Article

Synthetic Utility of [(CMe)Ln][(▯-Ph)BPh] in Accessing [(CMe)LnR] Unsolvated Alkyl Lanthanide Metallocenes, Complexes with High C–H Activation Reactivity

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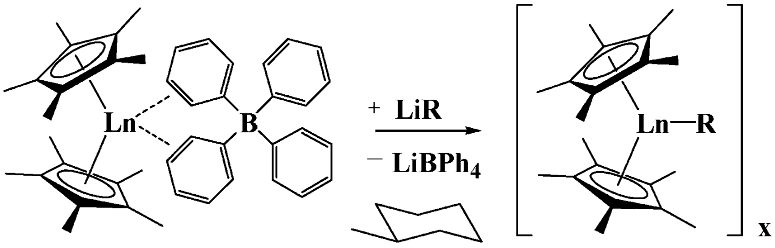

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ARTICLES

Synthetic Utility of $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ in Accessing $[(C_5Me_5)_2LnR]_x$ Unsolvated Alkyl Lanthanide Metallocenes, Complexes with High C−H Activation Reactivity

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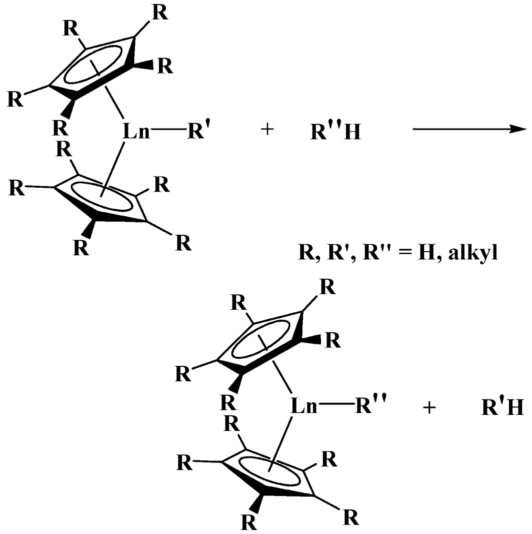
Abstract: The loosely ligated $[BPh_4]^{1-}$ ion in $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ can be readily displaced by alkyllithium or potassium reagents to provide access to unsolvated alkyl lanthanide metallocenes, $[(C_5Me_5)_2LnR]_x$, which display high C−H activation reactivity. $[(C_5Me_5)_2SmMe]_3$, $[(C_5Me_5)_2LuMe]_2$, $[(C_5Me_5)_2LaMe]_x$, $(C_5Me_5)_2Sm(CH_2Ph)$, $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$, and $[(C_5Me_5)_2SmPh]_2$ were prepared in this way. $[(C_5Me_5)_2SmMe]_3$ metalates toluene, benzene, $SiMe_4$, and $(C_5Me_5)^{1-}$ ligands to make $(C_5Me_5)_2Sm(CH_2Ph)$, $[(C_5Me_5)_2SmPh]_2$, $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$, and $(C_5Me_5)_6Sm_4[C_5Me_3(CH_2)_2]_2$, respectively. These C−H activation reactions can be done using an in situ synthesis of $[(C_5Me_5)_2LnMe]_x$ such that the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/LiMe/RH combination provides a facile route to a variety of unsolvated $[(C_5Me_5)_2LnR]_x$ products.

Introduction

One of the characteristic reactions of lanthanide metallocene alkyl complexes is metalation of C−H bonds, eq 1. While early studies of simple cyclopentadienyl complexes such as $[(C_5H_5)_2LnMe]_2$ (Ln = lanthanide and yttrium) showed reactivity with relatively acidic R″H hydrocarbons such as alkynes,[1−3] the advent of the solvent-free bis(pentamethylcyclopentadienyl) methyl complexes $[(C_5Me_5)_2LnMe]_x$ of the small metals (Ln = Lu,[4] Y,[5] Sc[6,7]) revealed spectacular reactivity with R″H substrates as weakly acidic as methane.[4−10]

Although the unsolvated bis(pentamethylcyclopentadienyl) methyl complexes of Lu, Y, and Sc have been known for many years,[4−7] no unsolvated analogues with larger lanthanide metals have been subsequently reported. This was understandable since, due to their greater steric unsaturation, methyl analogues of the larger metals should be even more reactive[11] than the Lu, Y, and Sc complexes which can metalate ethers, arenes, and even methane.[4−10] Historically, complexes of the larger lanthanides have been more challenging to isolate since they have higher reactivity. For example, with the larger metal samarium, even the more sterically saturated, *solvated*, methyl complex $(C_5Me_5)_2SmMe(THF)$ is known to metalate arenes and alkanes.[12] Due to the high reactivity of the known unsolvated $[(C_5Me_5)_2LnMe]_x$ complexes, literature syntheses of these species are challenging and involve multiple steps, e.g., Scheme 1.[4,5] This may have inhibited further investigation of their chemistry.[13,14]



(1)

Although $(C_5Me_5)_2LnR$ complexes with small alkyl R groups were not synthetically accessible, complexes in which the alkyl is the bulky $[CH(SiMe_3)_2]^{1-}$ ligand have been heavily studied.[15−18] The large size of the $[CH(SiMe_3)_2]^{1-}$ ligand as well as its propensity to engage in additional agostic interactions saturates the coordination sphere of the metal and makes these complexes

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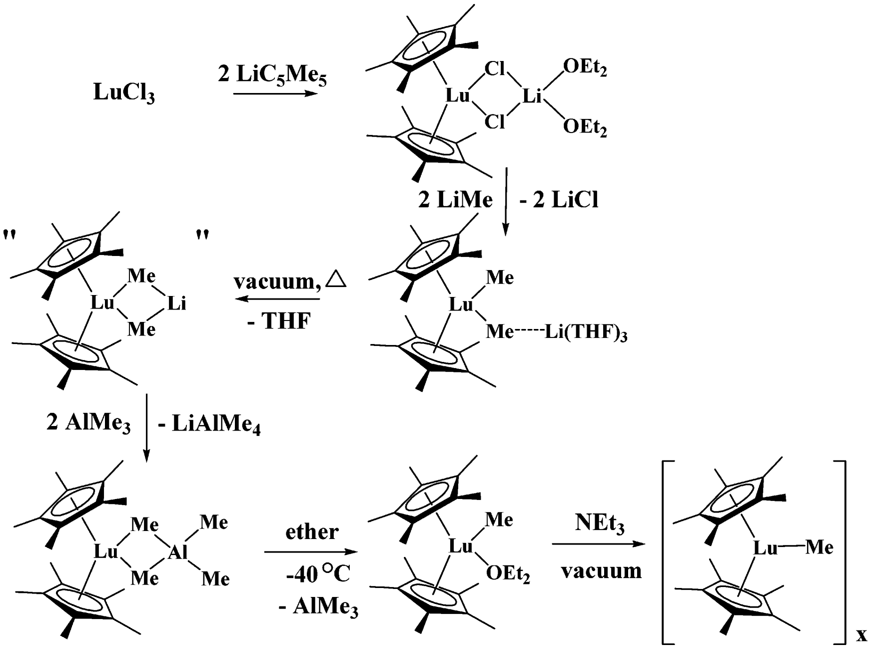
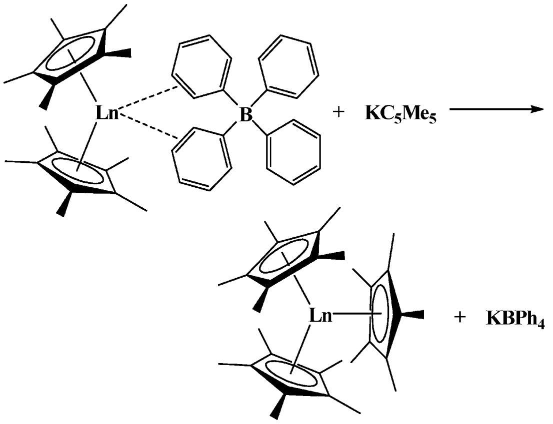
Scheme 1 . Original Synthesis of $[(C_5Me_5)_2LuMe]_2$, **3**



less reactive than $(C_5Me_5)_2LnR$ complexes with small alkyl groups. However, the $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ compounds also display some C−H activation activity particularly with the larger lanthanide complexes in which the metals are less saturated.[17,18] $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ complexes can be made from $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ and $LiCH(SiMe_3)_2$ which in turn is prepared from $ClCH(SiMe_3)_2$ or $CH_2(SiMe_3)_2$.[19,20]

