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COMMUNICATION

CYCLOPENTADIENYL RING METATHESIS WITH BIS(PENTAMETHYLCYCLOPENTADIENYL)CALCIUM AS A ROUTE TO MIXED RING ORGANOLANTHANIDE COMPLEXES; THE CRYSTAL STRUCTURE OF $(C_5Me_5)_2Nd(C_5H_5)$

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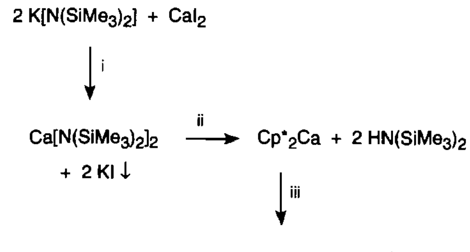
Abstract—Bis(pentamethylcyclopentadienyl)calcium, $(C_5Me_5)_2Ca$, can be made by the reaction of $Ca[N(SiMe_3)_2]_2$ with C_5Me_5H in toluene. It undergoes cyclopentadienyl ring metathesis with tris(cyclopentadienyl)lanthanide complexes, Cp_3Ln (Ln = La, Nd, Sm) in toluene to generate the mixed ring complexes $(C_5Me_5)_2LnCp$. The X-ray crystal structure of $(C_5Me_5)_2NdCp$ shows that the complex is a sterically crowded monomer with η^5-C_5Me_5 and Cp rings. The average Nd—C distances for both the C_5Me_5 and Cp rings are 2.76–2.79 Å.

Most cyclopentadienyl lanthanide complexes, including the intensively studied $Cp'_3Ln(ether)_n$ and $Cp'_2LnX(ether)_n$ species, contain only a single type of ring.[1] This is largely a consequence of their method of synthesis, which usually involves the metathetical reaction of alkali metal cyclopentadienides with lanthanide chlorides in ethers. Mixed cyclopentadienyl ring species (e.g. Cp'_2LnCp, $Cp'LnCp_2$) so far have proven inaccessible by halide metathesis; only one example has been crystallographically characterized (Cp^*_2SmCp; $Cp^* = C_5Me_5$), and it was formed by a redox process.[2] Such heteroleptic complexes are interesting synthetic targets, however, because they provide a means of probing the effects of various metal/ligand combinations on organolanthanide structure and reactivity. We report here a facile route to mixed ring organolanthanide complexes by *cyclopentadienyl ring metathesis*, using the organocalcium compound Cp^*_2Ca.

The originally reported synthesis of Cp^*_2Ca involved the reaction of NaCp* or KCp* and CaI_2 in Et_2O to form $Cp^*_2Ca(OEt_2)$, and the subsequent removal of the ether by the "toluene-reflux" method.[3,4] We have found that this synthesis is more effectively accomplished using the sequence of reactions given in Scheme 1. $Ca[N(SiMe_3)_2]_2$ was prepared by adopting the metathetical procedure developed by Boncella for the synthesis of $Ba[N(SiMe_3)_2]_2$.[5] This method provides a % yield (86%) comparable to that from the direct reaction of Ca and $Sn[N(SiMe_3)_2]_2$ described in the literature.[6] Subsequent reaction of $Ca[N(SiMe_3)_2]_2$ with Cp*H in toluene followed by sublimation or recrystalliz-



Scheme 1. Reagents and conditions: (i) Et_2O, overnight, 86% yield; (ii) 2 equiv. of HCp*, toluene, overnight, 76% yield; (iii) 1 equiv. Cp_3Ln, toluene, overnight, >50% yield. All temperatures *ca* 30°C.

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ation from hexane gives Cp$^*_2$Ca in good yield.† The reaction sequence can be readily scaled up to produce multigram quantities of the metallocene.

