Mono-, bis- and tris(t-butylcyclopentadienyl)lanthanoid complexes

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(Received September 18th, 1987; in revised form May 30th, 1988)

Abstract

Metathetical reactions of lanthanoid chlorides (La, Sm and Lu) with one, two and three equivalents of sodium t-butylcyclopentadienide allow the isolation of mono-, bis- and tris(t-butylcyclopentadienyl) lanthanoid complexes. Except for the amount of THF coordinated to the metal center, the synthetic chemistry of these complexes exactly parallels that observed for the parent unsubstituted Cp derivatives.

Attempts to exploit the increased steric bulk of the t-butyl substituted Cp ring in the synthesis of stable dialkyls of lutetium failed to yield isolable complexes.

Introduction

The organometallic chemistry of the lanthanoid elements is dominated by the cyclopentadienide derivatives of these metals. The first such examples of this class, the lanthanoid tris(cyclopentadienides), $LnCp_3$, now known for all of the lanthanoids, were synthesized by Birmingham and Wilkinson in 1954 [1,2]. The two remaining members of this general family of compounds, $[Cp_2LnCl]_2$ [3] and $CpLnCl_2 \cdot 3THF$ [4], were synthesized by Dubeck and co-workers several years later. Analogues of Cp_3Ln and $[Cp_2LnCl]_2$ have also been reported using the methylcyclopentadienide ligand [3, 5–10]. However, unlike the homoleptic $LnCp_3$ and $Ln(MeCp)_3$, heteroleptic mono- and bis-ring substituted compounds could not be synthesized for any early lanthanoid larger than samarium. Consequently, most recent synthetic efforts by researchers who wish to probe the chemistry of all members of these compound classes as a function of lanthanoid metal have focussed on stabilizing early lanthanoid derivatives of these complexes by incorporating bulky substituents on the cyclopentadienyl ring to disfavor ligand redistribution reactions.

In the first successful synthetic report using this strategy, Wayda and Evans [11], and Tilley and Andersen [12] working with the C_5Me_5 ligand were independently

able to synthesize Nd and La, Pr and Nd derivatives respectively incorporating two C_5Me_5 rings in the metal coordination sphere. Related complexes have also been reported by Watson [13] and Schumann [14]. Recent work by Bruno et al. [15] has produced mono- and bis-C_5Me_5 derivatives of La and Ce. In related work, Lappert and co-workers have utilized the bulky disubstituted silyl(cyclopentadienide) ligand, $(Me_3Si)_2C_5H_3$, to stabilize early lanthanoid derivatives of the bis(cyclopentadienides) [16]. Other approaches have used more exotic ring-substituted derivatives such as polymethylene-linked Cp rings (to yield early lanthanoid bis-ring derivatives) [17] and the extremely sterically hindered heptamethylindenide ligand (which has allowed Tsutsui and co-workers to isolate mono-, bis- and tris-ring derivatives of this ligand for the early lanthanoid Ce) [18].

Extending this generic line of investigation, we now report our preliminary studies on the utility of the t-butylcyclopentadienide ligand in synthesizing early, middle and late mono-, bis- and tris(t-butylcyclopentadienyl) lanthanoid complexes. We also report our unsuccessful attempts to exploit the greater steric saturation of $(t\text{-BuCp})LuCl_2 \cdot 2THF$ in the synthesis of stable dialkyls of this metal.

Results and discussion

All compounds were synthesized by the metathetical reaction of the anhydrous lanthanoid chlorides with one, two or three equivalents of sodium t-butylcyclopentadienide in THF at ambient temperature. Complexes were characterized by infrared and ^1H NMR spectroscopy and complexometric analysis [19*]. Syntheses were confined to NMR-accessible metal complexes (La, Sm and Lu) which allowed the effect of central metal ion size on product composition and identity to be probed systematically.

Our studies indicate that the synthetic effect of mono substitution of the Cp ring by a t-butyl group is minimal. Using this ligand, it still proves impossible to extend the synthesis of mono- and bis(cyclopentadienide) derivatives to the early lanthanoids.

The general properties of the new compounds parallel those of the parent cyclopentadienides. All complexes are characteristically colored (white or off-white for La and Lu-containing species and yellow or orange for the Sm compounds). They are freely soluble in ethereal solvents (Et_2O and THF) and moderately soluble in aromatic solvents (with the exception of $(t\text{-BuCp})LuCl_2 \cdot 2THF$ which, like the parent cyclopentadienide dichloride, is only soluble in THF). All complexes are insoluble in alkane solvents.