Although $LiCH(SiMe_3)_2$ is considerably more expensive than common alkyllithium reagents, $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ complexes have traditionally been used when unsolvated alkyls were needed since other alternatives were not available. For example, preparation of $[(C_5Me_5)_2LnH]_x$ by hydrogenolysis of $(C_5Me_5)_2LnR$ requires a THF-free system since the hydrides react with THF.[21] In the past, $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ complexes have been used for this purpose.[16] Recently, however, the allyl complexes, $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$,[16,22] have been advanced as readily accessible alternatives.[23] For example, they react with H_2 to make $[(C_5Me_5)_2LnH]_x$ complexes.[23]

An alternative approach to unsolvated alkyl complexes involves the tetraphenylborate salts of the unsolvated metallocene cations $[(C_5Me_5)_2Ln]^+$ namely, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$.[23] In these complexes, a tetraphenylborate anion is loosely ligated to the lanthanide via two bridging arene (not aryl) linkages. These compounds have proven to be good precursors for the difficult synthesis of sterically crowded $(C_5Me_5)_3Ln$ molecules, eq 2.[24] The $(C_5Me_5)_3Ln$ complexes must



(2)

be made in the absence of THF, which they ring open,[25] and they must be prepared in an environment in which no other sterically more acceptable products can form. The reaction of $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ and KC_5Me_5 in arenes meets these requirements, and the precipitation of the inert byproduct $KBPh_4$ facilitates the reaction. The $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes are good precursors since they can be made in high yield from the common organolanthanide precursors, $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2K(solvent)_2$, with $(CH_2CHCH_2)MgCl$ and $[Et_3NH][BPh_4]$ as shown in Scheme 2.[23]

We report here that $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes not only are useful for making sterically crowded $(C_5Me_5)_3Ln$ complexes but also are excellent precursors to unsolvated alkyl lanthanide metallocenes containing small alkyl groups. This has allowed the first synthesis of solvent-free $[(C_5Me_5)_2SmMe]_3$ and appears to be the best route to a variety of $[(C_5Me_5)_2LnR]_x$ species in which the alkyl group is smaller than $[CH(SiMe_3)_2]^{1-}$. Syntheses of a representative variety of unsolvated alkyl

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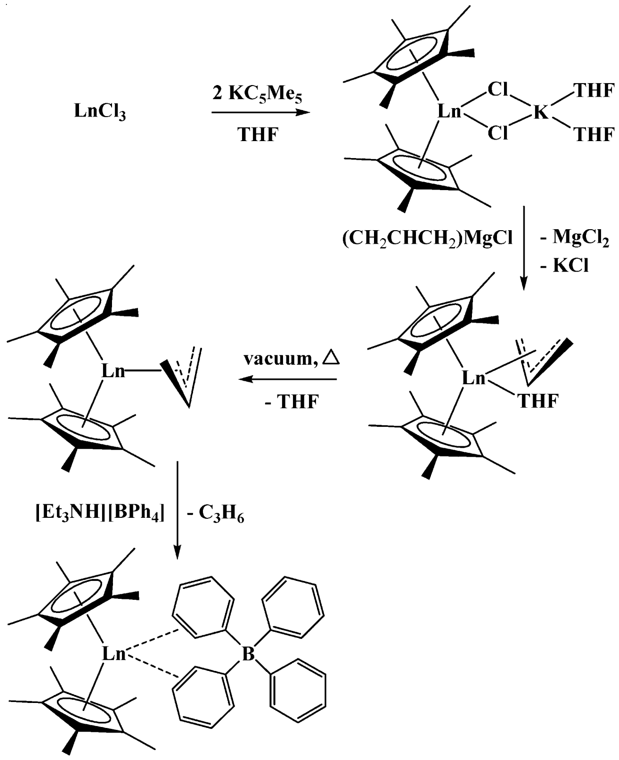
Scheme 2. Synthesis of [(C_5Me_5)$_2$Ln][(μ-Ph)$_2$BPh$_2$] Complexes.



complexes by this route are described as well as the extensive C−H activation chemistry that they reveal.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Therefore, the syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The argon glovebox used in these experiments was free of coordinating solvents. Glassware was treated with Siliclad (Gelest) to avoid formation of oxide decomposition products. Tetrahydrofuran, diethyl ether, toluene, hexanes, and benzene were saturated with UHP grade argon and dried by passage through Glasscontour drying columns.[26] Methylcyclohexane (99%) was purchased from Acros and distilled over NaK alloy prior to use. All deutero-solvents were dried over NaK alloy and vacuum transferred prior to use. The [(C_5Me_5)$_2$Ln][(μ-Ph)$_2$BPh$_2$] (Ln = La, Sm, **1**, Lu) precursors were prepared according to the literature[23] and were recrystallized from hot toluene before use.[27] LiMe was purchased as a 2.0 M solution in diethyl ether (Aldrich), and the solvent was removed under vacuum. The reagent was kept under vacuum until the resultant white solid achieved a constant weight. *meta*-Tolylcarboxylic acid and phenylacetic acid (Aldrich) were used as received. $LiCH_2SiMe_3$[19] and KCH_2Ph[28] were prepared as described previously. ^{1}H and ^{13}C NMR spectra were obtained on Bruker DRX 400 MHz and Omega 500 MHz spectrometers at 25 °C. Infrared analyses were acquired as thin films using an Applied Systems ReactIR 1000.[29] Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany) and complexometric titration.[30]

[(C_5Me_5)$_2$SmMe]$_3$, 2. In an argon glovebox, rose colored crystals of **1** (51 mg, 0.07 mmol) were combined with finely divided LiMe (2 mg, 0.10 mmol) in methylcyclohexane (5 mL). An orange colored suspension resulted within 2−3 h of stirring at 25 °C. After 5 h an orange solution was centrifuged to separate white solids. Volatiles were removed from the supernatant in vacuo to yield **2** (25 mg, 83%) as a glassy orange solid. ^{1}H NMR (500 MHz, C_6D_{12}) δ 0.33 (s, $\Delta\nu_{1/2} = 22$ Hz). IR (thin film from C_6H_{12}, cm^{-1}) 2961s, 2926s, 2853s, 2660w, 1660w, 1447s, 1378m, 1258s, 1080br,s, 1015br,s, 903m, 860m, 803s, 703m, 683m. Because of the high reactivity of **2**, analytical analysis was limited to in house methods. Anal. Calcd for $C_{63}H_{99}Sm_3$: Sm, 34.51. Found: Sm, 33.6. THF was added to **2** to form (C_5Me_5)$_2$SmMe(THF)[12] quantitatively by ^{1}H NMR spectroscopy. Single crystals of **2** suitable for X-ray diffraction were grown from methylcyclohexane at −38 °C.

[(C_5Me_5)$_2$LuMe]$_2$, 3. Colorless crystals of [(C_5Me_5)$_2$Lu][(μ-Ph)$_2$BPh$_2$] (80 mg, 0.10 mmol) were combined with finely divided LiMe (2 mg, 0.10 mmol) in methylcyclohexane (7 mL). After 2 h of stirring at 25 °C the colorless solution was centrifuged to remove white insoluble material and evaporated to dryness. **3** (36 mg, 75%) was recovered as a white solid identified by ^{1}H NMR spectroscopy in C_6D_{12}.[4] Single colorless crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated C_6D_{12} solution of **3** at 25 °C.

(C_5Me_5)$_2$Sm(CH_2Ph), 4. 1 (43 mg, 0.06 mmol) was combined with solid orange-red KCH_2Ph (7.6 mg, 0.06 mmol) in 5 mL of toluene. After the reaction mixture was stirred for 10 min at 25 °C, a yellow-brown suspension developed. Separation of the yellow-brown supernatant from white solids by centrifugation and removal of the solvent by rotary evaporation yielded **4** as a glassy yellow-brown solid (22 mg, 73%).[21] Red crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated *n*-hexane solution of **4** at 25 °C.

