Notes

4-*ansa*-Metallocene Complexes: Synthesis of 1,1,4,4-Tetramethyl-1,4-disilabutylene-Bridged Titanocene, Zirconocene, and Hafnocene Derivatives

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Summary: Titanocene, zirconocene, and hafnocene derivatives with an interannular 1,1,4,4-tetramethyl-1,4-disilabutylene bridge were synthesized by the reaction of the dilithium derivative of 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutane with titanium, zirconium, and hafnium tetrachlorides in THF. The identities of all new compounds have been documented by analytical as well as by spectroscopic (IR, MS, ^{1}H and ^{13}C NMR) data.

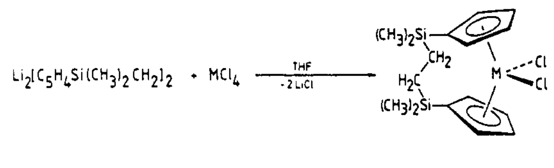
Linked cyclopentadienyl anions such as $[C_5H_4XC_5H_4]^{2-}$ (X = $(CH_2)_n$, n = 1-4; X = $Si(CH_3)_2$, $Si(H)(CH_3)$, $Ge(CH_3)_2$, ...) react with transition-metal halides to yield monomeric or polymeric metallocenes.[1-7] For example, the reaction between ferrous chloride and the dicyclopentadienylmethane dianion forms the oligomeric $[1^n]$-ferrocenes $[C_5H_4CH_2C_5H_4Fe]_n$ (n = 2-5).[7] However, the reaction of MCl_4 (M = Ti, Zr, Hf) with the cyclopentadienyl anions $[C_5H_4XC_5H_4]^{2-}$ yields the monomeric *ansa*-titanocene derivatives, as well as their higher homologues, where X is a covalent $(CH_2)_n$ link (n = 1-4) or a RR'E (E = C, Si, Ge; R = R' = CH_3, C_2H_5; R = CH_3, R' = H, ...)[1-6] unit. These are well-characterized compounds and have been used as model compounds for metallocene-based catalysis reactions.[1e,8,9] In this context, we report here the synthesis of the dilithium salt of the 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutylene dianion, $[C_5H_4Si(CH_3)_2CH_2]_2^{2-}$ (**2**), and a study of its reactions with the metal chlorides MCl_4 (M = Ti, Zr, Hf).

Results and Discussion of Reaction Chemistry

The 4-*ansa*-metallocene derivatives of type **3**, in which the ligand framework is stabilized by an interannular 1,1,4,4-tetramethyl-1,4-disilabutylene chelate ring, were prepared by the reaction of $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$ (**2**) and MCl_4 (M = Ti, Zr, Hf) in THF. **2** is easily accessible by

$$2\,C_5H_5Li + [ClSi(CH_3)_2CH_2]_2 \xrightarrow[0-25\,^\circ C]{THF} 2\,LiCl + \underset{\mathbf{1}}{[C_5H_5Si(CH_3)_2CH_2]_2} \quad (1)$$

$$\underset{\mathbf{1}}{[C_5H_5Si(CH_3)_2CH_2]_2} + 2\,n\text{-}BuLi \xrightarrow[0-45\,^\circ C]{THF} 2\,n\text{-}BuH + \underset{\mathbf{2}}{Li_2[C_5H_4Si(CH_3)_2CH_2]_2} \quad (2)$$



(3)

2 **3**

the lithiation of 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutane, which itself was prepared in 64% yield by the reaction of 2 mol of lithium cyclopentadienide with 1 equiv 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilabutane in THF. Reaction of **2** with the metal tetrachlorides MCl_4 (M = Ti, Zr, Hf) in THF and appropriate workup gave the air-stable 1,1,4,4-tetramethyl-1,4-disilabutylene-bridged metallocene derivatives **3a-c** in yields of around 30%. These low yields probably are due to competitive formation of insoluble polymeric products.

The compounds **3** are the only isolated products obtained by extraction of the reaction residue with dichloromethane. Atempted isolation of any other products by further extraction of the reaction residue with more polar solvents such as THF or DMSO was unsuccessful. The compounds **3** are monomeric, as cryoscopic molecular weight determinations in benzene have shown. In agreement with this observation is the FD mass spectrum of **3a**. However, for the zirconocene and hafnocene complexes **3b,c** a molecular ion that indicates a dimeric structure (M←Cl-M←Cl) was found in the FD mass spectrum.

