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Stability of cyclopentadienyl aryloxide complexes of calcium and barium

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To Professor William J. Evans, a mentor and friend.

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ABSTRACT

The synthesis of mono(cyclopentadienyl)aryloxide complexes of calcium and barium has been investigated. The reaction of ICa(ODipp)(thf)$_4$ (Odipp = [2,6-iPr-OC$_6$H$_3$O]$^-$) with K[C$_5$Me$_5$], (Cp^{3Si})$_2$Ca (Cp^{3Si} = C$_5$(SiMe$_3$)$_3$H$_2$) with K[ODipp], and IBa(BHT)(thf)$_3$ (BHT = [2,6-tBu-4-Me-C$_6$H$_2$O]$^-$) with K[C$_5$Me$_5$] in THF produces Cp*Ca(Odipp)(thf)$_3$, (Cp^{3Si})Ca(Odipp)(thf)$_2$, and Cp*Ba(BHT)(thf), respectively. The crystal structures of the two monomeric calcium complexes are reported. All three compounds are stable against Schlenk rearrangement in THF and aromatic solvents. DFT calculations suggest that the presence of THF has less of an effect on the thermodynamics of Schlenk rearrangements of the aryloxide systems than it does on comparable Cp′CaI compounds.

1. Introduction

Half-sandwich cyclopentadienyl complexes (Cp′MX) serve as useful synthons for the stoichiometric [1–3] and catalytic [4,5] chemistry of the heavy alkaline-earth metals calcium, strontium, and barium. Nevertheless, the highly electropositive character of these metals and the lack of valence electrons in their cations are associated with high kinetic lability in many Cp′MX compounds [6]. Archetypal examples include Cp′CaI(thf)$_n$ (Cp′ = C$_5$Me$_5$ or C$_5$Me$_4$Et) complexes, which undergo Schlenk-type rearrangement in THF solution to form 2:1:1 mixtures of Cp′CaI(thf)$_n$, Cp′$_2$Ca, and CaI$_2$, respectively [7,8]. The position of equilibrium can be shifted somewhat by the solvent (aromatic solvents favor the heteroleptic species) and by the use of “encapsulating” cyclopentadienyl rings such C$_5$(i-Pr)$_4$H (=Cp^{4i}) [1,3], C$_5$(SiMe$_3$)$_3$H$_2$ (=Cp^{3Si}) [2] and C$_5$(t-Bu)$_3$H$_2$ [9], which sterically interfere with the rearrangement process. The identity of the *X* ligand in Cp′CaX complexes also affects the position of Schlenk equilibrium, and the present work demonstrates how the use of aryloxide ligands can make possible the isolation of rearrangement-resistant complexes in the absence of encapsulating Cp′ rings or with easily displaceable Cp′ rings such as Cp^{3Si}.

2. Experimental

2.1. General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual resonances of C$_6$D$_6$ (δ 7.15 and 128.0) or THF-d_8 (δ 3.58 and 67.4). Infrared data were measured with KBr pellets as previously described [10]. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ or by Oneida Research Services, Whitesboro, NY.

2.2. Materials

2,6-Diisopropylphenol (HOdipp) and potassium hydride were purchased from Aldrich. K[Cp^{3Si}] [11], (Cp^{3Si})$_2$Ca [9] and IBa(BHT)(thf)$_3$ [12] were prepared as previously described. K[Odipp] and KCp* (Cp* = C$_5$Me$_5$) were prepared from potassium hydride and HOdipp or HCp*, respectively. ICa(Odipp)(thf)$_4$ was prepared from the reaction of CaI$_2$ and K[Odipp] in THF [13]. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were vacuum distilled from Na/K (22/78) alloy and stored over type 4A molecular sieves.

2.3. Synthesis of Cp*Ca(Odipp)(thf)$_3$

ICa(Odipp)(thf)$_4$ (0.781 g, 1.23 mmol) and KCp* (0.215, 1.23 mmol) were dissolved in THF (20 mL), and the reaction mixture was stirred overnight. The precipitate was allowed to settle, and the clear supernatant solution was decanted. The solution was concentrated under vacuum until the volume was reduced to about 5 mL. Slow evaporation of the remaining solvent under ambient pressure resulted in the isolation of 0.474 g (60% yield) of Cp*Ca(Odipp)(thf)$_3$ as air-sensitive, colorless crystals, mp 48–50 °C. Acceptable elemental analysis could not be obtained, perhaps