Formation of (C_5Me_5)$_2$Sm(CH_2Ph), 4, from [(C_5Me_5)$_2$SmMe]$_3$, 2, and Toluene. When [(C_5Me_5)$_2$SmMe]$_3$, **2** (19 mg, 0.014 mmol) was dissolved in neat toluene and stirred for 30 min at 25 °C, the solution color changes from orange to a yellow-brown. Volatiles were removed in vacuo to yield 20 mg of a glassy yellow-brown solid whose ^{1}H NMR spectrum in C_6D_{12} contained the resonances of (C_5Me_5)$_2$Sm(CH_2Ph),[21] as well as two other resonances in the 0−2 ppm C_5Me_5 region. Integration of the 0.94 ppm resonance of **4** versus the other peaks at δ 0.78 and 1.48 gave a 30:9:3 ratio, respectively.

[(C_5Me_5)$_2$Sm]$_2$(C_7H_6), 5. 1 (66 mg, 0.08 mmol) was combined with finely divided LiMe (2 mg, 0.10 mmol) in toluene (8 mL). An orange solution immediately resulted. Within 5 min the solution color turned bright yellow with formation of a white precipitate. After 30 min of stirring, a yellow-brown solution was separated from the insoluble material by centrifugation and the solvent was removed in vacuo to yield a glassy yellow-brown solid**.** The ^{1}H NMR spectrum is largely consistent with that reported previously for **4**,[21] but additional resonances were present. Red single crystals of **5** suitable for X-ray diffraction formed from hexanes at −38 °C. Crystallographic cell constants: monoclinic, *C*2/*c*, $a = 25.877(2)$ Å, $b = 14.0300(11)$ Å, $c = 11.7571(9)$ Å, $\beta = 103.682(1)$°, $V = 4147.3(6)$ Å^3. The disorder did not allow for a detailed discussion of the ligand between the two (C_5Me_5)$_2$Sm units.

[(C_5Me_5)$_2$Sm($O_2CC_6H_5$Me-*m*)]$_2$, 6. Addition of CO_2 to the orange-yellow product isolated from a [(C_5Me_5)$_2$Sm][(μ-Ph)$_2$BPh$_2$]/LiMe reaction in toluene immediately generated a bright yellow solution. The reaction was allowed to stir under 1 atm of CO_2 for 1 h at 25 °C. The reaction vessel was evacuated to dryness by rotary evaporation to yield a yellow powder. Single yellow crystals of **6** were grown from a mixture of hexanes, toluene, and pyridine at −38 °C and identified by X-ray crystallography.

Synthesis of 6 from (C_5Me_5)$_2$Sm(THF)$_2$ and *meta*-Tolylcarboxylic Acid. In a nitrogen filled glovebox, *meta*-tolylcarboxylic acid (20 mg,

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0.15 mmol) was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (86 mg, 0.15 mmol) in 7 mL of THF. Within 30 min the solution color turned golden yellow. Removal of the solvent by rotary evaporation left yellow solids. Recrystallization from toluene at −38 °C yielded **6** (67 mg, 79%). ^{1}H NMR (500 MHz, C_6D_6) δ 5.77 (d, $J_{HH} = 7.58$ Hz, 1H, *p*-C_6H_4Me), 5.60 (t, $J_{HH} = 7.58$ Hz, 1H, *m*-C_6H_4Me), 3.72 (d, $J_{HH} = 7.58$ Hz, 1H, *o*-C_6H_4Me), 3.60 (s, 1H, *o*-C_6H_4Me), 1.51 (s, 30H, C_5Me_5), 1.08 (s, 3H, MeC_6H_4). ^{13}C{^{1}H} (125 MHz, THF-d_8) δ 196.1 (O_2C), 138.0 (C_6H_4Me), 137.3 (C_6H_4Me), 131.5 (C_6H_4Me), 128.6 (C_6H_4Me), 127.8 (C_6H_4Me), 127.7 (C_6H_4Me), 113.3 (C_5Me_5), 43.4 (MeC_6H_4), 15.9 (C_5Me_5). IR (C_6D_6, cm^{-1}) 3034w, 2961s, 2918s, 2856s, 2725w, 1571s, 1401s, 1262s, 1089s, 1058s, 1015s, 803s, 676s. Anal. Calcd for $C_{56}H_{74}O_4Sm_2$: Sm, 27.04. Found: Sm, 26.8.

Synthesis of $[(C_5Me_5)_2Sm(O_2CCH_2C_6H_5)]_2$, 7, from $(C_5Me_5)_2Sm(THF)_2$ and Phenylacetic Acid. In a nitrogen filled glovebox, phenylacetic acid (19 mg, 0.14 mmol) was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (77 mg, 0.14 mmol) in 7 mL of THF. Within 10 min the solution color turned yellow. Removal of the solvent by rotary evaporation left yellow solids. Recrystallization from toluene at −38 °C yielded **7** (65 mg, 86%). ^{1}H NMR (500 MHz, C_6D_6) δ 5.89 (t, $J_{HH} = 7.4$ Hz, 1H, *p*-C_6H_5,), 5.56 (t, $J_{HH} = 7.9$ Hz, 2H, *m*-C_6H_5,), 3.70 (d, $J_{HH} = 8.0$ Hz, 2H, *o*-C_6H_5), 1.52 (s, 30H, C_5Me_5), −1.33 (s, 2H, $CH_2C_6H_5$). ^{13}C{^{1}H} (125 MHz, THF-d_8) δ 130.6 (*o*-C_6H_5), 128.6 (*m*-C_6H_5), 126.9 (*p*-C_6H_5), 113.2 (C_5Me_5), 43.3 ($CH_2C_6H_5$), 15.8 (C_5Me_5) (the ipso carbon was not located). IR (thin film from C_6D_6, cm^{-1}) 3023w, 2957s, 2922s, 2725w, 1567s, 1498m, 1397s, 1258s, 1077s, 942m, 799s, 702s, 579w. Anal. Calcd for $C_{56}H_{74}O_4Sm_2$: Sm, 27.04. Found: Sm, 26.3.

Synthesis of 7 from $(C_5Me_5)_2Sm(CH_2Ph)$, 4, and CO_2. In a J-Young NMR tube, glassy yellow-brown **4** (16 mg, 0.031 mmol) was dissolved in 0.5 mL of C_6D_6. The NMR tube was cooled to −196 °C using a liquid nitrogen bath. The headspace of the NMR tube was evacuated, and 1 atm of CO_2 was added. The solution turned bright yellow upon warming to 25 °C. A ^{1}H NMR spectrum revealed complete consumption of **4** with exclusive formation of **7**.

Formation of $[(C_5Me_5)_2Sm(C_6H_5)]_2$, 8, from $[(C_5Me_5)_2SmMe]_3$, 2, and Benzene. Complex **2** (20 mg, 0.015 mmol) was dissolved in neat benzene and stirred for 30 min at 25 °C. The solution changed from orange to yellow-brown. Volatiles were removed in vacuo, and $[(C_5Me_5)_2Sm(C_6H_5)]_2$[31−33] (21 mg, 92%) was isolated as a glassy yellow-brown solid and identified by ^{1}H NMR spectroscopy.

Synthesis of $[(C_5Me_5)_2Sm]_2(C_6H_4)$, 9, from 2 and Benzene. Glassy orange $[(C_5Me_5)_2SmMe]_3$, **2** (20 mg, 0.015 mmol), was dissolved in C_6D_{12} containing trace amounts of C_6H_6. Dark yellow crystals of **9** suitable for X-ray diffraction were grown from the NMR tube overnight in C_6D_{12} at 25 °C. Complex **9** was identified by X-ray crystallography. The structure matched that in the literature.[31]

Synthesis of $[(C_5Me_5)_2Sm]_2(C_6H_4)$, 9, from 2 and 8. An intimate mixture of $[(C_5Me_5)_2SmMe]_3$, **2** (16 mg, 0.012 mmol), and $[(C_5Me_5)_2Sm(C_6H_5)]_2$, **8** (18 mg, 0.012 mmol), were combined and dissolved in 0.5 mL of C_6D_{12}. ^{1}H NMR spectroscopy revealed complete conversion of **2** and **8** to $[(C_5Me_5)_2Sm]_2(C_6H_4)$, **9**, with concomitant formation of CH_4 at 0.18 ppm.