We observe chemical behavior which closely parallels that of the parent Cp complexes. Three exceptions warrant discussion.

For the smallest lanthanoid, lutetium, the metal is apparently too small to permit three bulky t-BuCp groups to coordinate. Syntheses directed toward the isolation of the expected $(t\text{-BuCp})_3Lu$ yield only the bis(cyclopentadienide) derivative, $[(t\text{-BuCp})_2LuCl]_2$. The synthesis of the mono(cyclopentadienide), $(t\text{-BuCp})LuCl_2$, proceeds as expected but is isolated as the bis- rather than the tris(tetrahydrofuranate) reflecting the effect of the greater steric bulk of t-BuCp on the isolated complex chemistry.

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* Reference number with asterisk indicates a note in the list of references.

For samarium, approximately in the middle of the series (on the basis of size), the metal is large enough to allow the isolation of $(t\text{-BuCp})_3\text{Sm}$ and $[(t\text{-BuCp})_2\text{SmCl}]_2$, but too large to support the stable coordination of only one ligand without ligand redistribution.

For lanthanum, as is the case in the unsubstituted systems, $(t\text{-BuCp})_3\text{La(THF)}$ can be isolated but the corresponding bis(cyclopentadienide) complex cannot.

These observations demonstrate a subtle synthetic point which merits comment, namely the influence of steric saturation on the amount of solvate THF retained by isolated complexes. In the parent Cp systems, metathetical syntheses which are conducted in THF usually yield the tris(cyclopentadienides) as the mono(tetrahydrofuranates) [1,2]. In contrast, we observe size dependent behavior for the t-butylcyclopentadienides. For the largest lanthanoid, lanthanum, the mono-THF adduct is indeed isolated. However, with samarium, as the metal size decreases and steric saturation increases, we isolate the unsolvated tris(cyclopentadienide) complex. In this regard, it should be noted that all work-ups, including removal of solvent to dryness were conducted under identical reduced pressure conditions (ambient temperature, $\sim 10^{-2}$ torr). Hence, it is assumed that the observed effects are not influenced by variations in product work-up procedure (although it is conceivable that a very weak THF adduct of the lanthanum complex would be destroyed by these mild handling conditions). Steric effects also presumably dictate the isolation of the bis(tetrahydrofuranate) of $(t\text{-BuCp})\text{LuCl}_2$ over the more congested tris(tetrahydrofuranate). We expect that other subtle steric effects will be observed as we continue our structural investigations on these and related compounds. We note that such effects have ample precedent in the chemistry of predominantly ionic Lewis-acidic organolanthanoid complexes [20*].

The synthesis of the more sterically saturated $t\text{-BuCpLuCl}_2 \cdot 2\text{THF}$ (as compared to $\text{CpLuCl}_2 \cdot 3\text{THF}$) allowed us to return to a problem which has interested us for sometime; the synthesis of stable dialkyls of lanthanoid cyclopentadienides. In earlier work, we had found that reaction of the parent Cp complex, $\text{CpLuCl}_2 \cdot 3\text{THF}$, with a variety of alkyl and heteroatom ligands failed to yield isolable dialkyl complexes (reactions were observed, but the only complexes isolated were ligand redistribution products which did not contain Cp) [21]. Unfortunately, the reaction chemistry of $t\text{-BuCpLuCl}_2 \cdot 2\text{THF}$ again mirrors the parent Cp complexes. Even for the bulky alkyls $\text{-C}\equiv\text{C-t-C}_4\text{H}_9$ and $\text{-CH(SiMe}_3)_2$, no isolable dialkyls were formed.

Conclusions

Metathetical reactions of lanthanoid chlorides with one, two and three equivalents of sodium t-butylcyclopentadienide allow the isolation of mono-, bis- and tris(t-butylcyclopentadienyl) lanthanoid complexes. Subtle steric effects distinguish these compounds from the parent Cp complexes, but, on the whole, their synthetic chemistry closely parallels the unsubstituted class of compounds. The increased bulk of the Cp ring does not allow the isolation of stable dialkyls of these materials.

Experimental

General

The compounds described are extremely air and moisture sensitive. Therefore, the syntheses and manipulations involving these materials are conducted using

standard Schlenk and high vacuum line techniques or are performed in the recirculated argon atmosphere of a Vacuum Atmosphere HE-43 Dri-Lab.

