Relative Importance of Oligomerized Structures and Donor–Acceptor Interactions in Electrophilic Cyclopentadienyl Compounds

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During the last several years, organometallic complexes featuring weak donor ligands such as N_2, alkenes and alkynes, and agostic alkyl groups (M—R(H)···M′) have been isolated in cyclopentadienyl complexes of the s- and f-block elements (e.g., $[Cp^*_2Sm]_2(\mu\text{-}N_2)$,[1] $Cp^*_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$,[2] and $Cp^*_2Yb(\mu\text{-}Me)BeCp^*$ [3] ($Cp^* = C_5Me_5$)), raising intriguing questions about the nature of the metal–ligand bonding. One of the problems is that the relationship between the stability of these interactions and donor basicity does not always vary in the same manner. For example, both Cp^*_2Ca and Cp^*_2Ba react with $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ in toluene to yield orange solutions containing spectroscopically identifiable adducts; on cooling, the calcium solution deposits a crystalline 1:1 complex,[2] whereas Cp^*_2Ba precipitates from its mixture and leaves a solution of the diyne.[4] Even when the metal does not change, adduct stability can differ considerably depending on other ligands present. For instance, $Cp_2Ca(THF)_2$ can be desolvated to produce base-free $[Cp_2Ca]_n$ by sublimation,[5] whereas THF cannot be completely removed from $Cp^*_2Ca(THF)_2$ by repeated sublimations or refluxing in toluene.[6]

When we attempted to extract the coordinated THF from $Cp^*_2Ca(THF)_2$ by a competition reaction with $AlMe_3$ (2.0 M in toluene, $AlMe_3$:THF = 1:1),[7,8] a white precipitate containing $Me_3Al{\cdot}THF$ immediately formed that was removed by centrifugation. Evaporation of the colorless supernatant to dryness yields a white, hexane-soluble solid analyzing as $Cp^*_2Ca(AlMe_3)(THF)$ in 69% yield.[9] Its proton NMR spectrum (C_6D_6, 300 MHz, 20 °C) contains peaks at δ 2.00 and −0.48 for the Cp* and $AlMe_3$ resonances (values for the free species are δ 1.91[10] and −0.30, respectively[11]); signals from coordinated THF are found at δ 3.27 and 1.22.[12] The IR spectrum (KBr) contains bands expected for Al–C stretches at 527 and 332 cm^{-1}.[13] Details of the interaction between the aluminum and calcium moieties were revealed in a single-crystal X-ray structure determination (Figure 1).[14]

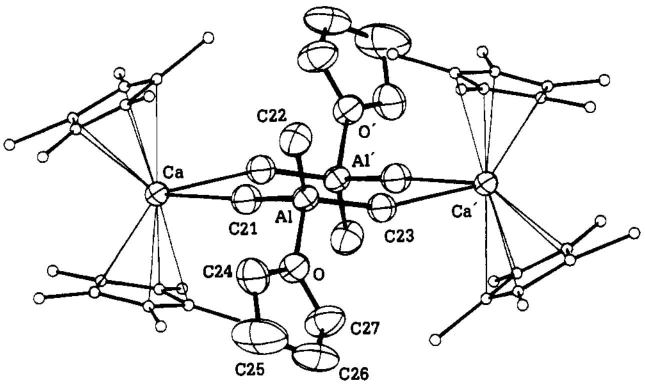

Figure 1. ORTEP view of $[(Me_5C_5)_2Ca(\mu\text{-}Me_3Al{\cdot}THF)]_2$. Thermal ellipsoids on the $Me_3Al{\cdot}THF$ unit have been drawn at the 30% probability level; the Cp* rings are rendered as lines, and only one of the disordered Cp* rings is shown.