$[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$, 10. 1 (73 mg, 0.1 mmol) was combined with $LiCH_2SiMe_3$ (9 mg, 0.1 mmol) in 7 mL of methylcyclohexane. The reaction mixture turned bright orange-yellow within 5 min of stirring at 25 °C. An orange-yellow solution was centrifuged to remove white solids. Rotary evaporation of the solvent yielded a bright orange powder. ^{1}H NMR (500 MHz, C_6D_{12}) δ 15.3 (s, 2H, CH_2SiMe_3), 1.04 (s, 30 H, C_5Me_5), −7.37 (s, 9 H, CH_2SiMe_3). ^{13}C{^{1}H} (125 MHz, C_6D_{12}) δ 119.4 (C_5Me_5), 18.5 (C_5Me_5), −7.9 (−SiMe_3). The methylene carbon resonance could not be located. IR (thin film from C_6H_{14}, cm^{-1}) 2961s, 2926s, 2860s, 2733w, 1449s, 1378m, 1247w, 903w, 865w, 757w, 726m. Anal. Calcd for $C_{24}H_{41}SiSm$: Sm, 29.6; C, 56.7; H, 8.1; Si, 5.5. Found: Sm, 28.80; C, 57.84; H, 8.35; Si, 5.30. Addition of 1 atm of H_2 to a C_6D_{12} solution of **10** forms $[(C_5Me_5)_2SmH]_2$[34] and $SiMe_4$ quantitatively by ^{1}H NMR. Orange crystals suitable for X-ray diffraction were grown from *n*-hexane at −38 °C. Crystallographic cell constants: triclinic, $P\bar{1}$, $a = 9.682(2)$ Å, $b = 10.421(2)$ Å, $c = 14.760(3)$ Å, $\alpha = 107.523(5)°$, $\beta = 95.611(6)°$, $\gamma = 90.546(6)°$, $V = 1412.6(7)$ Å^3. Unfortunately, a structure solution was not obtained. Due to the instability of **10** in solution, an accurate estimate of molecular weight was not obtainable through isopestic[35] determination.

Formation of 10 from $[(C_5Me_5)_2SmMe]_3$, 2, and $SiMe_4$. Complex **2** (10 mg, 0.008 mmol) was dissolved in 0.5 mL of C_6D_{12} and placed into a J-Young NMR tube. Tetramethylsilane (3.1 μL, 0.023 mmol) was added dropwise via microliter syringe, and the tube was sealed with a Teflon cap. After 2 h, formation of $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_n$, **10**, and CH_4 was complete as determined by ^{1}H NMR spectroscopy.

$[(C_5Me_5)_2Sm(CH_2SiMe_3)](THF)$. Bright orange crystals of **10** (40 mg) were loaded into a J-Young NMR tube and dissolved in 0.5 mL of C_6D_{12}. To the bright orange solution, THF (6.5 μL, 0.08 mmol) was added dropwise via a microliter syringe. The orange solution turned golden yellow upon addition of THF. ^{1}H NMR (500 MHz, C_6D_{12}) δ 8.14 (s, 2H, CH_2SiMe_3), 1.44 (s, 30H, C_5Me_5), 0.38 (s, 9H, CH_2SiMe_3), −1.10 (s, 4H, THF), −2.50 (s, 4H, THF). Attempts to obtain crystals of this complex generated $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[36,37] within 24 h.

$[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, 11. Bright orange crystals of **10** (28 mg) were loaded into a J-Young NMR tube and dissolved in 0.5 mL of C_6D_{12}. The NMR tube was cooled to −196 °C using a liquid nitrogen bath and evacuated, and 1 atm of CO_2 was added. The solution turned bright yellow upon warming to 25 °C with precipitation of yellow solids. Recrystallization of the yellow solids from hot toluene yielded **11** (31 mg, 0.028 mmol) as orange-yellow crystals. ^{1}H NMR (500 MHz, C_6D_6) δ 1.68 (s, 30H, C_5Me_5), −2.40 (s, 9H, CH_2SiMe_3). The CH_2-$SiMe_3$ methylene resonance could not be located. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 176.8 (O−*C*−O), 115.1 (C_5Me_5), 18.5 (C_5Me_5), −2.40 (CH_2SiMe_3). The CH_2SiMe_3 resonance was not located.

Formation of $(C_5Me_5)_6Sm_4[(C_5Me_3(CH_2)_2]_2$, 12. Black crystals of **12** formed in an NMR tube containing a C_6D_{12} solution of **10** (30 mg, 0.06 mmol) over several days at 25 °C. Complex **12** was also identified in ^{1}H NMR samples of **2** in C_6D_{12}. ^{1}H NMR (500 MHz, C_6D_{12}) δ 1.89 (s, 30H, C_5Me_5), 1.11 (s, 30H, C_5Me_5), 0.56 (s, 30H, C_5Me_5), −2.18 (s, 6H, $(CH_2)_2C_5Me_2Me$), −5.94 (s, 12H, $(CH_2)_2C_5Me_2Me$). The methylene resonances, $(CH_2)_2C_5Me_3$, could not be located. ^{13}C{^{1}H} NMR (125 MHz, C_6D_{12}) δ 120.8 (C_5Me_5), 115.7 (C_5Me_5), 114.7 (C_5Me_5), 24.1 (C_5Me_5), 19.3 (C_5Me_5), 19.0 (C_5Me_5). IR (thin film from C_6D_{14}, cm^{-1}) 2961s, 2910s, 2856s, 2725w, 2208m, 2096m, 1444s, 1378s, 1258s, 1258s, 1085s, 1019s, 914s, 857s, 803s, 703s. Anal. Calcd for $C_{80}H_{116}Sm_4$: Sm 35.82. Found: Sm 34.2. Crystallographic cell constants: monoclinic, $P2_1/n$, $a = 15.119(6)$ Å, $b = 13.285(5)$ Å, $c = 17.366(7)$ Å, $\beta = 99.107(7)°$, $V = 3444(2)$ Å^3. Unfortunately the crystal quality was insufficient to provide more than connectivity information.

Formation of $[(C_5Me_5)_2SmH]_2$ from $[(C_5Me_5)_2SmMe]_3$, 2, and H_2. An orange solution of **2** (10 mg, 0.008 mmol) in 0.5 mL of C_6D_{12} in a J-Young tube was cooled to −196 °C using a liquid nitrogen bath. The headspace of the NMR tube was evacuated, and 1 atm of H_2 was added. The ^{1}H NMR spectrum revealed complete consumption of **2** with exclusive formation of $[(C_5Me_5)_2SmH]_2$[34] and CH_4.

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Table 1. Experimental Data from the X-ray Diffraction Studies of $[(C_5Me_5)_2SmMe]_3$, **2**, $[(C_5Me_5)_2LuMe]_2$, **3**, $[(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)]$, **4**, $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, and $[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, **11**

	2·1.5(C_7H_{14})	**3**	**4**	**6**·C_6H_{14}	**7**	**11**
formula	$C_{63}H_{99}Sm_3$·1.5(C_7H_{14})	$C_{42}H_{66}Lu_2$	$C_{27}H_{37}Sm$	$C_{56}H_{74}O_4Sm_2$·C_6H_{14}	$C_{56}H_{74}O_4Sm_2$	$C_{50}H_{82}O_4Si_2Sm_2$
fw	1454.75	920.89	511.92	1198.02	1111.85	1104.04
temp (K)	163(2)	163(2)	163(2)	183(2)	293(2)	163(2)
cryst system	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	18.0097(9)	10.7702(5)	15.9095(15)	10.2195(5)	10.2254(9)	32.132(3)
b (Å)	16.9596(8)	27.0242(12)	9.9404(9)	11.0809(6)	10.5715(10)	21.368(2)
c (Å)	23.1091(11)	14.1407(6)	15.1263(14)	13.9199(7)	12.7887(12)	23.512(2)
α (deg)	90	90	90	104.5710(10)	87.415(2)	90
β (deg)	93.6400(10)	108.4590(10)	90	99.4930(10)	75.3380(10)	105.523(2)
γ (deg)	90	90	90	108.2190(10)	68.2230(10)	90
V (Å^3)	7044.1(6)	3904.0(3)	2392.2(4)	1397.33(12)	1240.1(2)	15555(3)
Z	4	4	4	1	1	12
D_{calcd}(Mg/m^3)	1.372	1.567	1.421	1.424	1.489	1.414
diffractometer	Bruker CCD	Bruker CCD	Bruker CCD	Bruker CCD	Bruker CCD	Bruker CCD
μ (mm^{-1})	2.505	5.054	2.464	2.125	2.388	2.328
wR2 (all data)	0.1076	0.0620	0.0503	0.0898	0.0894	0.0776