The most informative feature of the *ansa*-titanocene, -zirconocene, and -hafnocene dichloro derivatives [$C_5H_4XC_5H_4]MCl_2$ (M = Ti, Zr, Hf; X = $(CH_2)_n$, n = 1-4; X = $(CH_3)_2Si$, $(H)(CH_3)Si$, $(CH_3)_2Ge$, ...)[1-6] in their ^{1}H NMR spectra is the appearance of an AA'XX' resonance pattern for the cyclopentadienyl protons. Similar observations have been made for all of the compounds **3**: They

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show two pseudotriplets with J values of 2.7 Hz in the region δ 6–7 ppm. For the $(CH_3)_2SiCH_2CH_2Si(CH_3)_2$ link the ^1H NMR spectra show the expected simplicity with the resonance signals of the methyl protons at around δ 0.3 ppm and of the methylene protons in the region δ 0.8–1.1 ppm.

In the carbon-13 NMR spectra two signals around δ −1.7 and 7.2 ppm are found for the 1,1,4,4-tetramethyl-1,4-disilabutylene bridge. The carbon atoms of the cyclopentadienyl rings of each of the compounds **3** show two C_5H_4R methine signals (d, J(C–H) = 172–175 Hz) and one ipso C_5H_4R singlet around δ 121–129 ppm. The ipso carbon atom is deshielded and resonates at lower field. All of the compounds **3** show the C^i, $C^{2,5}$, and $C^{3,4}$ resonances downfield from those of the parent C_5H_5 complex. This deshielding is attributed to electron withdrawal by the $(CH_3)_2SiCH_2$ group.[10]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or a Vacuum Atmospheres HE-43 Dri-Lab glovebox. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl, *n*-pentane, *n*-hexane, and diethyl ether were purified by distillation from lithium aluminum hydride, and dichloromethane was purified by distillation from phosphorus pentoxide.

Infrared spectra were obtained with a Perkin-Elmer 1430 double-beam grating spectrometer. Proton nuclear magnetic resonance spectra were recorded on a JEOL FX-90 spectrometer, and carbon-13 NMR spectra were recorded on a Bruker WM-270 spectrometer operating at 67.9 MHz in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethysilane with the solvent as the reference signal. EI mass spectra were recorded on a Finnigan 3200 mass spectrometer operating at 70 eV, whereas field desorption mass spectra were recorded on a Finnigan MAT 731 mass spectrometer operating in the positive ion mode. Melting points were determined with use of analytically pure samples, which were sealed in nitrogen-purged capillaries, on a Büchi melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Samples were sent sealed in evacuated vials.

Synthesis of 1,4-Dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutane (1). To lithium cyclopentadienide, prepared from 5.77 g of *n*-butyllithium (93 mmol, 37.2 mL of 2.5 M *n*-butyllithium in *n*-hexane) and 6.15 g (93 mmol) of freshly cracked cyclopentadiene in 200 mL of THF, was added a solution of 10.0 g (46.45 mmol) of 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilabutane[11] in 20 mL of THF, slowly at 0 °C. After it had been warmed to room temperature and stirred overnight, the reaction mixture was treated with 100 mL of ice water and the organic layer was separated. The water layer was washed three times with a total of 150 mL of diethyl ether, and the combined organic layers were dried over anhydrous magnesium sulfate. Solvent was removed under reduced pressure, leaving a pale yellow oil, which was distilled with use of a 10-cm Vigreux column. The compound **1**, $[C_5H_5Si(CH_3)_2CH_2]_2$, distilled at 90–95 °C (0.1 mmHg) as a colorless liquid, yield 8.1 g (29.5 mmol, 64%). IR (CCl_4): 3095 w, 2960 s, 2914 m, 2900 m, 1295 vw, 1250 s, 1138 m, 1115 vw, 1092 vw, 1060 m, 972 s, 953 s, 905 w, 898 w, 885 vw cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.11 (s, 12 H, $Si(CH_3)_2$), 0.44 (s, 4 H, $SiCH_2$), 3.02 (broad, 2 H, C_5H_5), 6.56 (broad, 8 H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ −4.7 (q, J(C–H) = 119 Hz, 4 C, $Si(CH_3)_2$), 8.2 (t, J(C–H) = 119 Hz, 2 C, $SiCH_2$), 58.6 (d, J(C–H) = 139 Hz, 2 C, C_5H_5), 130.1 (d, J(C–H) = 168 Hz, 4 C, C_5H_5), 132.6 (d, J(C–H) = 168 Hz, 4 C, C_5H_5). EI mass spectrum: molecular ion at m/e (relative intensity) 274 (23), $M^+ - CH_3$ 279 (1), $M^+ - 2CH_3$ 244 (1), $M^+ - 3CH_3$ 229 (1), $M^+ - 4CH_3$ 214 (1), $C_5H_5Si(CH_3)_2CH_2CH_2Si(CH_3)_2^+$ 209 (41), $C_5H_5Si(CH_3)_2CH_2CH_2SiCH_3^+$ 194 (21), $C_5H_5Si(CH_3)_2CH_2CH_2Si^+$ 179 (16), $C_5H_5SiCH_3CH_2CH_2Si^+$ 164 (16), $[(CH_3)_2SiCH_2]_2^+$ 144 (88), $C_5H_5Si(CH_3)_2^+$ 123 (100), $C_5H_5SiCH_3^+$ 109 (16), $C_5H_5Si^+$ 93 (48), $Si(CH_3)_3^+$ 73 (35), $Si(CH_3)_2^+$ 58 (20), $SiCH_3^+$ 43 (19). Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.54. Found: C, 69.69; H, 9.66.

