Double Deprotonation of a Cyclopentadienyl Alkene to Form a Polydentate Trianionic Cyclopentadienyl Allyl Ligand System

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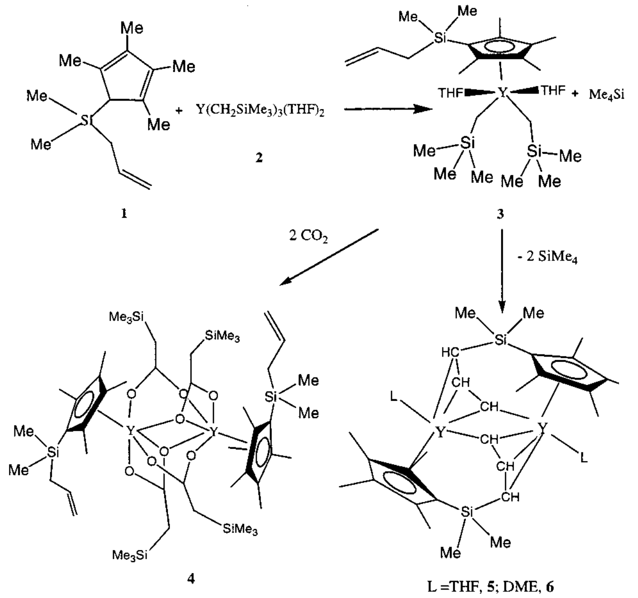
An important part of the evolution of metallocene chemistry and metallocene-based polymerization chemistry has been the development of cyclopentadienyl ligands to which other donor functionalities have been attached.[1−14] Ligand systems have been designed which involve monoanionic cyclopentadienides attached to neutral ether, amine, and hydrocarbon groups as well as dianionic ansa ligands in which the cyclopentadienide is attached to another anionic donor such as a cyclopentadienide or amide. These have provided additional coordination opportunities and in some cases unique and high reactivity in olefin polymerization.[4−9]

Among the tethered systems, those that incorporate olefinic functionality are attractive for elucidating metal olefin interactions and reaction pathways pertinent to olefin polymerization. For example, Okuda has examined $[C_5Me_4(CH_2CH_2CH{=}CH_2)]^-$ with titanium,[10] and Royo has studied $[(C_5H_4)SiMe_2(CH_2CH{=}CH_2)]^-$ with zirconium.[11] Olefins tethered to alkyl and alkoxide ligands have also been studied with yttrium and zirconium by Casey, $[CH_2CH_2CH_2C(Me){=}CH_2]^-$,[12,13] and Jordan, $(OCMe_2CH_2CH_2CH{=}CH_2)^-$.[14]

In efforts to examine the metal olefin chemistry of yttrium and the lanthanide metals in a well-defined cyclopentadienyl system, we have prepared complexes of an alkene-substituted tetramethylcyclopentadienide. We report here the surprising hydrocarbon elimination chemistry that occurred when yttrium alkyl complexes of this ligand were prepared. Intramolecular hydrocarbon elimination reactions are well-known from the work of Schrock and others to have the potential to generate unusual results and new ligand systems.[15−19] The formation of a new type of cyclopentadienyl ligand is reported as well as reaction chemistry unusual for metallocene-based olefin polymerization systems.

Scheme 1



The alkene-substituted tetramethylcyclopentadiene $(C_5Me_4H)SiMe_2(CH_2CH{=}CH_2)$, **1**, was synthesized by standard methods[20−23] from $Me_2Si(C_5Me_4)Cl$[24] and allylmagnesium chloride. To avoid the separation of the alkali metal byproducts of ionic metathesis reactions involving metal chlorides,[25] the ligand was attached to yttrium by reacting **1** with $Y(CH_2SiMe_3)_3(THF)_2$, **2**.[26,27] In the course of these studies, it was established that this readily available yttrium alkyl starting material exists as the octahedral facial trisolvate, $Y(CH_2SiMe_3)_3(THF)_3$, when crystallized in the presence of THF.[28]

The neutral diene **1** reacts directly with **2** in C_6D_6 to evolve one equivalent of $SiMe_4$ and form the bright yellow complex $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]Y(CH_2SiMe_3)_2(THF)_2$, **3**, Scheme 1.[29]