Formation of $[(C_5Me_5)_2LaH]_x$ from $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$/LiMe and H_2. Pale yellow needles of $[(C_5Me_5)_2La][BPh_4]$ (55 mg, 0.075 mmol) were combined with finely divided LiMe (2 mg, 0.077 mmol) and dissolved in 5 mL of methylcyclohexane. After 4 h of stirring at 25 °C, a golden yellow solution was centrifuged from off-white solids. Removal of the solvent in vacuo yielded a glassy yellow solid, whose ^{1}H NMR spectrum in C_6D_{12} contained a C_5Me_5 resonance at 1.85 ppm. The instability of this product led us to convert it to the previously characterized derivative, the $[(C_5Me_5)_2LaH]_x$ hydride.[16] A solution of this product, presumably $[(C_5Me_5)_2LaMe]_x$ in 0.5 mL of C_6D_{12} in a J-Young tube, was cooled to −196 °C. The headspace of the NMR tube was evacuated, and 1 atm of H_2 was added. The solution turned pale yellow upon warming to 25 °C. The ^{1}H NMR spectrum contained the resonances of $[(C_5Me_5)_2LaH]_x$[16] and CH_4 and none of the residual 1.85 ppm peak. Crystals of $[(C_5Me_5)_2LaH]_x$ were obtained from hexane at −38 °C. Crystallographic cell constants: monoclinic, $C2/c$, $a = 17.25(3)$ Å, $b = 14.48(3)$ Å, $c = 16.66(3)$ Å, $\beta = 106.01(3)°$, $V = 4005(23)$ Å^3. The quality of the data was insufficient for a structure solution.

Formation of $[(C_5Me_5)_2LuH]_2$ from $[(C_5Me_5)_2LuMe]_2$, 3, and H_2. A colorless solution of $[(C_5Me_5)_2LuMe]_2$ (12 mg, 0.013 mmol) in 0.5 mL of C_6D_{12} in a J-Young NMR tube was cooled to −196 °C. The headspace of the NMR tube was evacuated, and 1 atm of H_2 was added. No resonances for **3** were present in the ^{1}H NMR spectrum of the resulting colorless solution. Only resonances for $[(C_5Me_5)_2LuH]_2$[4] and CH_4 were observed.

X-ray Data Collection, Structure Determination, and Refinement. A typical procedure is given for **2**. All other structures were done similarly except as noted. Table 1 presents the crystallographic data.

$[(C_5Me_5)_2SmMe]_3$, 2. An orange crystal of approximate dimensions 0.10 × 0.20 × 0.22 mm^3 was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[38] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[39] and SADABS[40] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[41] program. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[42] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were 1.5 molecules of methylcyclohexane present per formula unit. The solvent molecules were disordered and included using multiple components with partial site-occupancy factors. Hydrogen atoms associated with the solvent molecules were not included in the refinement. At convergence, wR2 = 0.1076 and GOF = 1.064 for 648 variables refined against 14376 data (0.80 Å). As a comparison for refinement on F, R1 = 0.0445 for those 9456 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2LuMe]_2$, 3. A colorless crystal of approximate dimensions 0.08 × 0.22 × 0.34 mm^3 was handled as described above for **2**. The diffraction symmetry was $2/m$, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct. Hydrogen atoms either were located from a difference Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. At convergence, wR2 = 0.0620 and GOF = 1.062 for 409 variables refined against 9334 data. As a comparison for refinement on F, R1 = 0.0250 for those 7990 data with $I > 2.0\sigma(I)$.

$(C_5Me_5)_2Sm(CH_2Ph)$, 4. A red crystal of approximate dimensions 0.16 × 0.26 × 0.29 mm^3 was handled as described above for **2**. The diffraction symmetry was mmm, and the systematic absences were consistent with the orthorhombic space group $Pna2_1$ which was later determined to be correct. Hydrogen atoms either were located from a difference Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. At convergence, wR2 = 0.0503 and GOF = 1.082 for 281 variables refined against 4866 data (0.80 Å). As a comparison for refinement on F, R1 = 0.0188 for those 4611 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.[43]

$[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, 6. A yellow crystal of approximate dimensions 0.11 × 0.20 × 0.32 mm^3 was handled as described above for **2**. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center ($Z = 1$). There was one molecule of hexane solvent present which was also located about an inversion center. At

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[38] *SMART Software Users Guide*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

[39] *SAINT Software Users Guide*, version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.

[40] Sheldrick, G. M. *SADABS*, version 2.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

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[42] International Tables for X-ray Crystallography; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.

[43] Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876.

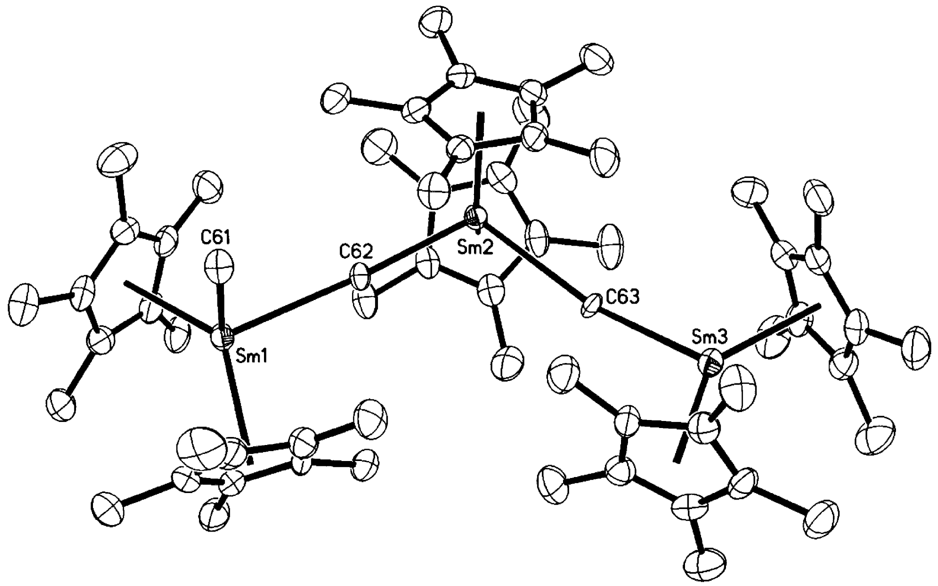


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2SmMe]_3$, **2**, drawn at the 50% probability ratio.

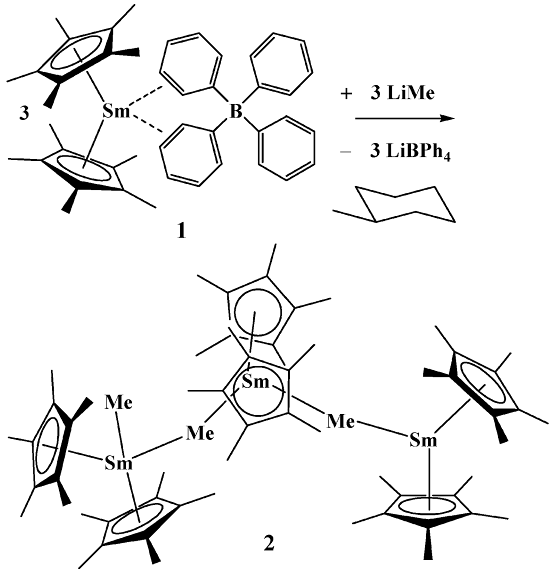
convergence, wR2 = 0.0898 and GOF = 1.106 for 307 variables refined against 5693 data (0.80 Å). As a comparison for refinement on *F*, R1 = 0.0324 for those 5235 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, 7. A yellow crystal of approximate dimensions 0.06 × 0.18 × 0.23 mm^3 was handled as described above for **2**. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. Carbon atoms C(1)−C(20) and C(24)−C(28) were disordered and included using multiple components with partial site-occupancy factors. The samarium and oxygen atoms were refined anisotropically. At convergence, wR2 = 0.0894 and GOF = 1.076 for 244 variables refined against 5746 data. As a comparison for refinement on *F*, R1 = 0.0346 for those 5130 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, 11. A yellow crystal of approximate dimensions 0.16 × 0.21 × 0.24 mm^3 was mounted on a glass fiber and handled as described above. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc and C*2/*c*. It was later determined that the centrosymmetric space group *C*2/*c* was correct. There was one molecule located in a general position and one located about an inversion center. This was consistent with *Z* = 12. At convergence, wR2 = 0.0776 and GOF = 1.070 for 784 variables refined against 17158 data (0.78 Å). As a comparison for refinement on *F*, R1 = 0.0301 for those 12420 data with $I > 2.0\sigma(I)$.