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because of the high air-sensitivity of the compound. ^{1}H NMR (C_6D_6, 20 °C): δ = 7.22 (d, *J* = 6 Hz, 2H, meta-(OAr)), 6.84 (t, *J* = 6 Hz, 1H, para-(OAr)), 2.23 (s, 15H, Cp-CH_3), 1.37 (d, *J* = 6 Hz, 12H, CH*Me*$_2$). ^{1}H NMR (THF-d_8, 20 °C): δ = 6.70 (d, *J* = 7 Hz, 2H, meta-(OAr)), 6.18 (t, *J* = 7 Hz, 1H, para-(OAr)), 3.45 (septet, *J* = 7 Hz, 2H, C*H*Me$_2$), 2.02 (s, 15H, Cp-CH_3), 1.07 (d, *J* = 7 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C): δ = 161.7 (*i*Pr-*C*(Ar)), 135.8 (O-*C*(Ar)), 122.5 (meta-*C*(Ar)), 112.3 (para-*C*(Ar)), 111.5 (ring-CCH_3), 25.9 (*C*H(*i*Pr)), 24.7 (CH_3(*i*Pr)), 11.6 (Cp-CH_3). Principal IR bands (KBr, cm^{-1}): 2966 (vs, br), 2871 (s), 1587 (w), 1438 (vs), 1342 (br, m), 1263 (m), 1042(br, s), 885 (w), 748 (w), 543 (br, w). Crystals for X-ray structural analysis were grown by slow evaporation of a saturated THF solution of Cp*Ca(Odipp)(thf)$_3$ at room temperature.

2.4. Synthesis of (Cp^{3Si})Ca(Odipp)(thf)$_2$

(Cp^{3Si})$_2$Ca (0.320 g, 0.53 mmol) and K[Odipp] (0.117, 0.54 mmol) were dissolved in THF (40 mL), and the reaction mixture was stirred overnight, evaporated to dryness, and the residue extracted with toluene. The extract was filtered, and the filtrate evaporated to an oil that crystallized upon standing, yielding (Cp^{3Si})Ca(Odipp)(thf)$_2$ as air-sensitive, colorless crystals (0.277 g, 81%), mp 102–104 °C. Anal. Calcd. for $C_{34}H_{62}CaO_3Si_3$: C, 63.49; H, 9.72. Found: C, 64.27; H, 9.87. ^{1}H NMR (THF-d_8, 20 °C): δ = 6.92 (s, 2H, ring-C*H*), 6.72 (d, *J* = 7 Hz, 2H, meta-(OAr)), 6.26 (t, *J* = 7 Hz, 1H, para-(OAr)), 3.35 (septet, *J* = 7 Hz, 2H, C*H*Me$_2$), 1.12 (d, *J* = 7 Hz, 12H, CH*Me*$_2$), 0.31 (s, 18H, Si(CH_3)$_3$), 0.16 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75.5 MHz, THF-d_8, 20 °C): δ = 160.9 (*i*Pr-*C*(Ar)), 135.7 (O-*C*(Ar)), 131.3 (2C, ring-*C*H), 126.8 (ring-CSi(CH_3)$_3$), 122.7 (ring-CSi(CH_3)$_3$), 122.5 (meta-C(Ar)), 113.3 (para-C(Ar)), 26.5 (*C*H(*i*Pr)), 24.6 (CH3(*i*Pr)), 2.6 (Si(CH_3)$_3$), 1.1 (Si(CH_3)$_3$). Principal IR bands (KBr, cm^{-1}): 2952 (vs, br), 2895 (s), 1587 (w), 1434 (vs), 1345 (m), 1281 (m), 1248 (s, sh), 1093 (m), 1028 (s), 942 (w), 844 (vs, br), 748 (s), 687 (m), 420 (s). Crystals for X-ray structural analysis were grown by slow evaporation of a saturated toluene solution of (Cp^{3Si})Ca(Odipp)(thf)$_2$ at room temperature.

