

# Formation and Crystal Structure of a Cationic Mono(cyclopentadienyl) Complex of Calcium, [(C<sub>5</sub>Me<sub>5</sub>)Ca(OPPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>I<sup>-</sup>

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**Summary:** When the neutral Lewis base triphenylphosphine oxide reacts with (C<sub>5</sub>Me<sub>5</sub>)CaI(thf)<sub>2</sub> in THF, the halide is displaced from the calcium to generate the stable cation [(C<sub>5</sub>Me<sub>5</sub>)Ca(OPPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>. The latter exhibits a "piano stool" geometry and displays only modest air sensitivity.

Organometallic compounds of the alkali-metal and alkaline-earth-metal elements are usually designed to maximize the electrostatic interactions between the metal cations and their anionic ligands.<sup>1,2</sup> Consequently, the charges are balanced so that the resulting complexes are neutral; examples of anionic,<sup>3–5</sup> and especially cationic,<sup>6</sup> compounds are much less common. We now have found that a sufficiently basic neutral donor ligand L can successfully substitute for a halide ligand in an organocalcium complex, thereby generating the isolable cationic species [RCaL<sub>n</sub>]<sup>+</sup>. The complex with R = C<sub>5</sub>-Me<sub>5</sub> and L = OPPh<sub>3</sub> (n = 3) possesses substantial air stability and allows the first detailed examination of the structure of a cationic mono(cyclopentadienyl) compound of a heavy alkaline-earth metal.<sup>7</sup>

The reaction of (C<sub>5</sub>Me<sub>5</sub>)CaI(thf)<sub>2</sub><sup>8</sup> prepared in situ with 3 equiv of OPPh<sub>3</sub> in THF at room temperature generates a yellow solution that on removal of the solvent produces the complex [(C<sub>5</sub>Me<sub>5</sub>)Ca(OPPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup>I<sup>-</sup> in high yield.<sup>9</sup> In the solid state, the compound remains unchanged in air for up to 6 h, which is unusually high stability for a mono(cyclopentadienyl)calcium complex; other examples of Cp'CaX complexes (Cp' = C<sub>5</sub>Me<sub>5</sub>, C<sub>5</sub>(t-Pr)<sub>4</sub>H, C<sub>5</sub>(SiMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub>) degrade within minutes in air.<sup>8,10,11</sup> It has good solubility in THF but is only slightly soluble in aromatic hydrocarbons. The <sup>1</sup>H NMR spectrum of the

complex in C<sub>6</sub>D<sub>6</sub> contains a singlet for the pentamethylcyclopentadienyl protons at δ 2.36 and multiplets centered at δ 7.0 and 7.6 from the phenyl ring protons. <sup>1</sup>H NMR spectra of crystalline samples consistently contain a peak at δ 2.17, which may indicate the presence of some (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ca(OPPh<sub>3</sub>)<sub>n</sub>,<sup>12</sup> it might arise from Schlenk-type redistribution (i.e., [MCp']<sup>+</sup> + X<sup>-</sup> ⇌ MCp'X ⇌ 1/2MCp'<sub>2</sub> + 1/2MX<sub>2</sub>).<sup>13</sup> The <sup>31</sup>P NMR shift of δ 32.9 ppm is slightly, but significantly, moved downfield from free OPPh<sub>3</sub> at δ 28.4,<sup>14</sup> which suggests that the complex remains largely intact in solution. The infrared P–O stretch in the solid state at 1178 cm<sup>-1</sup> is reduced by 12 cm<sup>-1</sup> from that in the free ligand (1190 cm<sup>-1</sup>).<sup>15</sup>

Replacement of a halide on a main-group-metal center by a phosphine oxide has been described in other systems,<sup>16,17</sup> and the present results make it clear that OPR<sub>3</sub> can compete effectively with an anionic ligand in binding to alkaline-earth metal centers. In separate experiments, we have found that OPPh<sub>3</sub> will not displace an amido ligand from Ca[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>12</sup> the phosphine oxide's ability to substitute for I<sup>-</sup> and THF but not [C<sub>5</sub>Me<sub>5</sub>]<sup>-</sup> or [N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> on calcium is thus consistent with the approximate pK<sub>b</sub> of the bases (i.e., -12