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(28) $Y(CH_2SiMe_3)_3(THF)_3$ crystallizes from hexanes/THF in the space group $P2_1/n$ with $a = 10.5929(7)$ Å, $b = 16.3536(11)$ Å, $c = 19.0604(12)$ Å, $\alpha = 90°$, $\beta = 91.1260(10)°$, $\gamma = 90°$, $V = 3301.2(4)$ Å^3 and $\rho_{cacld} = 1.141$ Mg/m^3 at 158 K. At convergence, wR2 = 0.0755 and GOF = 1.044 for 289 variables refined against 8020 unique data. As a comparison for refinement on F, R1 = 0.0324 for those 6355 data with $I > 2.0\sigma(I)$. Average Y−C(CH_2SiMe_3): 2.427(19) Å. Y−O(THF): 2.4512(14), 2.4567(13) and 2.5000(13) Å. The latter elongated Y−O distance may explain the coordination lability of the third THF molecule which can be removed under vacuum.

(29) **1** (67 mg, 0.303 mmol) was added to a colorless solution of **2** (150 mg, 0.303 mmol) dissolved in 1 mL of C_6D_6 in a greaseless resealable NMR tube. The color changed to bright yellow within 30 min and ^{1}H NMR spectroscopy indicated that the reaction was complete after 45 min. **3** can be isolated as a yellow/orange oily solid in > 90% yield. ^{1}H NMR δ (C_6D_6): −0.67 (d, J_{YH} = 4 Hz, 4 H, CH_2SiMe_3), 0.00 (s, 12 H, $SiMe_4$, formed during reaction), 0.25 (s, 18 H, CH_2SiMe_3), 0.46 (s, 6 H, $C_5Me_4SiMe_2$), 1.32 (m, 8 H, THF), 1.82 (d, J_{HH} = 8 Hz, 2 H, $CH_2CH{=}CH_2$), 1.93 (s, 6 H, ring *Me*), 2.21 (s, 6 H, ring *Me*), 3.60 (m, 8 H, THF), 4.94 (m, 2 H, $CH_2CH{=}CH_2$), 5.83 (m, 1 H, $CH_2CH{=}CH_2$). ^{13}C NMR (C_6D_6) δ: 0.3 (s, $SiMe_4$), 0.5 ($C_5Me_4SiMe_2$), 4.8 (s, CH_2SiMe_3), 11.8 (s, ring *Me*), 15.0 (s, ring *Me*), 25.5 (s, THF), 26.5 (s, $CH_2CH{=}CH_2$), 34.7 (d, J_{YC} = 50 Hz, CH_2SiMe_3), 52.8 (s, ring Si-*C*), 69.7 (s, THF), 113.5 (s, $CH_2CH{=}CH_2$), 123.6 (s, ring *C*-Me), 126.8, (s, ring *C*-Me), 136.1 (s, $CH_2CH{=}CH_2$). IR (thin film): 690 w, 802 s, 833 s, 891 m, 992 w, 1034 s, 1154 m, 1251 s, 1328 m, 1444 m, 1629 m, 2860 s, 2914 s, 2957 s, 3076 w, 3655 w, 3694 w cm^{-1}.

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The oily nature of **3** frustrated attepts at definitive crystallographic characterization, but the NMR spectra (complete with the expected Y−C and Y−H coupling) were consistent with this composition. No evidence for an yttrium olefin interaction was observed by NMR spectroscopy. Further chemical confirmation of the composition of **3** was obtained by derivatization with CO_2. $\{[Me_2Si(C_5Me_4)(CH_2CH{=}CH_2)]Y(O_2CCH_2SiMe_3)_2\}_2$, **4**, the result of CO_2 insertion into each of the yttrium alkyl bonds, was isolated and structurally characterized, Scheme 1.[30]