2.5. Synthesis of Cp*Ba(BHT)(thf)

IBa(BHT)(thf)$_3$ (0.82 g, 1.17 mmol) and KCp* (0.20 g, 1.17 mmol) were combined in 20 mL of THF in an Erlenmeyer flask. The white reaction mixture was stirred for 8 h and then set aside to allow the precipitate to settle. The clear supernatant liquid was transferred to another flask with a pipet and the THF was removed under vacuum to a volume of 2 mL; a white solid precipitated as the THF was removed. The remaining THF solution was decanted, and the solid was allowed to dry at ambient pressure, giving 0.51 g (77% yield) of Cp*Ba(BHT)(thf) as an ivory powder. Anal. Calcd. for $C_{29}H_{46}BaO_2$: C, 61.76; H, 8.22; Ba, 24.35. Found: C, 62.44; H, 8.45; Ba, 24.59. ^{1}H NMR (C_6D_6): δ 7.19 (s, 2 H, Ar-*H*); 3.54 (t, *J* = 6.5 Hz, 4 H, α-C_4*H*$_8$O); 2.41 (br s ($\omega_{1/2}$ = 30 Hz), 3 H, Ar-CH_3); 1.79 (br s ($\omega_{1/2}$ = 60 Hz), 15H, Cp-CH_3); 1.52 (br s ($\omega_{1/2}$ = 30 Hz), 18 H, Ar-C(CH_3)$_3$); 1.39 (m, 4 H, β-C_4*H*$_8$O). ^{1}H NMR (THF-d_8): δ 6.61 (br s, 2 H, Ar-*H*); 3.60 (m, 4 H, α-C_4H_8O); 2.04 (br s, 3 H, Ar-CH_3); 1.94 (br, partially resolved doublet, 15 H, Cp-CH_3); 1.76 (m, 4 H, β-C_4*H*$_8$O); 1.35 (br, partially resolved doublet, 18 H, Ar-C(CH_3)$_3$). ^{13}C NMR (THF-d_8): δ 165.7 (Ar-1); 136.2 (Ar-2,6); 125.0 (Ar-3,5); 120.3 (Ar-4); 112.8 (Cp ring-CCH_3); 68.2 (α-C_4H_8O); 35.3 (Ar-*C*(CH_3)$_3$); 31.9 (Ar-C(CH_3)$_3$); 26.4 (β-C_4H_8O); 21.6 (Ar-CH_3); 11.5 (Cp-CH_3). Principal IR bands (KBr, cm^{-1}): 2901 (s, vbr), 2723 (m, sh), 1602 (w), 1548 (w), 1421 (s), 1380 (s), 1343 (m), 1286 (s, br), 1216 (m), 1199 (m), 1035 (s), 886 (s), 818 (s), 800 (s), 667 (w), 577 (w), 498 (m).

2.6. X-ray crystallography

Data collection and structure solution were conducted at the X-ray Crystallographic Laboratory at the University of Minnesota. Details of the data collection and refinement can be found in Section 5.

2.7. Computational details

All calculations were performed with the Gaussian 03W suite of programs [14]. For geometry optimization and energy calculations, the B3PW91 functional, which incorporates Becke's three-parameter exchange functional [15] with the 1991 gradient-corrected correlation functional of Perdew and Wang [16] was used. For C, H, and O, the standard 6-31G(d) basis set was used. For Ca, the TZV basis of Ahlrich [17] was supplemented with five *d* functions (the diffuse *d* (α = 0.013) was not included); [18] for Ba and I, the Stuttgart/Dresden ECPs were employed [19]. Frequency calculations confirmed that structures were either minima on their potential energy surfaces or, in the case of the some barium complexes and solvated calcium species, had relatively minor (<–24 cm^{-1}) imaginary frequencies. In the latter case, structures were reoptimized using an ultrafine grid, which left only positive or very small negative (<–9 cm^{-1}) frequency values. The same grid type (regular or ultrafine) was used for the energy calculations in the separate reactions.

3. Results and discussion

3.1. Synthesis of Cp*Ca(Odipp)(thf)$_3$

The reaction of ICa(Odipp)(thf)$_4$ with one equivalent of KCp* generates the mono(ring)calcium aryloxide complex Cp*Ca(Odipp)(thf)$_3$ (Eq. (1)).

$$\mathrm{ICa(Odipp)(thf)_4 + KCp^* \rightarrow\ Cp^*Ca(Odipp)(thf)_3 + KI\downarrow} \qquad (1)$$

The compound was characterized with spectroscopic methods and X-ray crystallography. It is stable against rearrangement in both THF and aromatic solvents.