(9) A solution of [Ca(C<sub>5</sub>Me<sub>5</sub>)I(thf)<sub>2</sub>] was prepared in THF (30 mL) by mixing K[C<sub>5</sub>Me<sub>5</sub>] (0.059 g, 0.34 mmol) and CaI<sub>2</sub> (0.100 g, 0.342 mmol). After the mixture had been stirred for 2 h, the solution was filtered to remove precipitated KI, and solid triphenylphosphine oxide (0.283 g, 1.02 mmol) was added, upon which the solution immediately became yellow. The solution was then evaporated under reduced pressure. The crude product was recrystallized from toluene/THF. [Ca(C<sub>5</sub>Me<sub>5</sub>)OPPh<sub>3</sub>]<sup>+</sup>I<sup>-</sup> was obtained as yellow blocks, which contained 0.5 equiv of toluene per calcium (0.32 g, 80%), mp 169–173 °C. Anal. Calcd for C<sub>67.5</sub>H<sub>64</sub>CaIO<sub>3</sub>P<sub>3</sub>: C, 68.52; H, 5.45. Found: C, 68.05; H, 5.64. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C): δ 2.10 (s, toluene), 2.34 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 6.89–7.08 (br m, OPPh<sub>3</sub> and toluene), 7.59–7.65 (br m, 18 H, OPPh<sub>3</sub>). <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C): δ 13.1 (C<sub>5</sub>Me<sub>5</sub>), 21.4 (toluene), 111.0 (C<sub>5</sub>Me<sub>5</sub>), 125.6 (toluene), 128.5 (d, J = 0.2 Hz, OPPh<sub>3</sub>), 131.7 (d, J = 0.03 Hz, OPPh<sub>3</sub>), 132.4 (d, J = 0.1 Hz, OPPh<sub>3</sub>), 137.8 (toluene). <sup>31</sup>P NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C): δ 32.9 (s, OPPh<sub>3</sub>). Principal IR bands (KBr, cm<sup>-1</sup>): 2911 (s), 2846 (s), 1589 (m, sh), 1484 (m, sh), 1436 (s, sh), 1313 (w, sh), 1178 (s, br), 1119 (s, sh), 1092 (m), 1073 (m).

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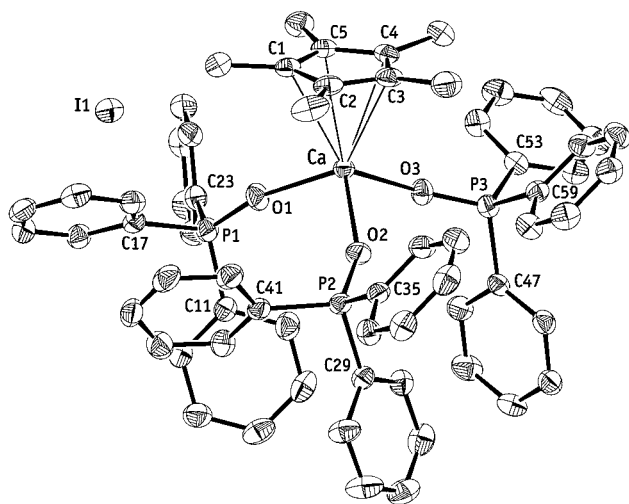
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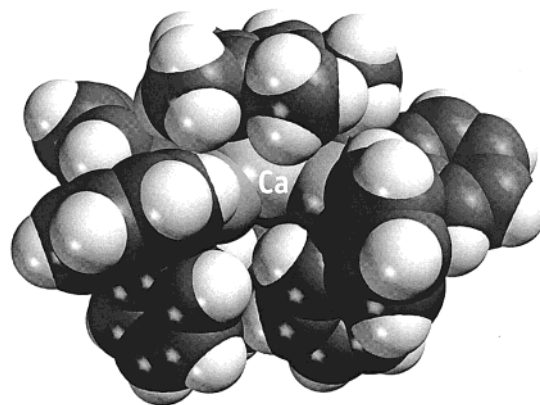
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**Figure 1.** ORTEP plot of  $[(C_5Me_5)Ca(OPPh_3)_3]^+I^- \cdot 1/2C_7H_8$ , with ellipsoids drawn at the 50% probability level. For clarity, neither hydrogen atoms nor the lattice toluene are shown. Selected bond distances (Å) and angles (deg): Ca–C1, 2.694(2); Ca–C2, 2.683(2); Ca–C3, 2.677(2); Ca–C4, 2.687(2); Ca–C5, 2.681(2); Ca–O1, 2.254(2); Ca–O2, 2.282(1); Ca–O3, 2.300(2); P1–O1, 1.506(2); P2–O2, 1.510(2); P3–O3, 1.508(2); (C<sub>5</sub> ring centroid)–Ca–O1 = 114.6, (C<sub>5</sub> ring centroid)–Ca–O2 = 124.2, (C<sub>5</sub> ring centroid)–Ca–O3 = 116.1.