Bis(pentamethylcyclopentadienyl)calcium reacts in toluene with tris(cyclopentadienyl)lanthanides (Ln = La, Nd, Sm) to form Cp$^*_2$LnCp complexes in moderate to high yields (Scheme 1).‡ Cp$^*_2$SmCp has been reported before, although not by this route;[2] the other complexes are new. The driving force for the reaction is the precipitation of $\mathrm{Cp_2Ca}$, which is insoluble in toluene.[7] The importance of $\mathrm{Cp_2Ca}$ precipitation as a driving force for the reaction is emphasized by the absence of ring metathesis between Cp$^*_2$Mg and $\mathrm{Cp_3Ln}$, presumably because $\mathrm{Cp_2Mg}$ is soluble in hydrocarbons.

Attempts to use an excess of Cp$^*_2$Ca to form Cp$^*_3$Ln complexes[8] (eq. 1) were not successful; the reactions stop with Cp$^*_2$LnCp.

$$3\,\mathrm{Cp}^*_2\mathrm{Ca}+2\,\mathrm{Cp}_3\mathrm{Ln}\overset{\text{toluene}}{\not\longrightarrow}2\,\mathrm{Cp}^*_3\mathrm{Ln}+3\,\mathrm{Cp}_2\mathrm{Ca}\downarrow \qquad (1)$$

The failure of Cp$^*_2$LnCp to react with Cp$^*_2$Ca is probably a consequence of steric crowding at the lanthanide center; there is apparently not enough room for a third Cp* ring to approach closely enough to displace the remaining Cp ligand.

Cp$^*_2$NdCp forms photochromic crystals (green in artificial light, salmon in sunlight). The structure of the complex was determined by X-ray crystallography on a single crystal grown from hexane, a view of which is presented in Fig. 1.§ The compound consists of monomeric units with η^5-Cp* and Cp rings, and is isostructural with the samarium analog Cp$^*_2$SmCp.[2] The average Nd—C distances for both the Cp* and Cp rings (2.76–2.79 Å) are the same within error, and are comparable to the distances observed in other (cyclopentadienyl) neodymium complexes (*cf* 2.79(1) Å in $\mathrm{[(MeCp)_3Nd]_4}$,[9] and 2.76(1) Å in Cp$^*_2$NdCH(SiMe$_3$)$_2$[10]). The (Cp* centroid)—Nd—(Cp* centroid) angle of 127.3° is indistinguishable from the analogous value in Cp$^*_2$SmCp (127.0°);[2] both are small for a Cp$^*_2$LnX complex (typical values are 135–140°[11]), and are a consequence of the steric crowding generated by the presence of the η^5-Cp ring on the same metal as the two bulky Cp* rings. The Cp* rings are almost perfectly staggered (twist angle = 32.7°), also a consequence of steric congestion.

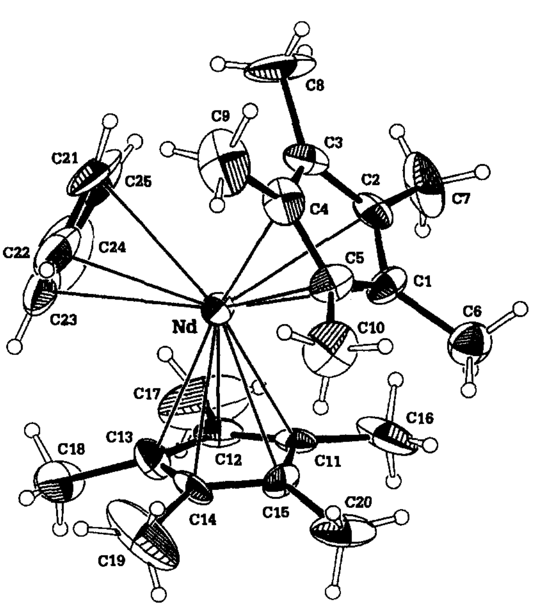

Fig. 1. ORTEP view of Cp$^*_2$NdCp with thermal ellipsoids at the 30% probability level and hydrogen atoms at an arbitrary size. Selected bond distances and angles are: (av.) Nd—Cp*(1) (C1—C5) = 2.79(2) Å, (av.) Nd—Cp*(2) (C11—C15) = 2.76(2), (av.) Nd—Cp (C21—C25) = 2.77(3) Å, (Cp*(1) centroid)—Nd—(Cp*(2) centroid) = 127.3°, (Cp*(1) centroid)—Nd—(Cp centroid) = 116.8°, (Cp*(2) centroid)—Nd—(Cp centroid) = 116.0°, Nd— (plane of ring centroids) = 0.096 Å.