3.2. Synthesis of (Cp^{3Si})Ca(Odipp)(thf)$_2$

The stability of Cp*Ca(Odipp)(thf)$_3$ suggests that related [Odipp]$^-$-containing complexes with other Cp′ rings should also be stable. In fact, early attempts to isolate (Cp^{3Si})Ca(Odipp)(thf)$_n$ from the reaction of (Cp^{3Si})CaI(thf) and K[Odipp] were unsuccessful, owing to facile ring loss from calcium (Eq. (2)) [2]. A reinvestigation of the system indicates that the direct reaction of K[Cp^{3Si}] and ICa(Odipp)(thf)$_4$ does form the mono(ring)calcium aryloxide complex (Cp^{3Si})Ca(Odipp)(thf)$_n$, but in low yield (23%; Eq. (3)); the majority of the starting materials remains unreacted. When the same reactants are mixed in toluene, (Cp^{3Si})Ca(Odipp)(thf)$_n$ is produced in 63% yield, but K[Cp^{3Si}] and ICa(Odipp)(thf)$_n$ are also present in the reaction mixture (Eq. (4)).

$$\mathrm{(Cp^{3Si})CaI(thf) + K[Odipp] \xrightarrow{THF} K[Cp^{3Si}] + ICa(Odipp)(thf)_4} \qquad (2)$$

$$\mathrm{ICa(Odipp)(thf)_4 + K[Cp^{3Si}] \xrightarrow{THF} (Cp^{3Si})Ca(Odipp)(thf)_2 + KI\downarrow} \qquad (3)$$

$$\mathrm{(Cp^{3Si})CaI(thf) + K[Odipp]}$$
$$\mathrm{\xrightarrow{toulene} (Cp^{3Si})Ca(Odipp)(thf)_2 + K[Cp^{3Si}]\ + ICa(Odipp)(thf)_{\mathit{n}}} \qquad (4)$$

An effective synthesis for (Cp^{3Si})Ca(Odipp)(thf)$_n$ was found in the reaction of (Cp^{3Si})$_2$Ca [9] with K[Odipp] (Eq. (5)).

$$\mathrm{(Cp^{3Si})_2Ca + K[Odipp] \xrightarrow{THF} (Cp^{3Si})Ca(Odipp)(thf)_2 (81\%) + K[Cp^{3Si}]} \qquad (5)$$

With this approach, the potassium cyclopentadienide is intentionally formed and can subsequently be removed from the desired product by extraction with toluene. (Cp^{3Si})Ca(Odipp)(thf)$_2$ was characterized with spectroscopic methods and X-ray crystallography. The ^{1}H NMR resonances for the [Cp^{3Si}]$^-$ and [Odipp]$^-$ ligands are shifted from those of the corresponding homoleptic compounds [9]. As with the related mono(ring) alkaline-earth iodide (Cp^{3Si})CaI(thf), the aryloxide derivative is resistant to ligand redistribution in both THF and aromatics.

3.3. Synthesis of Cp*Ba(BHT)(thf)

The reaction of IBa(BHT)(thf)$_3$ with one equiv of KCp* generates the off-white mono(ring)barium alkoxide complex Cp*Ba(BHT)(thf) (Eq. (6)). As with the other heteroleptic alkaline-earth alkoxides described above, the mono(ring) complex was isolated by precipitation from small volumes of THF.

$$\mathrm{IBa(BHT)(thf)_3 + KCp^* \xrightarrow{THF} Cp^*Ba(BHT)(thf) + KI\downarrow} \qquad (6)$$

Satisfactory elemental analysis was obtained for the compound, and spectroscopic data (^{1}H and ^{13}C NMR, IR) were consistent with its proposed formulation. Attempts to obtain crystals of