The complex crystallizes as a centrosymmetric dimer consisting of two Cp^*_2Ca units linked by bridging $Me_3Al{\cdot}THF$ groups, thereby generating an eight-membered $[Ca{-}C(H_3){-}Al{-}C(H_3){-}]_2$ ring. Two of the methyl groups of each $Me_3Al{\cdot}THF$ moiety bridge the calcium centers; the third group remains terminal. Adduct formation at the Al center has been observed to enhance the carbanionic character of alkyl groups in AlR_3 species.[15] It is apparently this property that allows $AlMe_3$ to display bifunctional behavior toward $Cp^*_2Ca(THF)_2$, first as a Lewis acid (in extracting the THF from the calcium center) and second as a neutral base (interacting through the methyl groups of the THF adduct).

The Ca–(μ-Me) distances of 2.948(7) and 2.999(7) Å are 0.25–0.30 Å greater than the average Ca–Cp* distance of 2.70(1) Å and considerably longer than the analogous values reported for $Cp_2Yb(\mu\text{-}Me)_2AlMe_2$ (Yb–(μ-Me) = 2.58(3) Å),[16] $[Cp^*_2Y(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2$ (Y–(μ-Me) = 2.66(3) Å),[17] or $[Cp^*_2Sm(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2$ (Sm–(μ-Me) = 2.75(1) Å),[18] even allowing for differences in metal radii (0.985 Å (Yb^{3+}), 1.02 Å

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(12) The existence of only one peak in the ^{1}H NMR spectrum for the $AlMe_3$ protons indicates that the $AlMe_3{\cdot}THF$ moiety is undergoing a process that renders the hydrogens equivalent. In the ^{13}C NMR spectrum, cooling a sample in toluene-d_8 to −83 °C causes the methyl resonance to shift from δ −7.4 (20 °C) to δ −8.0 and to broaden slightly, but no further structure is evident. Thus we cannot reliably distinguish by this means between a dissociative exchange mechanism and an intramolecular fluxional process for the methyl groups on the aluminum.

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(14) Crystals of $[(Me_5C_5)_2Ca(\mu\text{-}Me_3Al{\cdot}THF)]_2$ grown from hexane are monoclinic, space group $P2_1/n$, with a = 11.396(2) Å, b = 20.112(1) Å, c = 12.627(2) Å, β = 97.20(1)°, and D_{calcd} = 1.052 g cm^{-3} for Z = 2 (dimers). Data were collected on a Rigaku AFC6S diffractometer at 293 K using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Continuous θ–2θ scans with fixed backgrounds were used to collect a total of 4664 intensities (4418 unique) in the range $6° < 2\theta < 120°$, of which 3028 had $F > 3\sigma(F)$. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved with a combination of direct methods (MITHRIL, DIRDIF) and Fourier techniques. One C_5Me_5 ring in the molecule was rotationally disordered. The electron density was fitted to two rigid idealized C_5Me_5 rings to refine the occupancies (0.56/0.44); the constraints were then removed, and the positions of the atoms were refined isotropically. With the exception of the atoms involved in the disorder, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the methyl groups bonded to aluminum were clearly visible on difference Fourier maps, and their isotropic thermal parameters were allowed to refine. The positions of the remaining hydrogen atoms were calculated using idealized geometries based on packing considerations and d(C–H) = 0.95 Å. The positions were fixed for the final cycles of refinement. $R(F)$ = 0.086, and $R_w(F)$ = 0.112.

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(Y^{3+}), 1.08 Å (Sm^{3+}), and 1.14 Å (Ca^{2+}) (all CN = 8)).[19] Part of the difference may reflect the existence of the formal ion pair $[Cp'_2M]^+[AlMe_4]^-$ in the lanthanide analogues, whereas the calcium complex is a neutral donor–acceptor adduct. The calcium–methyl distances are thus more directly comparable to the metal–diyne contacts in $Cp^*_2Ca(Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$ (2.878(5)–3.024(5) Å)[2] and $Cp^*_2Yb(MeC{\equiv}CMe)$ (2.829(5), 2.871(5) Å),[20] the 2.872(7)-Å bridging Yb···Me interaction in $[(Me_3Si)_2C_5H_3)_2Yb]_n$,[16] and especially the Yb···(μ-C_2H_5) separations observed in $Cp^*_2Yb{\cdot}Al(C_2H_5)_3(THF)$ (2.854(18), 2.939(21) Å).[7]