Reaction between 1,4-Dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutane and *n*-Butyllium. *n*-Butyllithium (36.42 mmol; 14.6 mL of a 2.5 M *n*-hexane solution) was added dropwise to a solution of 5.0 g (18.21 mmol) of 1,4-dicyclopentadienyl-1,1,4,4-tetramethyl-1,4-disilabutane in 100 mL of THF at 0 °C. After 5 min of stirring at 0 °C the reaction mixture was warmed to room temperature and stirred at reflux for 45 min to give the $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$ reagent.

Reaction between Titanium Tetrachloride and $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$. To the above-synthesized $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$ was added 3.46 g (18.22 mmol) of titanium tetrachloride dissolved in 100 mL of toluene at 0 °C. The reaction mixture slowly turned red. It was warmed to room temperature and stirred for 14 h, followed by stirring at reflux for 2 h. After the mixture was cooled to 25 °C, the solvents were evaporated under high vacuum and the resulting dark red residue was extracted first with a total of 300 mL of dichloromethane and filtered through a pad of silica gel. Evaporation of dichloromethane under reduced pressure gave 2.0 g (5.11 mmol) of **3a** as a red, air-stable, crystalline solid in 28% yield. Recrystallization from dichloromethane/*n*-pentane gave pure material (1.65 g, 4.22 mmol, 23%), mp 253 °C dec. Further extraction of the reaction residue with THF or DMSO did not afford additional compounds. IR (KBr): 3082 s, 2948 s, 2916 m, 2889 m, 2855 s, 2840 sh, 2788 vw, 1440 vw, 1409 vw, 1395 s, 1370 s, 1317 w, 1248 s, 1239 vs, 1197 vw, 1171 s, 1168 sh, 1104 m, 1069 vw, 1051 s, 1040 s, 957 w, 936 w, 915 w, 893 s, 845 sh, 832 vs, 818 vs, 805 sh, 771 vs, 714 s, 684 m, 647 w, 635 w, 618 w, 596 w, 582 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.26 (s, 12 H, $Si(CH_3)_2$), 0.83 (s, 4 H, $SiCH_2$), 6.66 (t, J(H–H) = 2.7 Hz, 4 H, C_5H_4), 6.98 (t, J(H–H) = 2.7 Hz, 4 H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −1.6 (q, J(C–H) = 120 Hz, 4 C, $Si(CH_3)_2$), 7.4 (t, J(C–H) = 120 Hz, 2 C, $SiCH_2$), 126.0 (d, J(C–H) = 175 Hz, 4 C, C_5H_4), 127.4 (d, J(C–H) = 175 Hz, 4 C, C_5H_4), 128.8 (s, 2 C, C_5H_4). FD mass spectrum (10 mA, CH_2Cl_2): molecular ion at m/e 390. Molecular weight determination (in benzene, cryoscopic): calcd 391.3; found 380. Anal. Calcd for $C_{16}H_{24}Cl_2Si_2Ti$: C, 49.11; H, 6.18. Found: C, 49.09; H, 6.13.