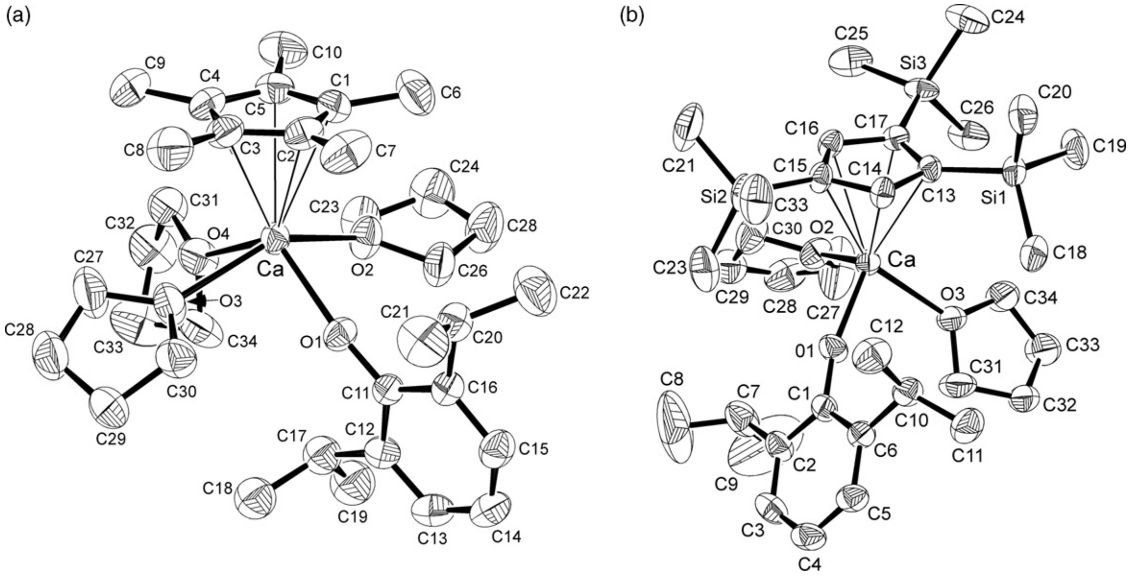

Fig. 1. ORTEP diagrams of Cp*Ca(Odipp)(thf)$_3$ (a) and (Cp^{3Si})Ca(Odipp)(thf)$_2$ (b), with thermal ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

Cp*Ba(BHT)(thf) suitable for an X-ray structural analysis have been unsuccessful.

The proton NMR resonances for the [Cp*]$^-$ and [BHT]$^-$ ligands in both C_6D_6 and THF-d_8 are shifted from those of the corresponding homoleptic compounds [20,21]. Interestingly, the peaks of the ^{1}H NMR spectra in both solvents are substantially broadened; such broadening is especially unusual for the methyl proton resonance of the [Cp*]$^-$ ligand ($\omega_{1/2}$ as high as 60 Hz), which is normally a sharp singlet in related compounds [22,23]. It is possible that the wider lines reflect some aggregation in solution; no broadening of the resonances is observed in the ^{13}C NMR spectra of the complex in THF-d_8, however. Also unusual is the upfield shift observed for the [Cp*]$^-$ resonance in C_6D_6 (1.79 ppm), when compared to the analogous peak for the metallocene Cp*$_2$Ba (1.97 ppm). This contrasts with that of the corresponding mono(ring) complexes of calcium Cp*CaX(thf)$_n$, which have [Cp*]$^-$ resonances shifted downfield from the same peak for Cp*$_2$Ca [7,8].

C_6D_6 and THF-d_8 solutions of isolated Cp*Ba(BHT)(thf) allowed to stand for up to 72 h under ambient conditions do not exhibit any noticeable changes in their ^{1}H NMR spectra. However, removal of toluene from a solution of Cp*Ba(BHT)(thf) under vacuum leads to partial desolvation and subsequent decomposition of the complex in solution, as proton NMR spectra (C_6D_6) now contain resonances for the corresponding homoleptic products Cp*$_2$Ba(thf)$_n$ [23] and Ba(BHT)$_2$(thf)$_n$ [21].

3.4. Solid state structure of Cp*Ca(Odipp)(thf)$_3$·THF

Cp*Ca(Odipp)(thf)$_3$ crystallizes from THF solution as a monomer in which each calcium atom is coordinated by one η^5-Cp* ring, one [Odipp]$^-$ ligand, and three thf molecules; a THF of crystallization is also present in the lattice (Fig. 1a). The Ca–O(aryloxide) bond distance of 2.177(2) Å is comparable to that of 2.1063(16) Å in (Cp^{3Si})Ca(Odipp)(thf)$_2$ when the difference in the radii between 6- and 7-coordinate Ca^{II} (1.00 Å and 1.06 Å, respectively) is considered [24]. The average Ca–C(ring) and the Ca–centroid bond lengths of 2.731(8) Å and 2.45 Å are longer than those in [Cp*CaI(thf)$_2$]$_2$ (2.67(1) Å) [7]. The average Ca–O(thf) distance of 2.443(5) Å is also slightly longer than the average Ca–O(thf) distances of 2.422(6) Å and 2.387(7) Å in [Cp*CaI(thf)$_2$]$_2$.

