids are drawn to 50% probability, and the hydrogen atoms have been removed for clarity. For **6b** only one of the two crystallographically distinct molecules in the asymmetric unit is shown, and metrical parameters are averages. For the "top view" (B, D) all Co−C bonds have been removed and the C−C bonds in the Cp ring are dashed for clarity. A schematic of the cobaltoarenophane is given (E) defining the indicated angles. Bond lengths (Å), angles (deg): **6a**: Co(1)−$C_{(Cp)}$ 2.027(2) (av), Co(1)−$C_{(Cb*)}$ 1.971(2) (av), $C_{(Cb*)}$−CH_3 1.488(2) (av), C(6)−C(10) 1.506(2), Si(1)−C(10) 1.914(2), Si(1)−C(1) 1.883(2), Si(1)−C(14) 1.888(2), Si(1)−C(17) 1.893(2), α = 15.9, β = 4.6, β' = 20.6, δ = 163.7, τ = 22; **6b**: Co(1)−$C_{(Cp)}$ 2.067(3) (av); Co(1)−$C_{(Cb*)}$ 1.973(2) (av); $C_{(Cb*)}$−CH_3 1.490(4) (av), C(6A)−C(10A) 1.409(4), Si(A)−C(10A) 1.906(3); Si(A)−C(1A) 1.877(3), Si(A)−C(14A) 1.862(3), Si(A)−C(15A) 1.862(3), α = 16.8, β = 4.0, β' = 19.1, δ = 166.7, τ = 18.9.

The solid state structures of **6a** and **6b** confirmed the expected connectivity indicated by the spectroscopic data. The average Cb*−Co distance is slightly shorter than that of the Cp−Co distance (**6a**, 1.971(2) vs 2.027(2) Å; **6b**, 1.973(2) vs 2.067(3) (Å) and is consistent with the solid state structure of other unbridged mixed sandwich complexes (Co−$C_{(Cb*)}$, 1.97 Å; Co−$C_{(Cp)}$, 2.07 Å).[6,8] The α angle is greater than that of the corresponding silicon-bridged [2]ferrocenophane (**6a**, 15.9°; **6b**, 16.8° vs 11.8°).[5a] However the value falls short of the two crystallographically characterized cationic [2]cobaltocenophanes (24.8°; 22.9°).[9] This indicates that there is indeed ring strain in derivatives of **6**. However subsequent ring opening to form the corresponding polymers may be restricted. Although both the C_{ipso}−CH_2 and C_{ipso}−Si bonds are distorted from the plane of