Samples of **3** change color to dark red over several days at room temperature or in 4 h at 65 °C with the further evolution of tetramethylsilane. No $(Me_3SiCH_2)^-$ ligand peaks remain in the NMR spectrum of the product and the cyclopentadienyl resonances broaden into the baseline even at low temperature.[31] Crystals of the dark red compound could be isolated as both THF and dimethoxyethane (DME) adducts. Each revealed that *double* metalation of the tetramethylcyclopentadienyl(dimethylsilylallyl) ligand had occurred to form a new type of *trianionic* cyclopentadienyl allyl ligand, $[Me_2Si(C_5Me_4)(C_3H_3)]^{3-}$,[32] in the complexes $\{[Me_2Si(C_5Me_4)(C_3H_3)]Y(L)\}_2$ (L = THF, **5**; L = DME, **6**), Scheme 1.[33] Precedent for multiple hydrocarbon elimination reactions has been shown by Schrock to occur in polyalkylmetal complexes to form, for example, carbynes.[15−19,34] The formation of **5** and **6** suggests that multiple metalation can occur with olefins in metallocene environments.

The structures of the THF adduct, **5**, and the DME ligated complex, **6** (Figure 1), are similar. Each trianionic $[Me_2Si(C_5Me_4)(C_3H_3)]^{3-}$ ligand bridges the two yttrium atoms by coordinating $\eta^5{:}\eta^1$ to one metal and η^3 to the other. One hydrogen atom was found on each of the allyl carbon atoms, C12, C13, and C14 in **6**. GC/MS analysis of the product of deuteriolysis of **5** is consistent with the trideuteride $Me_2Si(C_5Me_4D)C_3H_3D_2$.

It is evident that the trianion is sterically flexible since it can crystallize with DME or THF giving yttrium formal coordination numbers of both 7 and 8 in **5** and **6**, respectively. The DME structure has uniformly longer Y−ligand distances including a 3.7231(5) Å Y···Y distance versus 3.48(2) Å in **5** and 3.53 and 3.58(1) Å in the simple methyl-bridged yttrium dimers $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$[35] and $[(1,3,\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$,[36] respectively. The 2.651(9) and 2.716(3) Å Y−C(ring) average distances in **5** and **6** are in the normal range,[37] although the range in **6**, 2.630(3) to 2.780(3) Å, is large. The Y−(ring centroid) distances in **5**, 2.360 Å, and **6**, 2.432 Å, can be compared to those in the chelating $(C_5Me_4R)^{2-}$ complexes $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)Y(CH_2SiMe_3)(THF)$,[27] 2.333(7) Å, and $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)Y\{CH(Me)C_6H_4\text{-}4\text{-}{}^tBu\}(THF)$,[27] 2.347(6) Å. The 2.398(6) Å THF Y−O distance in **5** is similar to the 2.319(5) and 2.374(4) Å distances in the latter two complexes.[27]

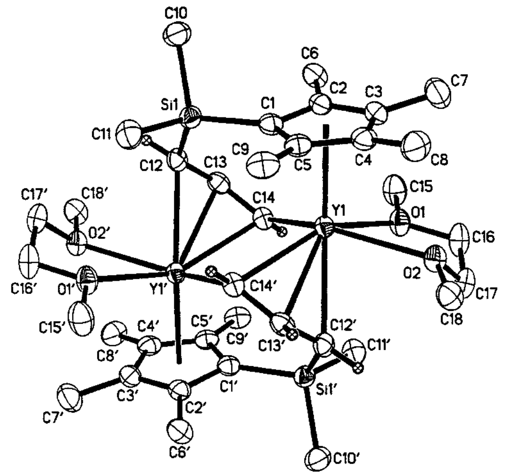

Figure 1. Structure of $\{[Me_2Si(C_5Me_4)(C_3H_3)]Y(DME)\}_2$, **6**, with thermal ellipsoids drawn at the 50% probability level.

The 2.399(9) and 2.456(3) Å Y−C distances of the CH moiety which is closest to Y1, namely C14, in **5** and **6** can be compared with the bridging methyl distances of 2.553(10) and 2.537(9) Å in $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$ and $[(1,3,\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$, respectively, and the 2.468(7) and 2.427(19) Å terminal Y−C distances in $(C_5Me_5)YCH(SiMe_3)_2$[38] and $Y(CH_2SiMe_3)_3(THF)_3$.[28] The allylic carbons C12′, C13′, and C14′ are found 2.573(9), 2.599(9), and 2.484(8) Å, respectively, from Y1 in **5** and 2.622(3), 2.593(3), and 2.536(3) Å from Y1 in **6**. This range of distances is well within the range found in the substituted allyl compounds such as $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = Me,Ph) and $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3{:}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$[39] when the difference in radial size of the metal is taken into account.[40] The C−C distances of the allyl moiety in **6** are 1.429(4) Å for C12−C13 and 1.382(4) Å for C13−C14, but in **5**, they are indistinguishable within the error limits: 1.422(12) and 1.382(12) Å.