3.5. Solid state structure of (Cp^{3Si})Ca(Odipp)(thf)$_2$

(Cp^{3Si})Ca(Odipp)(thf)$_2$ crystallizes from THF solution as a monomer in which each calcium atom is coordinated by one η^5-Cp^{3Si} ring, one [Odipp]$^-$ ligand, and two thf molecules (Fig. 1b). The average Ca–C(ring) and the Ca–centroid bond distances of 2.706(4) and 2.42 Å are slightly longer than those in [(Cp^{3Si})CaI(thf)]$_2$ (2.65(4) and 2.36(2) Å), [(C$_5$(*t*Bu)$_3$H$_2$]CaI(thf)$_2$ (2.677(4) and 2.39 Å), and {[(C$_5$(*t*Bu)$_3$H$_2$]CaI(thf)}$_2$ (2.63(2) Å and 2.34 Å) [25]. This lengthening is similar to that observed in Cp*Ca(Odipp)(thf)$_3$. As noted above, the Ca–O(aryloxide) bond distance in (Cp^{3Si})Ca(Odipp)(thf)$_3$ of 2.1063(16) Å is comparable with the analogous distance observed in Cp*Ca(Odipp)(thf)$_3$ when the difference in coordination number-adjusted radii Ca^{II} are considered [24]. The same is true of the average Ca–O(thf) distances (i.e., 2.36(2) Å in (Cp^{3Si})Ca(Odipp)(thf)$_3$; 2.443(5) Å in Cp*Ca(Odipp)(thf)$_3$). The Ca–O(1)–C(1) angle of 166.76(16)° is indistinguishable from the analogous angle in Cp*Ca(Odipp)(thf)$_3$ (166.6(2)°), suggesting that the steric interactions between the aryloxide and thf ligands are similar in the two complexes [12].

3.6. Computational results

The energetics of the exchange reactions of the mono(aryloxide) complexes were studied with model systems and DFT methods. As a first level of approximation, the models were kept as simple as possible (Cp′ = C_5H_5; OAr = OC_6H_5) to remove undue influence from steric effects. The dissociation of CpCaOPh into Cp_2Ca and $Ca(OPh)_2$ is found to be slightly endothermic ($\Delta H^\circ = +3.8\ \mathrm{kcal\,mol^{-1}}$) and nonspontaneous ($\Delta G^\circ = +4.8\ \mathrm{kcal\,mol^{-1}}$) (Fig. 2). The same reaction with barium ($2\ \mathrm{CpBaOPh} \rightleftharpoons \mathrm{Cp_2Ba}$ and $\mathrm{Ba(OPh)_2}$) is essentially thermoneutral ($\Delta H^\circ = -0.7\ \mathrm{kcal\,mol^{-1}}$) but still nonspontaneous ($\Delta G^\circ = +3.9\ \mathrm{kcal\,mol^{-1}}$). Adding a THF molecule to each complex (i.e., $2\ \mathrm{CpMOPh(thf)} \rightleftharpoons \mathrm{Cp_2M(thf)} + \mathrm{M(OPh)_2(thf)}$) leaves the energetics of CpMOPh exchange essentially unaltered ($\Delta H^\circ = +3.8\ \mathrm{kcal\,mol^{-1}}$; $\Delta G^\circ = +3.3\ \mathrm{kcal\,mol^{-1}}$ for M = Ca; $\Delta H^\circ = +1.7\ \mathrm{kcal\,mol^{-1}}$; $\Delta G^\circ = +3.0\ \mathrm{kcal\,mol^{-1}}$ for M = Ba). The energetics of an even more fully solvated calcium system are not appreciably different; for