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(7) For the synthesis of **5**: To a stirred *n*-hexane solution (60 mL) of freshly sublimed Cb*CoCp (1.00 g; 4.31 mmol) was added freshly distilled PMDETA (2.70 mL; 13 mmol; 3 equiv) and ^{n}BuLi (1.6 M in *n*-hexane; 8.0 mL; 13 mmol) at RT. The reaction mixture was stirred at RT for 16−20 h, after which the precipitate was allowed to settle. The supernatant solution was removed, and the precipitate was washed with *n*-hexanes (2 × 20 mL) followed by *n*-pentane (5 × 15 mL) until no visible color was extracted into the *n*-pentane layer. The light brown solid was dried for 18 h *in vacuo* to give $[Co(\eta^4\text{-}Me_3C_4CH_2Li)(\eta^5\text{-}C_5H_4Li)]\cdot$PMDETA (**5**): yield 1.19 g, 66%. Anal. Calcd for $C_{22}H_{38}N_3Co_1Li_2$ (found): C 63.32 (63.20), H 9.18 (8.78), N 10.07 (9.41). For the synthesis of **6a/b**: To an *n*-hexane solution of **5** (0.500 g; 1.20 mmol; 80 mL) was added an *n*-hexane (60 mL) solution of R_2SiCl_2 (**6a**: R = ^{i}Pr, 0.216 mL, 1.20 mmol; **6b**: R = Me, 0.145 mL; 1.20 mmol) dropwise at −40 °C. The reaction mixture was stirred at −30 °C for 3 h, warmed to 10 °C, then filtered through Celite. The volatiles were removed from the filtrate *in vacuo*. Crystals were grown from a saturated solution of **6a** in pentane at −30 °C or by Et_2O/*n*-hexane vapor diffusion (**6b**) at −30 °C. **6a**: yield 0.132 g, 20%; mp 62 °C; ^{1}H NMR (C_6D_6; δ (ppm)) 5.06 (*p*t, 2H, C_5H_4), 4.98 (*p*t, 2H, C_5H_4), 1.77(s, 6H, CH_3(Cb*)), 1.67(s, 2H, CH_2Si), 1.37 (overlapping singlet/septet, 5H, CH_3(Cb*) and $(CH_3)_2CH$), 1.22 (d, 6H, $CH(CH_3)_2$, ^1J = 7.8 Hz), 1.17(d, 6H, $CH(CH_3)_2$, ^1J = 7.8 Hz,); $^{13}C\{^1H\}$ NMR (C_6D_6; δ(ppm)) 88.2 ($CH_{(\alpha-Cp)}$), 82.6 ($CH_{(\beta-Cp)}$), 79.9 ($C_{ipso(Cp)}$), 77.0 (Cb* and $C_{ipso(Cb*)}$), 72.6 (Cb*) 18.7 ($(CH_3)_2CH$), 18.6 ($(CH_3)_2CH$), 14.0 ($(CH_3)_2CH$), 11.4 (CH_3-(Cb*)), 10.83 and 10.78 either (CH_3(Cb*)) or (CH_2Si). A definitive assignment cannot be made from 1-D or 2-D NMR spectroscopic techniques. ^{29}Si NMR (C_6D_6; δ ppm) 8.5; EI-MS *m/z* (%) 344 (100). Crystal data: $C_{19}H_{29}Co_1Si_1$; M = 344.44 g mol^{-1}, monoclinic, $P2_1/c$, a = 12.898(3) Å, b = 17.481(4) Å, c = 8.291(2) Å, β = 103.99(3)°, V = 1813.9(6) Å^3, T = 150(2) K, Z = 4, D_c = 1.261, measured reflections 7821, unique 4163 (R_{int} = 0.0319), refined parameters 195, $R[I > 2\sigma I]$ = 0.0350, $wR_2(F^2)$ = 0.1097. **6b**: yield 0.076 g, 22%; mp 59 °C; ^{1}H NMR (C_6D_6; δ (ppm)) 5.04 (*p*t, 2H, C_5H_4), 4.96 (*p*t, 2H, C_5H_4), 1.75 (s, 6H, CH_3 (Cb*), 1.55 (s, 2H, CH_2-Si), 1.37 (s, 3H, CH_3(Cb*)) 0.35 (s, 6H, $(CH_3)_2$Si); $^{13}C\{^1H\}$ NMR (C_6D_6; δ (ppm)) 87.4 ($CH_{(\alpha-Cp)}$), 83.0 ($C_{ipso(Cp)}$), 82.5 ($CH_{(\beta-Cp)}$), 77.1 (Cb*), 76.7 ($C_{ipso(Cb*)}$), 72.7 (Cb*) 16.5 (CH_2Si), 11.4 (CH_3(Cb*)), 10.9 (CH_3(Cb*)), 0.2 (CH_3Si); ^{29}Si NMR (C_6D_6; δ ppm) 1.3; EI-MS *m/z* (%) = 288 (63%), 273 (100%, −CH_3). Crystal data: $C_{15}H_{21}Co_1Si_1$; M = 288.34 g mol^{-1}, triclinic, $P\bar{1}$, a = 8.098(1) Å, b = 8.956(1) Å, c = 20.855(3) Å, α = 87.957(2)°, β = 103.99(3)°, γ = 77.611(2)°, V = 1476.4(3) Å^3, T = 193(2) K, Z = 4, D_c = 1.297, measured reflections 12 352, unique 6618 (R_{int} = 0.0201), refined parameters 313, $R[I > 2\sigma I]$ = 0.0360, $wR_2(F^2)$ = 0.1190. Satisfactory elemental analysis could not be achieved even from single crystals. The extreme solubility of both **6a** and **6b** in all organic solvents prevented the effective washing of the bulk powder or single crystals. Furthermore, **6a** and **6b** readily sublime at RT, therefore precluding the efficient drying of bulk material *in vacuo*. Representative ^{1}H NMR spectra are available in the Supporting Information as an indication of the level of purity obtained.

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their respective arene rings (**6a**, $\beta = 4.6°$, $\beta' = 20.6°$; **6b**, $\langle\beta\rangle = 4.0°$, $\langle\beta'\rangle = 19.1°$), no upfield shift is observed in the ^{13}C-{^{1}H} NMR spectra, an additional mark of imposed ring strain. Rather, a slight downfield shift is noted for both *ipso*-carbon centers as compared to the parent Cb*CoCp (**6a**/**6b** (ppm): Cp, 79.87/82.99; Cb*, 77.04/76.70 vs 80.01 and 74.83, respectively). Furthermore, DSC experiments utilizing repeated heating and cooling cycles show only melting transitions with no indication of ring opening. Increasing the ring strain should be readily imposed by the incorporation of smaller bridging atoms.

The mixed sandwich [2]cobaltoarenophanes (**6a**; **6b**) represent the first example of neutral, late transition metal *ansa*-metalloarenocenes. We are currently examining the chemistry of these unique molecules, modifying the bridging elements, and pursuing the synthesis and isolation of a [1]cobaltoarenophane analogue.

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Supporting Information Available: Samples of multinuclear NMR spectra, DSC traces, tables of X-ray crystallographic data, as well as detailed notes on a modified experimental procedure for the synthesis of Cb*CoCp (**4**) are available free of charge on the Internet at http://pubs.acs.org.

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