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† All reactions were performed under nitrogen. A toluene solution of $\mathrm{Ca[N(SiMe_3)_2]_2}$ (0.20 g, 0.55 mmol) was stirred overnight at room temperature with $\mathrm{C_5Me_5H}$ (0.15 g, 1.1 mmol). Removal of the solvent *in vacuo* followed by washing with a minimal amount of hexane gave Cp$^*_2$Ca (0.13 g, 76% yield), identified by its ^{1}H NMR spectrum.

‡ In a typical preparation, Cp$^*_2$Ca (0.307 g, 0.989 mmol) and $\mathrm{Cp_3Nd}$ (0.222 g, 0.654 mmol) were added to toluene (30 cm^3) and the mixture stirred for 12 h. The solution was then filtered and the filtrate evaporated to leave bright green Cp$^*_2$NdCp (yield = 0.164 g, 52%). ^{1}H NMR data (300 MHz, $\mathrm{C_6D_6}$): δ 8.15 (s, $\mathrm{C_5Me_5}$), −1.29 (s, $\mathrm{C_5H_5}$). Found: C, 62.6; H, 7.2. Calc. for $\mathrm{C_{25}H_{35}Nd}$: C, 62.6; H, 7.3%. IR (KBr pellet): 2917 (s), 1685 (w), 1654 (s), 1560 (s), 1541 (w), 1508 (w), 1458 (m), 1240 (w), 1085 (s), 770 (s) cm^{-1}. The analogous compounds with La and Sm were formed similarly.

§ *Crystal data* for Cp$^*_2$NdCp. $\mathrm{C_{25}H_{35}Nd}$: M_r = 479.79, monoclinic, space group $P2_1/n$, a = 9.374(3), b = 14.238 (7), c = 17.429(7), β = 102.11(3)°, V = 2274(2) Å^3, Z = 4, D_{calc} = 1.401 g cm^{-3}; structure solution and refinement on the basis of 1905 reflections with $F > 3\sigma(F)$ (Mo-$K\alpha$, λ = 0.71069 Å, 20°C), $R(F)$ = 0.062, $R_w(F)$ = 0.084 (235 variables). Unresolvable disorder was evident in the $\mathrm{C_5H_5}$ ring, causing larger than normal variation in the Nd-ring distances; the $\mathrm{C_5Me_5}$ rings were unaffected by the disorder. Tables of atomic coordinates, thermal parameters, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

The usefulness of Cp_2^*Ca in these cyclopentadienyl ring metatheses stems from its hydrocarbon solubility (aromatics and alkanes) in contrast to that of the parent Cp_2Ca complex (hydrocarbon insoluble). Thus rather than relying on the insolubility of a metal *halide*, these reactions depend on the insolubility of a *metallocene* for their effectiveness. This suggests roles for organo-alkaline-earth reagents where it is important to avoid halide complexation and the formation of "-ate" complexes (e.g. $M^+[Cp_2LnX_2]^-$).[12,13]

In preliminary work, we have found that Cp_2^*Ca can efficiently displace cyclopentadienyl rings from *p*-block metallocenes such as Cp_2Sn and Cp_2Pb.[14] We are currently exploring the extent of applicability of heavy alkaline-earth compounds as cyclopentadienyl metathesis reagents with other organo-*p*-, *d*- and *f*-block metal complexes.

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