Materials

Hydrated rare earth chlorides, $LnCl_3 \cdot 6H_2O$ were obtained from Research Chemicals, Phoenix, Arizona and were dehydrated by the method of Taylor and Carter [22]. THF, toluene (both Aldrich Sure-Seal grade) and Et_2O (Mallinckrodt) were distilled from sodium benzophenone ketyl under argon. Pentane (Aldrich Sure-Seal grade) was distilled from sodium benzophenone ketyl (stabilized by the addition of tetraglyme) under argon. NMR solvents (benzene-d_6 and THF-d_8) were dried over sodium benzophenone ketyl, degassed by vacuum transfer and stored over activated 4 Å sieves in the dry box. $(t-C_4H_9)C_5H_5$ (t-BuCp) was prepared according to literature procedures [23]. Na-t-BuCp was prepared by the reaction of t-BuCpH with dry NaH in THF.

Measurements

Infrared spectra were recorded on a Nicolet 5DX-FTIR with solid samples that had been mulled with dry, degassed Nujol and sandwiched between 25×4 mm NaCl plates protected from the atmosphere in an O-ring sealed Barnes Presslok holder. ^1H NMR spectra were recorded on a JEOL FX-90Q with all shifts referenced to the residual protons contained in the deuterated solvents (δ 7.15 for benzene-d_6 and 3.58 for THF-d_8). Complexometric analyses were conducted as previously described [24].

La(t-BuCp)₃(THF)

To a stirred slurry of anhydrous $LaCl_3$ in THF (0.5256 g, 2.14 mM) was slowly added a clear light pink solution of Na-t-BuCp dissolved in THF (0.9272 g, 6.43 mM). As the addition proceeded, no change was noted in the appearance of the solution. After addition was completed, the cloudy solution was stirred for 24 h at ambient temperature. At the end of this time, a fine white precipitate was observed and the supernatant liquid had assumed a clear light gold color. The precipitated NaCl was then separated by gravity filtration of the reaction mixture through a fine porosity frit. Removal of solvent from the clear gold filtrate by rotary evaporation yielded 0.8375 g (68% yield) of free-flowing light yellow analytically pure La(t-BuCp)₃(THF). Anal. Found: La, 23.62. $LaC_{31}H_{47}O$ calc: La, 24.17%. ^1H NMR (benzene-d_6): δ 6.05 (m, 12H, $t-C_4H_9-C_5H_4$), 3.56 (m, 4H, α-THF), 1.41 (m, 4H, β-THF), 1.19 (s, 27H, $t-C_4H_9-C_5H_4$). IR (Nujol, cm^{-1}) 1359s, 1278m, 1200w, 1156m, 1040s, 1025s, 915m, 868m, 818s, 746s, 668m.

Sm(t-BuCp)₃

To a stirred slurry of anhydrous $SmCl_3$ in THF (0.5135 g, 2.00 mM) was slowly added a clear light pink solution of Na-t-BuCp dissolved in THF (0.8652 g, 6.00 mM). Addition of the first few drops of the cyclopentadienide solution produced an intense yellow color. Continued additon produced a bright orange-colored reaction mixture. No further change in appearance was observed upon completion of addition. After stirring overnight at ambient temperature, NaCl was separated from the reaction mixture by gravity filtration through a fine porosity frit. Evaporation of solvent from the resultant bright clear orange filtrate produced a thick viscous

sludge of orange product. Addition of pentane followed by evaporation of the solution to dryness produced 0.8660 g of free-flowing bright orange analytically pure Sm(t-BuCp)$_3$ in 84% yield. Anal. Found: Sm, 27.65. SmC$_{27}$H$_{39}$ calc: Sm, 29.25%. ^{1}H NMR (benzene-d_6): δ 21.46 (br s, 6H, t-C$_4$H$_9$-C$_5$H$_4$), 13.91 (br s, 6H, t-C$_4$H$_9$-C$_5$H$_4$), −3.82 (s, 27H, t-C$_4$H$_9$-C$_5$H$_4$). No evidence for coordinated THF was seen in either the ^{1}H NMR or the IR spectrum. IR (Nujol, cm^{-1}) 1359s, 1278m, 1200w, 1156m, 1043m, 1018w, 971w, 915m, 828s, 759s, 671m.