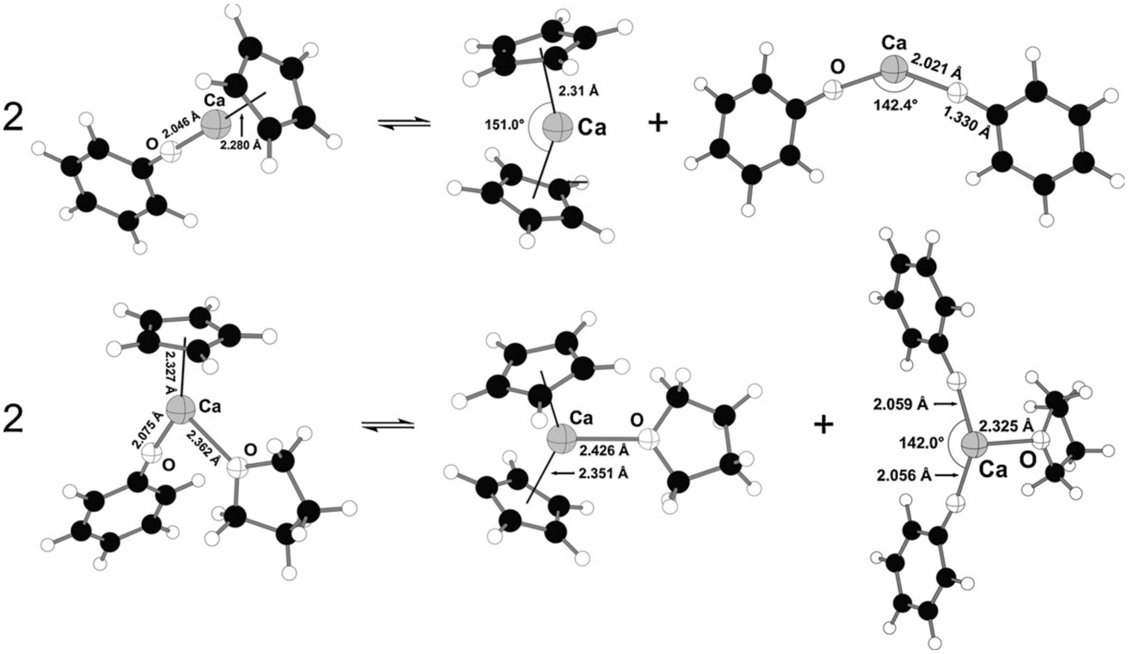

Fig. 2. Calculated structures for the organocalcium species (see the text). The structures of the barium analogues are similar, but with ca. 15% longer M–L bond lengths.

the reaction 2 $CpCaOPh(thf)_2 \rightleftharpoons Cp_2Ca(thf)_2 + Ca(OPh)_2(thf)_2$, $\Delta H^\circ = +3.4$ kcal mol^{-1} and $\Delta G^\circ = +5.6$ kcal mol^{-1}.

Analogous calculations on the 2 $CpCaI(thf)_n \rightleftharpoons Cp_2Ca(thf)_n + CaI_2(thf)_n$ system reveal a more substantial change in the free energy on the addition of THF. For the unsolvated system, $\Delta G^\circ = +15.9$ kcal mol^{-1}; with one THF ligand on each metal center, ΔG° decreases to +9.6 kcal mol^{-1}. The fully solvated reaction 2 $CpCaI(thf)_3 \rightleftharpoons Cp_2Ca(thf)_2 + CaI_2(thf)_4$ is both exothermic ($\Delta H^\circ = -5.5$ kcal mol^{-1}) and spontaneous ($\Delta G^\circ = -7.0$ kcal mol^{-1}), which is consistent with the observation of extensive Schlenk equilibrium in THF solutions of mono(cyclopentadienyl)calcium iodides [7,8]. Although a larger variety of systems need to be studied to extend this point, evidently the addition of solvent has less of an effect on the thermodynamics of the aryloxide systems than on their iodide counterparts.

4. Conclusions

Cyclopentadienyl mono(aryloxide) complexes provide a unique platform for studying the organometallic chemistry of the heavier alkaline-earth metals. Although the use of sterically demanding, “encapsulating” cyclopentadienyl rings can be used to produce $Cp'MX(thf)_n$ complexes that are resistant to rearrangement reactions in solution (this includes X = aryloxide [1]), the present work demonstrates that such bulky rings are not always necessary with aryloxide derivatives. As the bonding in these systems is considered highly polar, the enhanced stability compared to related cyclopentadienyl iodide compounds may be attributed to the superior match of the hard, Lewis acidic metal center with the hard, basic aryloxide ligand rather than to the softer iodide ligand. This phenomenon, also observed in the ability of neutral phosphine oxide ligands to displace a charged iodide ligand from calcium [26], should be an important principle in the design of new organoalkaline-earth systems.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC 690299 and 690300, for $Cp^*Ca(Odipp)(thf)_3 \cdot THF$ and $(Cp^{3Si})Ca(Odipp)(thf)_2$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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