To our knowledge this is the first example of a trianionic cyclopentadienyl allyl ligand system. Its formation demonstrates that multiple metalation of alkene-substituted cyclopentadienyl ligands is a new route to polyanionic organometallic ligands. It also shows that in the proper coordination environment, allyl moieties can be multiply metalated. This may be of interest in regard to recent studies of allyl units on surfaces[41] as well as reactivity considerations involving olefins in cyclopentadienyl-based polymerization systems. The high reactivity of **5** and **6** is currently under investigation.

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Supporting Information Available: Complete experimental details, including tables of crystal data, positional parameters, bond distances and angles, and thermal parameters; listing of observed and calculated structure factor amplitudes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Full experimental details are given in the Supporting Information.

(31) As described above, **1** (67 mg, 0.303 mmol) was added to **2** (150 mg, 0.303 mmol) in 1 mL of C_6D_6. **3** was generated in situ, and the sample was monitored over a 3-day period by ^1H NMR spectroscopy during which time the color gradually changed from yellow to dark red. The ligand peaks broadened into the baseline after 48 h, and the only new peaks observed were free THF and tetramethylsilane. After 4 days, X-ray quality crystals of **5** were formed in the tube. A separate sample was prepared by the same procedure in toluene-d_8 and cooled to −80 °C in the NMR probe. No new ligand peaks were observed at low temperature. **5** can also be prepared in 90% yield by generating a sample of **3** in arenes and heating the solution to 65 °C for 4 h. IR (thin film): 679 br, 833 br, 1023 br, 1251 s, 1328 m, 1378 w, 1444 w, 1620 br, 2860 s, 2922 s, 2957 s. Anal. Calcd for $C_{36}H_{58}O_2Si_2Y_2$: C, 57.13. H, 7.72. Y, 23.49. Found C, 56.24. H, 7.93 (Desert Analytics). Y, 21.3 (complexometric). **6** was prepared by crystallizing a sample of **5** in a toluene/hexanes/DME (80:15:5) mixture. Compounds **5** and **6** are soluble in arenes and ethers and partially soluble in alkanes.

(32) The closest example we could find in the literature was the fulvene-derived metallacyclobutane system in $(\eta^5\text{-}C_5Me_5)[\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CMe(CH_2)_2]$-Ti. Brinkmann, P. H. P.; Prosenc, M.; Luinstra, G. A. *Organometallics* **1995**, *14*, 5481−5482.

(33) **5** crystallizes in the space group $P2_1/n$ with $a = 9.1930(6)$ Å, $b = 13.6616(10)$ Å, $c = 14.4241(10)$ Å, $\alpha = 90°$, $\beta = 96.561(2)°$, $\gamma = 90°$, $V = 1799.7(2)$ Å^3 and $\rho_{calcd} = 1.397$ Mg/m^3 for $Z = 2$ at 183 K. At convergence, wR2 = 0.1769 and GOF = 0.0634 for 191 variables refined against 3062 unique data. (As a comparison for refinement on F, R1 = 0.0634 for those 1720 data with $I > 2.0\sigma(I)$.) The high value for wR2 was probably due to the weakness of the data set. The best quality crystal obtained was a very thin plate. The data set was truncated at a resolution of 0.85 Å. **6** crystallizes in the space group $P2_1/n$ with $a = 8.8433(3)$ Å, $b = 14.5482(6)$ Å, $c = 16.9272(6)$ Å, $\alpha = 90°$, $\beta = 98.2430(10)°$, $\gamma = 90°$, $V = 2155.26(14)$ Å^3 and $\rho_{calcd} = 1.364$ Mg/m^3 for $Z = 2$ at 163 K. At convergence, wR2 = 0.0955 and GOF = 1.049 for 359 variables refined against 5266 data. As a comparison for refinement on F, R1 = 0.0384 for those 3795 data with $I > 2.0\sigma(I)$.

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