The $Me_3Al{\cdot}THF$ unit is slightly distorted from a tetrahedral geometry, and the μ-Al–Me bond lengths of 1.968(7) Å (C21) and 1.963(7) Å (C23) differ by less than 0.02 Å from the terminal Al–Me (C22) distance of 1.949(8) Å. This small variation is much less than the 0.17-Å difference between bridging and terminal Me–Al groups observed in the $[AlMe_3]_2$ dimer[21] or the 0.09–0.17-Å difference typically found in complexes with terminal and bridging Al–Me groups.[17,18,22] It reflects the weakness of the attraction of the aluminum methyl groups to the calcium center.[23] The Ca–C–Al angles of 176.7(4) and 159.7(3)° compare favorably with those found in other Cp* complexes containing μ-Me groups, such as $Cp^*_2Yb(\mu\text{-}Me)BeCp^*$ (177.2°),[3] $[Cp^*_2Sm(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2$ (175.2 and 177.8°),[18] $[Cp^*_2Y(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2$ (176 and 177°),[17] and $Cp^*_2Lu(\mu\text{-}Me)Lu(Me)Cp^*$ (170°).[24]

That the calcium/aluminum system forms an isolable complex is in marked contrast to many other electrophilic cyclopentadienyl complexes, which relieve the coordinative unsaturation occasioned by loss of ethers by oligomerizing (as seen in the formation of $[Cp_2Ca]_n$,[5] $[(MeC_5H_4)_3(Ce, Nd)]_4$,[8,25] $[Cp_3M]_n$ (M = Sc,[26] Y,[27] La,[28] Pr[29]), and $[(Me_3Si)_2C_5H_3)_2(Yb, Eu)]_n$.[30] In these structures, effective increases in coordination number occur through interaction with adjacent Cp′ rings.[31] The intermolecular M···Cp′ interactions are sufficiently strong to overwhelm weaker metal–donor adducts. Consistent with this, when we allowed $Cp_2Ca(THF)_2$ to react with $AlMe_3$ in toluene, we isolated the base-free polymer $[Cp_2Ca]_n$[5] rather than a $Me_3Al{\cdot}THF$ adduct. In this case (and in the analogous reaction of $(MeC_5H_4)_3Ce(THF)$ with $AlMe_3$ to yield the tetrameric $[(MeC_5H_4)_3Ce]_4$[8]), oligomerization of the complex through the Cp′ rings extrudes the potential $Me_3Al{\cdot}THF$ donors from the coordination sphere of the metals.

In contrast to the case of Cp_2Ca, the sterically imposed monomeric nature of Cp^*_2Ca[6] leaves the methyl groups of $Me_3Al{\cdot}THF$ as the only available nucleophiles after removal of THF from the metal. Similar behavior was observed in the reaction of $Cp^*_2Yb(THF)$ with $Al(C_2H_5)_3$ to yield $Cp^*_2Yb{\cdot}Al(C_2H_5)_3(THF)$[7] rather than the monomeric Cp^*_2Yb.[32] The kinetic stability of these weak donor adducts, and those of other Cp*-based metallocenes, evidently depends on a delicate relationship between ring and metal size: the Cp* rings must block oligomerization yet not completely interfere with donor binding.[33] This structural balance must be considered along with electronic factors in rationalizing the stability of such complexes.

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Supplementary Material Available: A textual presentation of the crystallographic data collection and tables giving crystal data, data collection parameters, fractional coordinates, bond distances and angles involving non-hydrogen atoms, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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