Reaction between Zirconium Tetrachloride and $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$. To $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$ (for preparation and reaction scale see above) was added 4.25 g (18.24 mmol) of zirconium tetrachloride as a suspension in 100 mL of toluene. The reaction mixture gradually turned pale yellow. Appropriate workup, similar to that used for the analogous titanium compound (see above), gave 2.5 g (5.75 mmol) of **3b** as colorless needles in 32% yield; mp 218 °C dec. No further compounds could be isolated, even by extracting the reaction residue with more polar solvents such as THF and DMSO. IR (KBr): 3088 w, 2943 s, 2921 m, 2887 m, 2855 m, 1435 w, 1402 m, 1366 m, 1310 w, 1292 vw, 1242 vw, 1196 vw, 1170 s, 1126 s, 1095 vw, 1055 s, 1035 vs, 925 w, 896 s, 880 w, 846 sh, 816 vs, 800 sh, 772 vs, 754 sh, 718 s, 698 s, 679 s, 663 m, 634 sh, 625 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.25 (s, 12 H, $Si(CH_3)_2$), 0.87 (s, 4 H, $SiCH_2$), 6.48 (t, J(H–H) = 2.7 Hz, 4 H, C_5H_4), 6.75 (t, J(H–H) = 2.7 Hz, 4 H, C_5H_4). ^{13}C NMR ($CDCl_3$): δ −1.8 (q, J(C–H) = 120 Hz, 4 C, $Si(CH_3)_2$), 7.0 (t, J(C–H) = 120 Hz, 2 C, $SiCH_2$), 121.6 (d, J(C–H) = 172 Hz, 4 C, C_5H_4), 122.5 (s, 2 C, C_5H_4), 124.1 (d, J(C–H) = 172 Hz, 4 C, C_5H_4). FD mass spectrum (10 mA, CH_2Cl_2): molecular ion at m/e 868. Molecular weight determination (in benzene, cryoscopic): calcd 434.7; found, 424. Anal. Calcd for $C_{16}H_{24}Cl_2Si_2Zr$: C, 44.21; H, 5.57. Found: C, 44.49; H, 5.64.

Reaction between Hafnium Tetrachloride and $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$. To $Li_2[C_5H_4Si(CH_3)_2CH_2]_2$ (for preparation and reaction scale see above) was added 5.85 g (18.26 mol) of hafnium tetrachloride as a suspension in 100 mL of toluene. Workup similar to that described earlier yielded only colorless **3c** in 29% yield (2.8 g, 5.36 mmol); mp 248 °C dec. IR (KBr): 3088 m, 3066 vw, 2956 sh, 2940 m, 2921 sh, 2895 w, 2885 sh, 2859 m, 2765 vw, 1438 vw, 1403 s, 1399 s, 1365 s, 1307 w, 1251 vs, 1245 vs, 1192 m, 1173 vs, 1126 vs, 1065 s, 1053 vs, 1031 vs, 919 w, 894 vs, 878 m, 815 vs, 775 vs, 720 vs, 699 vs, 635 s, 625 s cm^{-1}. ^1H NMR ($CDCl_3$):

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δ 0.45 (s, 12 H, $Si(CH_3)_2$), 1.04 (s, 4 H, $SiCH_2$), 6.07 (t, J(H-H) = 2.7 Hz, 4 H, C_5H_4), 6.62 (t, J(C-H) = 2.7 Hz, 4 H, C_5H_4). FD mass spectrum (10 mA, CH_2Cl_2): molecular ion at m/e 1044. Molecular weight determination (in benzene, cryoscopic): calcd 521.9; found, 512. Anal. Calcd for $C_{16}H_{24}Cl_2HfSi_2$: C, 36.82; H, 4.64. Found: C, 37.37; H, 4.71.

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Registry No. 1, 130904-26-6; **3a**, 130904-27-7; **3b**, 130904-28-8; **3c**, 130904-29-9; cyclopentadiene, 542-92-7; 1,4-dichloro-1,1,4,4-tetramethyl-1,4-disilabutane, 13528-93-3; titanium tetrachloride, 7550-45-0; zirconium tetrachloride, 10026-11-6; halfnium tetrachloride, 13499-05-3.