$[(C_5Me_5)]^- < -2$   $[(N(SiMe_3)_2)]^- < \sim 8$   $(OPPh_3) < \sim 12$   $(THF) < \sim 24$   $(I^-)$ .<sup>18</sup>

The solid-state structure of  $[(C_5Me_5)Ca(OPPh_3)_3]^+I^-$  was obtained on a yellow crystal slowly grown from THF/toluene solution.<sup>19</sup> The complex crystallizes as a monomeric species with the calcium coordinated by an  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ring and the three triphenylphosphine oxide ligands in a classic “piano stool” arrangement (Figure 1). The C<sub>5</sub> ring plane and the plane defined by the three oxygen atoms are almost parallel, with a dihedral angle of 6.1°. The average Ca–C distance of 2.684(4) Å is longer than that usually observed in neutral complexes with a formally six-coordinate Ca<sup>2+</sup> center (cf. 2.63(2) Å in  $[C_5(t-Bu)_3H_2]CaI(thf)_2$ <sup>20</sup>) and is similar to that found in seven-coordinate species (e.g., 2.678(9) Å in  $[1,3-(SiMe_3)_2C_5H_3]_2Ca(thf)$ <sup>21,22</sup> and 2.67(1) Å in  $[(C_5Me_5)-Ca(\mu-I)(thf)_2]_2$ <sup>8</sup>). The Ca–O distances range from 2.254-



**Figure 2.** Space-filling drawing of the  $[Ca(C_5Me_5)(OPPh_3)_3]^+$  cation, with the most exposed portion of the calcium toward the viewer. The C<sub>5</sub>Me<sub>5</sub> ring is at top.

(2) to 2.300(2) Å, and the Ca–O–P angles are bent from 150.99(9) to 166.4(1)°. There is no relationship between the Ca–O–P angles and the P–O bond lengths; the latter are indistinguishable (average 1.508(3) Å) and are slightly longer than in free OPPh<sub>3</sub> (1.483(2) Å).<sup>23</sup> The iodide anion is completely removed from the coordination sphere of the calcium, with its closest contact to a phenyl carbon atom at 4.02 Å. As with the decaisopropylated group 2 metallocenes  $[(i-Pr)_5C_5]_2Ae$  (Ae = Ca, Sr, Ba),<sup>24</sup> the reduced air sensitivity of the cation evidently stems from the heavy shielding of the metal center by the ligands (Figure 2).

Density functional theory calculations<sup>25</sup> on the model compound  $[(C_5H_5)Ca(OPMe_3)_3]^+$  were completed to evaluate the extent of interaction between the Ca<sup>2+</sup> center and the cyclopentadienyl and OPPh<sub>3</sub> ligands. In the optimized structure of the model, the average Ca–C and Ca–O distances (2.670 and 2.276 Å, respectively) reproduce the experimental values well (2.684(4) and 2.279(3) Å). Considering that the calcium in the model is much less sterically encumbered than in the experimentally known complex, the lengthened Ca–Cp' distance in the latter is likely a consequence of electron donation from the OPPh<sub>3</sub> ligands, although the degree of charge transfer is difficult to quantify. The calculated NPA charge<sup>29,30</sup> on the calcium center is +1.78, which would suggest that the bonding in the molecule is still largely ionic. Consistent with this, the charge on the Cp<sup>-</sup> ligand is –0.90 and that on each OPMe<sub>3</sub> group is only +0.04 (collectively +0.12). The charge on the oxygen atoms themselves is –1.20, however, which is increased somewhat from that calculated for the free ligand (–1.08) and is a sign of the importance of the  $O^{\delta-} \equiv P^{\delta+}R_3$  resonance form.

In summary, we have found that consideration must be given to the relative Lewis basicities of ligands, rather than simply to their nominal charge, in the design of cationic organocalcium compounds. The use of phosphine oxide ligands may provide a general means

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(19) Crystals of  $[(C_5Me_5)Ca(OPPh_3)_3]^+I^- \cdot 1/2C_7H_8$  are triclinic, space group P1, with  $a = 11.0960(8)$  Å,  $b = 12.3103(9)$  Å,  $c = 22.466(2)$  Å,  $\alpha = 83.514(2)^\circ$ ,  $\beta = 76.376(2)^\circ$ ,  $\gamma = 78.521(2)^\circ$ ,  $V = 2915.7(4)$  Å<sup>3</sup>,  $Z = 2$ , and  $\rho_{\text{calcd}} = 1.348$  g cm<sup>-3</sup> for  $f_w = 1183.08$ . Refinement of 12 878 reflections collected at the University of Minnesota at 173(2) K with  $I > 2.0\sigma(I)$  led to residuals of  $R(F^2) = 0.0352$  and  $R_w(F^2) = 0.0655$ . A molecule of toluene was found disordered on an inversion center; thus, it is present half as often as the calcium complex.

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for synthesizing  $[\text{Cp}'\text{AeL}_n]^+$  species, allowing the reactions of heavy group 2 cationic complexes, including their potential to serve as Lewis acid catalysts, to be studied more fully.

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**Supporting Information Available:** Tables of atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for  $[(\text{C}_5\text{Me}_5)\text{Ca}(\text{OPPh}_3)_3]^+\text{I}^- \cdot 1/2\text{C}_7\text{H}_8$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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