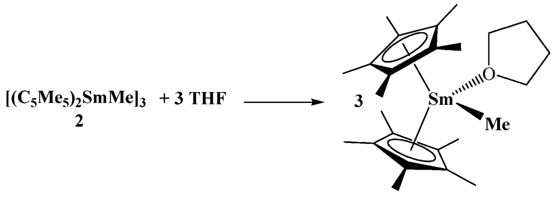
Results

Synthesis of $[(C_5Me_5)_2LnMe]_n$ Complexes. Initial studies showed that $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$, **1**, reacts readily with alkyllithium reagents, LiR, in arene solvents, but the reaction is not useful for the synthesis of $[(C_5Me_5)_2SmR]_x$ products because they immediately metalate the arene solvent as described in a later section. To avoid metalation of the solvent, reactions must be conducted in cyclohexane or methylcyclohexane. The latter solvent was preferred since it allowed for low-temperature crystallizations. Although $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$ has lower solubility in cyclohexanes, reaction occurs between **1** and LiMe to form the desired $[(C_5Me_5)_2SmMe]_x$ product, **2**, as shown in eq 3.



(3)

The ^{1}H NMR spectrum of **2** was not particularly informative and contained only a broad singlet ($\Delta\nu_{1/2}$ = 22 Hz) at δ 0.33 in C_6D_{12}. No additional information was obtained down to −90 °C in methylcyclohexane-d_{14}, and decomposition to $(C_5Me_5)_6Sm_4[C_5Me_3(CH_2)_2]_2$, **12**, described later, occurred at high temperature. However, addition of THF to **2** gave quantitative conversion to the solvate, $(C_5Me_5)_2SmMe(THF)$, eq 4, which had previously been characterized by X-ray crystallography.[12]



(4)

Despite the high reactivity of **2** (see below), X-ray quality

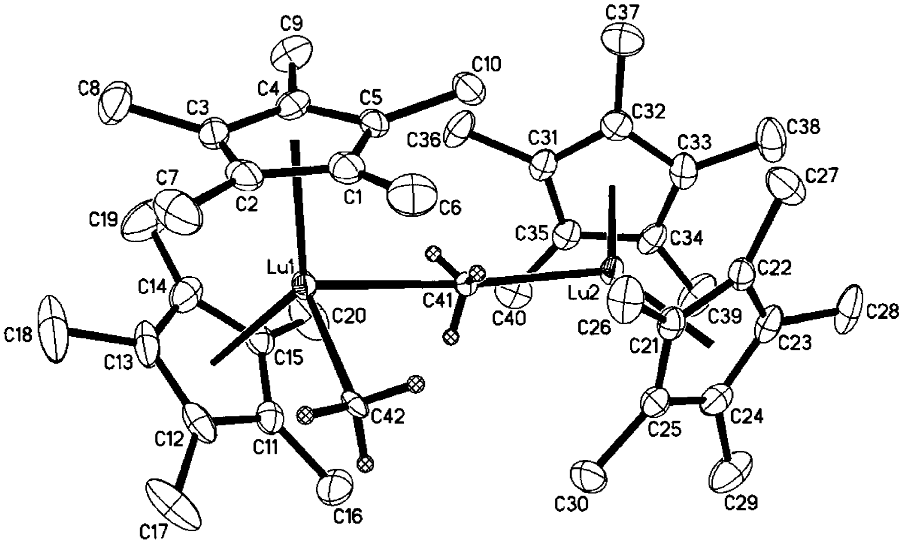
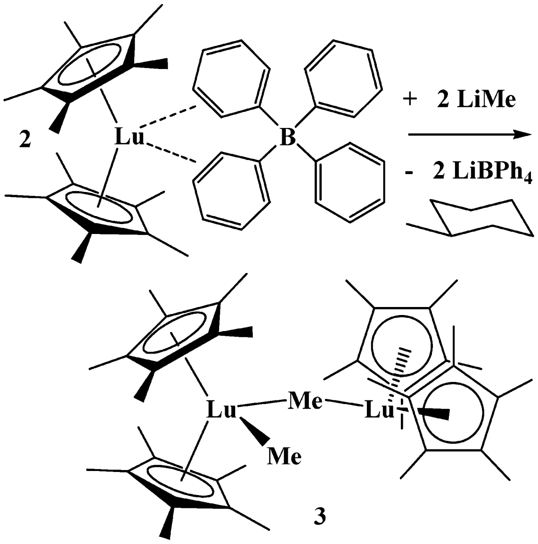


Figure 2. Thermal ellipsoid plot of $[(C_5Me_5)_2LuMe]_2$, **3**, drawn at the 50% probability ratio. Although all hydrogens were located, the C_5Me_5 hydrogens are not shown for clarity.

crystals were obtained which confirmed the composition and revealed the value of x as three in the solid state, Figure 1. The structure is discussed below.

LiMe reactions analogous to eq 3 were conducted with $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$ and $[(C_5Me_5)_2Lu][(\mu\text{-}Ph)_2BPh_2]$ to demonstrate the viability of this method to make unsolvated methyl complexes with the largest and smallest members of the lanthanide series. If this approach was successful with these two extremes and the intermediate-sized Sm, it is likely that the reaction would be general for the rest of the series.

$[(C_5Me_5)_2Lu][(\mu\text{-}Ph)_2BPh_2]$[27] reacts with LiMe in methylcyclohexane to make $[(C_5Me_5)_2LuMe]_2$, **3**, according to eq 5. Complex **3** was previously made by the series of reactions shown in Scheme 1.[4,5] Complex **3** was identified by ^1H NMR spectroscopy and fully defined by X-ray crystallography, Figure 2. Since the details of the X-ray crystal structure of **3** are not published,[4,5,8] this information is included here and discussed along with the structure of **2** in the next section.



(5)

The reaction of LiMe with $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$ gives a product that has a reactivity consistent with that of $[(C_5Me_5)_2LaMe]_x$, but definitive X-ray data were not obtainable so far on this compound. The complex does react with hydrogen to make the known lanthanum hydride, $[(C_5Me_5)_2LaH]_x$,[16] eq 6. This product was identified by comparison of its ^1H NMR spectrum with the literature value.[16]

$$[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2] \xrightarrow[-\ LiBPh_4]{+\ MeLi} \text{"}[(C_5Me_5)_2LaMe]_x\text{"} \xrightarrow{+\ H_2} [(C_5Me_5)_2LaH]_x + CH_4 \quad (6)$$

Structures of $[(C_5Me_5)_2LnMe]_x$ Complexes. As shown in Figure 1, $[(C_5Me_5)_2SmMe]_3$, **2,** crystallizes as an asymmetric trimer, $(C_5Me_5)_2MeSm(\mu\text{-}Me)Sm(C_5Me_5)_2(\mu\text{-}Me)Sm(C_5Me_5)_2$, in the solid state. This contrasts with lutetium analogue, **3**, which crystallizes as the asymmetric dimer, $(C_5Me_5)_2MeLu(\mu\text{-}Me)Lu(C_5Me_5)_2$, Figure 2, and the samarium chloride and hydride analogues of **2**, $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$[44] and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[34] which crystallize as symmetrical trimers and dimers, respectively, Scheme 3. Bond distances and angles are compared in Table 2.

The Sm(1)−Sm(2)−Sm(3) angle in **2** is 112.1° with the samarium centers connected by Sm−(μ-Me)−Sm bridges which have 176.2(3)° and 162.2(2)° Sm−C(Me)−Sm angles for the five coordinate C(62) and C(63), respectively. The first angle is similar to the linear Sm−C(Me)−Al bridging angles in $[(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2]_2$,[12] while the second angle is similar to the 162−165° Ln−(μ-Cl)−Ln angles in $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$[45] and the $[(C_5Me_5)_2ClSm(\mu\text{-}Cl)SmCl(C_5Me_5)_2]^-$ anion in the complicated structure of $(C_5Me_5)_{10}Sm_5Cl_5$(tetraglyme), Scheme 3.[44] The variability of these angles even within the structure of **2** is consistent with the flexibility of coordination geometry possible with lanthanides. Directed orbital interactions are less important than electrostatic and steric packing optimization.