Tungsten(0) Complexes of Bis(dialkoxyphosphino)methylamines. Crystal and Molecular Structure of the Novel Cycloheptatriene-Bridged Dimer $[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$

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Summary: The cycloheptatriene-bridged ditungsten complexes $[(mer\text{-}W(CO)_3(CH_3N(P(OR)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$ (R = CH_3 (**1**), $CH(CH_3)_2$ (**2**), CH_2 (**3**)) have been identified as minor products of the reaction of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ with $CH_3N(P(OR)_2)_2$. Slow reaction of **1** with carbon monoxide occurs to form *cis*-$[W(CO)_4(CH_3N(P(OCH_3)_2)_2)]$. The crystal structure of **1** (triclinic $P\bar{1}$, a = 14.256 (4) Å, b = 14.629 (4) Å, c = 9.737 (4) Å, α = 97.51 (3)°, β = 96.89°, γ = 64.25 (2)°, Z = 2, 3106 data ($I \geq 3\sigma(I)$), R = 0.034, R_w = 0.045) shows the two $[mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2)]$ moieties to be bonded to the same face of the cycloheptatriene ring, which adopts a tub conformation, via the two nonadjacent carbon-carbon double bonds. Metal-metal bonding is absent.

Few tungsten complexes containing simple η^2-olefin ligands are known[1-11] and even fewer have been structurally characterized.[1,7,10,11] The number of bimetallic complexes bridged solely by a cyclic polyolfin where metal-metal bonding is absent is also small, and to the best of our knowledge, the only examples previously reported are $[(Fe(CO)_4)_2(\mu\text{-}\eta^2{:}\eta^2\text{-ol})]$ (ol = cycloocta-1,3,6-triene,[12] cycloocta-1,5-diene,[13] 1,1′-diphenylfulvalene[14]), $[(cpFe(CO)_2)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_4)]$,[15] and $[(ML_n)_2(\mu\text{-hexafluorobicyclo[2.2.0]hexa-1,4-diene})]$ (ML_n = $Pd(PPh_3)_2$, $Pt(PPh_3)_2$, $Rh(acac)(C_2H_4)$).[16] Of these, only two are structurally characterized.[13,14] We report here the synthesis and structural characterization of what appears to be the first example of a ditungsten complex, $[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$, containing a bridging cyclic polyolefin and the first fully characterized example of this mode of coordination for cycloheptatriene.

Experimental Section

All manipulations were preformed under an atmosphere of purified nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert atmosphere prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on an IBM/Bruker AF200 spectrometer at 200.132 and 81.015 MHz, respectively, and referred to tetramethylsilane (δ 0.0) and 85% H_3PO_4 (δ 0.0) as external standards. Positive chemical shifts are downfield of the standard. Literature methods were used to prepare $[W(CO)_3(\eta^6\text{-}C_7H_8)]$[17] and $CH_3N(P(OR)_2)_2$ (R = $CH_3(L_2)$,[18] $CH(CH_3)_2(L'_2)$,[19] $CH_2(L''_2)$[19]).

$[(mer\text{-}W(CO)_3(CH_3N(P(OCH_3)_2)_2))_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_7H_8)]$ (1). A toluene solution (10 mL) of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (0.300 g, 0.833 mmol) and $CH_3N(P(OCH_3)_2)_2$ (0.269 g, 1.250 mmol) was stirred for 6 h at room temperature. The solvent was removed in vacuo (25 °C) to give a yellow oil that was taken up in a few drops of toluene and chromatographed on a 1.5 × 20 cm column of Brockman I alumina. Development with hexane followed by elution with hexane/diethyl ether (4:1, v:v) removed a yellow band that was shown by ^{31}P NMR to be a mixture of 1 and *cis*-$[W(CO)_4(L_2)]$.[19] Futher elution with hexane/diethyl ether (1:1, v:v) afforded a second fraction containing more 1 together with a large quantity of *mer*-$[W_2(CO)_6(L_2)_2(\mu\text{-}L_2)]$[19] and a small amount of *mer*-$[W(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]$.[19] Yellow, air-sensitive crystals of 1 could be obtained by slow evaporation of both fractions followed by cooling, but those from the second fraction proved to be more satisfactory for the crystallographic study. Total yield estimated to be ca. 30% by NMR. Anal. Calcd for $C_{23}H_{38}O_{14}P_4N_2W_2$: C,

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