[(t-BuCp)$_2$SmCl]$_2$

To a stirred slurry of anhydrous SmCl$_3$ in THF (0.8596 g, 3.34 mM) was slowly added a clear light pink solution of Na-t-BuCp dissolved in THF (0.9656 g, 6.69 mM). As in the previous reaction, addition of the cyclopentadienide solution produced an immediate yellow color. This color persisted until toward the end of the addition when the solution assumed a slight orange cast. After stirring overnight at ambient temperature, precipitated NaCl was removed from the reaction mixture by careful gravity filtration through a fine porosity frit. Removal of solvent from the resultant clear yellow-orange filtrate produced a fine free-flowing orange-yellow powder. The orange cast of the product suggested and the ^{1}H NMR spectrum of the material revealed that it was contaminated with a small amount of Sm(t-BuCp)$_3$. Since the latter is much more soluble in pentane than the title complex, it was easily removed by washing the crude product several times with pentane. This allowed the isolation of analytically pure bright yellow [(t-BuCp)$_2$SmCl]$_2$ in 67% yield. Anal. Found: Sm, 34.91. SmC$_{18}$H$_{26}$Cl calc: Sm, 35.11%. ^{1}H NMR (benzene-d_6): 17.46 (br s, 4H, t-C$_4$H$_9$-C$_5$H$_4$), 12.31 (br s, 4H, t-C$_4$H$_9$-C$_5$H$_4$), −1.89 (s, 18H, t-C$_4$H$_9$-C$_5$H$_4$). IR (Nujol, cm^{-1}) 1362s, 1275m, 1206m, 1190w, 1156m, 1046m, 1037m, 915m, 834s, 768s, 681s.

[(t-BuCp)$_2$LuCl]$_2$

To a stirred slurry of anhydrous LuCl$_3$ in THF (0.6766 g, 2.41 mM) was slowly added a clear light pink solution of Na-t-BuCp dissolved in THF (0.6935 g, 4.81 mM). After several drops of the cyclopentadienide solution had been added, the LuCl$_3$ was observed to disappear and the solution assumed a light champagne-colored cast. As addition proceeded, the solution clouded, but an observable precipitate was not produced. Continued additon of the reagent solution produced no further change. The solution was then stirred overnight at ambient temperature. Evaporation of the solvent from the cloudy ginger-ale colored solution produced a free-flowing light yellow powder. Extraction of this crude product with pentane (or Et$_2$O) quantitatively left behind NaCl. Removal of solvent from the clear ginger-ale colored extract resulted in the isolation of 0.779 g (72% yield) of cream white, analytically pure [(t-BuCp)$_2$LuCl]$_2$. Anal. Found: Lu, 37.65. LuC$_{18}$H$_{26}$C calc: Lu, 38.64%. ^{1}H NMR (benzene-d_6): δ 6.44 (m, 4H, t-C$_4$H$_9$-C$_5$H$_4$), 6.14 (m, 4H, t-C$_4$H$_9$-C$_5$H$_4$), 1.28 (s, 18H, t-C$_4$H$_9$-C$_6$H$_4$). IR (Nujol, cm^{-1}) 1359s, 1275m, 1200m, 1156m, 1040m, 1021m, 918m, 831s, 781s, 675s.

(t-BuCp)LuCl$_2$ · 2THF

To a stirred slurry of anhydrous LuCl$_3$ in THF (2.0393 g, 7.25 mM) was slowly added a clear light pink solution of Na-t-BuCp dissolved in THF (1.0451 g, 7.25 mM). During the addition, the reaction mixture became increasingly cloudy. After addition was complete, the solution had assumed a cloudy light yellow cast. The

solution was then stirred overnight at ambient temperature. At the end of this time, a precipitate remained suspended in the solution. Concentration on the rotary evaporator and cooling of the reaction solution resulted in the deposition of a fine white crystalline mass which could be isolated from the cloudy supernatant by quick filtration. A first crop of white analytically pure $(t\text{-BuCp})LuCl_2 \cdot 2THF$ (0.821 g, 22% yield) could be isolated in this manner. Second and third crops were collected by a similar procedure. Anal. Found: Lu, 33.97. $LuC_{17}H_{29}O_2$ calc: Lu, 34.22%. ^1H NMR (THF-d_8) δ 5.96 (m, 4H, t-C_4H_9-C_5H_4), 1.22 (s, 9H, t-C_4H_9-C_5H_4). The resonances of coordinated THF protons were superimposed on those of residual proton THF. Accurate integrations could not be obtained due to this superposition of peaks and the low solubility of the compound. IR (Nujol, cm^{-1}) 1343w, 1296w, 1246w, 1178m, 1037m, 1009s, 953w, 915m, 853s, 721w, 675m.

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