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(45) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554.

Scheme 3. Structures of Some Oligomeric $[(C_5Me_5)_2LnX]_x$ Complexes and the $[(C_5Me_5)_2ClSm(\mu\text{-}Cl)SmCl(C_5Me_5)]^{1-}$ Anion in $(C_5Me_5)_{10}Sm_5Cl_5[Me(OCH_2CH_2)_4OMe]$[44]

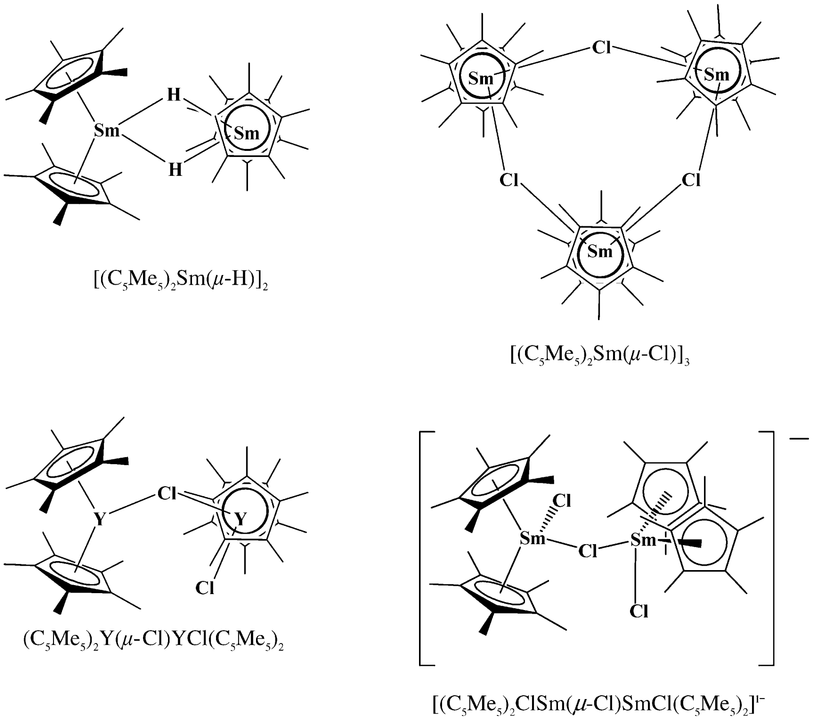

Table 2. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2SmMe]_3$, **2**, and $[(C_5Me_5)_2LuMe]_2$, **3**

compound	2	3
Ln−C(Me) bridging		
	Sm(1)−C(62): 2.889(6)	Lu(1)−C(41): 2.737(3)
	Sm(2)−C(62): 2.577(6)	Lu(2)−C(41): 2.442(3)
	Sm(2)−C(63): 2.880(7)	
	Sm(3)−C(63): 2.625(5)	
Ln−C(Me) terminal	Sm(1)−C(61): 2.474(4)	Lu(1)−C(42): 2.423(3)
Ln−C(ring) average		
Ln(1)	2.747(7)	2.649(3)
Ln(2)	2.738(7)	2.584(3)
Ln(3)	2.687(7)	
Ln−ring centroid		
Ln(1)	2.459, 2.480	2.367, 2.348
Ln(2)	2.460, 2.454	2.278, 2.289
Ln(3)	2.398, 2.404	
(ring centroid)−Ln−(ring centroid)		
Ln(1)	133.6	135.9
Ln(2)	135.7	138.8
Ln(3)	137.0	
Ln−C(Me)−Ln	C(62): 176.2(3)	169.47(16)
	C(63): 162.2(2)	

The locations of the bridging methyl carbons C(62) and C(63) are not symmetrical between the two samarium centers they-bridge, with 2.889(6)/2.577(6) and 2.880(7)/2.625(5) Å pairs of distances, respectively. Hence, these connections do not involve a *symmetrical* 3 center 2 electron bond for the five-coordinate carbon atoms. As expected, these bridging methyl distances are longer than the single Sm−terminal methyl distance involving Sm(1)−C(61), which is 2.474(7) Å in length. This terminal distance is similar to the 2.484(14) Å terminal Sm−Me distance in the solvated analogue of **2**, $(C_5Me_5)_2SmMe(THF)$,[12] which also has a formally eight-coordinate metal center. The long and short bridging lengths are arranged so that Sm(1) and Sm(2) each have a long and a short Sm−Me distance and the single Sm(3)−bridging Me distance is short. In this sense, the molecule is clearly comprised of three $(C_5Me_5)_2SmMe$ units, each of which has a short Sm−Me bond, which link together via long distance connections using the "backside" of the methyl group.

As expected, the Sm−C(C_5Me_5) average and Sm−(C_5Me_5 ring centroid) distances for the formally seven-coordinate Sm(3), 2.687(7) Å and 2.401 Å, respectively, are smaller than those for the eight-coordinate centers, Sm(1) (2.747(7) and 2.470 Å) and Sm(2) (2.738(7) and 2.457 Å). For both coordination numbers, the values are in the usual range found for organosamarium complexes.[46] The (C_5Me_5 ring centroid)−Sm−(C_5Me_5 ring centroid) angles are also in the normal range for seven- and eight-coordinate $(C_5Me_5)_2LnX$ and $(C_5Me_5)_2LnXL$ metallocenes (X = anionic ligand, L = neutral ligand).

Like **2**, $(C_5Me_5)_2MeLu(\mu\text{-}Me)Lu(C_5Me_5)_2$, **3**, contains both seven- and eight-coordinate metal centers, but with this smaller metal there is only one of each. The overall structure is similar to that of $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$,[45] Scheme 3. As shown in Table 2, the Lu−C(C_5Me_5) average and Lu−(C_5Me_5 ring centroid) distances for comparable seven- and eight-coordinate metal centers in **3** are shorter than those in **2** by the difference in their ionic radii: Lu(III) is 0.102 Å smaller than Sm(III).[47]

Although these Sm and Lu C_5Me_5 distances compare as expected, the distinct Lu−Me distances are not as regular. Hence, the 2.423(3) Å Lu−C(terminal methyl) distance is only 0.05 Å smaller than the analogous bond in **2**. The 2.737(3) and 2.442(3) Å Lu−C(bridging methyl) distances are dissimilar as in **2**, but they are 0.13−0.18 Å shorter. The 169.47(16)° Lu−Me−Lu angle is intermediate between the 162.2(2)° and 176.2(3)° in **2**. In comparison, the analogous angle in $(C_5Me_5)_2$-

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(46) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.
(47) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

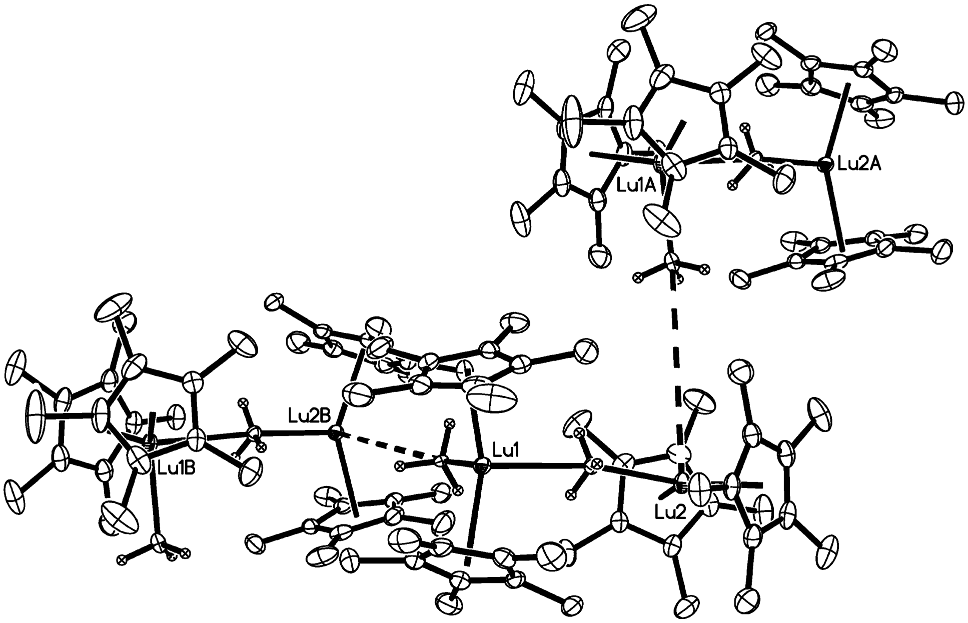

Figure 3. Portion of the packing diagram of $[(C_5Me_5)_2LuMe]_2$, **3**, showing the intermolecular orientation of the dimers.

$ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$[45] is 162.8(2)°. The 2.423(3) Å Lu−C(terminal methyl) distance can be compared with a 2.390(5) Å Lu−C(terminal Me) distance in $(C_5Me_4{}^iPr)_2LuMe(THF)$.[48]

Although locating hydrogen atoms in the presence of heavy metals is difficult, the structural data on **3** allowed location and refinement of the H positions on the five-coordinate C(41). The data indicate that the three hydrogen atoms are not located symmetrically between Lu(1) and Lu(2). Instead, they are oriented toward Lu(1). This means that the shorter 2.442(3) Å Lu(2)−C(41) connection has a Lu−Me unit with a more conventional tetrahedral arrangement around carbon than is normal for a μ-Me group. The long 2.737(3) Å Lu(1)−C(41) connection involves the backside of the methyl, i.e., Lu(1)···$H_3C(41)$−Lu(2). A similar methyl bridged structure has been observed for the Yb···H_3C−Be interaction in $(C_5Me_5)_2Yb(\mu\text{-}Me)Be(C_5Me_5)$.[49] Neutron diffraction studies of $LiBMe_4$ showed similar bridging.[50]

Interestingly, the somewhat longer than expected Lu−C distance in **3** involves a methyl group directed at the seven-coordinate metal center of another molecule in the unit cell as shown in Figure 3. This generates a network with intermolecular connections similar to the intramolecular Lu−Me···Lu analogue in **3**. These intermolecular Lu−Me···Lu angles are 170.9°. Although oriented for interaction, the intermolecular C(Me)·····Lu distance is 5.38 Å, a length too long to be appropriate for a bond.

Once the extended oligomeric structure for **3** was identified, the intermolecular arrangement of **2** was examined. Indeed, the terminal methyl group in **2**, C(61), is oriented toward a seven-coordinate Sm(3) center to make a continuous intermolecular oligomeric chain. Again the 5.364 Å C(61)·····Sm(3) distance is too long for a normal bond.

Arene Metalation Chemistry. Toluene. The reaction of **1** with LiMe in toluene occurs much faster than the reaction in methylcyclohexane perhaps because **1** has better solubility in this solvent. The product initially isolated from this reaction had the NMR characteristics of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$, **4**, which had been previously isolated from the reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with toluene.[21] The earlier studies of **4** had not provided crystallographic data on this compound, and only its THF adduct, $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2Ph)(THF)$, was characterized by X-ray methods.[21]

However, crystallization of this **1**/LiMe/toluene reaction product over several weeks gave **5**, whose X-ray crystal structure is shown in Figure 4. Complex **5** contains a disordered C_7 unit located between two $(C_5Me_5)_2Sm$ moieties which suggests a dimetalated toluene product, $[(C_5Me_5)_2Sm]_2(CH_2C_6H_4)$. Since dimetalated arene complexes have been identified with samarium metallocenes, both in this study (see below) and in the literature,[31] and since the **1**/LiMe reaction generates a powerful metalation reagent, this is not unreasonable. However, the ^1H NMR spectrum was consistent with $(C_5Me_5)_2Sm(CH_2Ph)$, and the X-ray data did not provide detailed information on the toluene derived ligand.

Furthermore, attempts to make a more crystalline derivative of **5** to prove the dimetalation by trapping with CO_2 gave crystals of monocarboxylates not dicarboxylates. In addition, the carboxylate crystallized from the reaction of CO_2 with the $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/LiMe/toluene product mixture was the carboxylate derived from *meta*-metalation of toluene, i.e., $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, Figure 5. The system was further complicated by the fact that the NMR spectrum of the solution from which **6** was crystallized did not match that expected for **6**.

To obtain more information on this system, **6** was independently synthesized from $(C_5Me_5)_2Sm(THF)_2$ and *meta*-tolylcarboxylic acid according to eq 7. Synthesis of samarocene carboxylates by this route was previously well established.[51]

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(48) Schumann, H.; Keitsch, M. R.; Winterfeld, J.; Mühle, S.; Molander, G. A. *J. Organomet. Chem.* **1998**, *559*, 181.

(49) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853.

(50) Rhine, W. E.; Stucky, G. D.; Peterson, S. W. *J. Am. Chem. Soc.* **1975,** *97*, 6401.

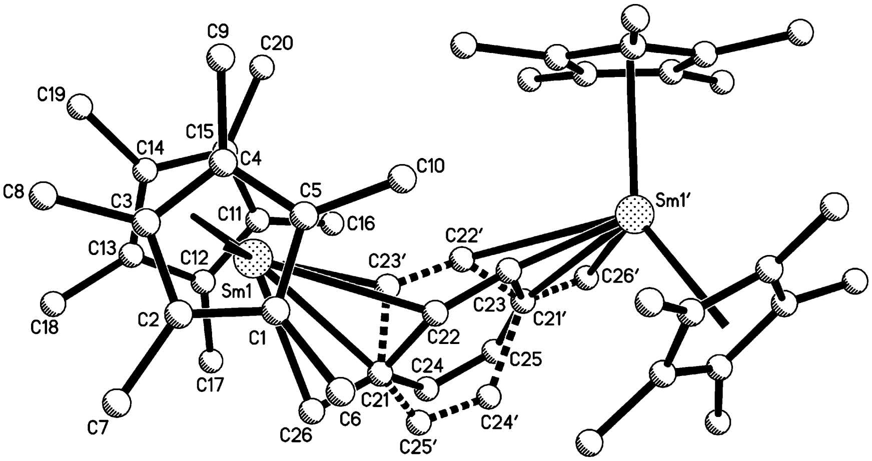


Figure 4. Ball-and-stick figure of disordered $[(C_5Me_5)_2Sm]_2(C_7H_6)$, **5**.

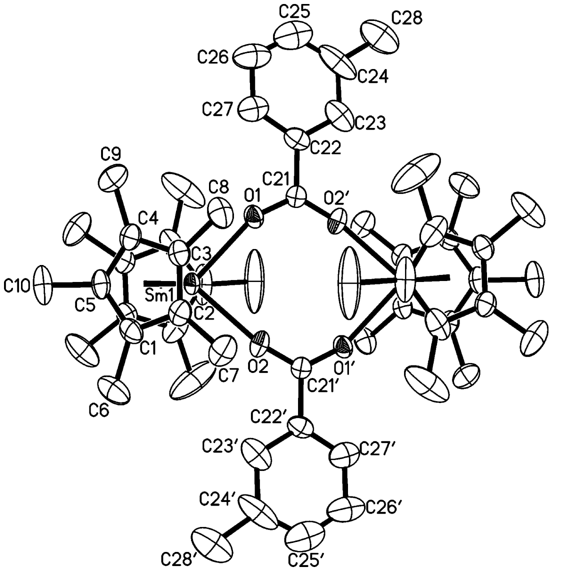
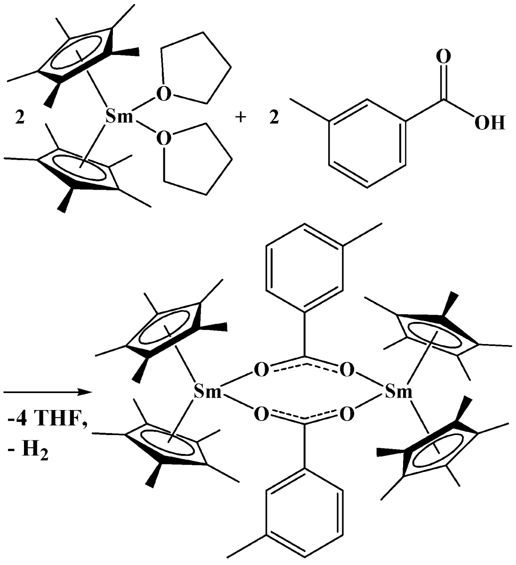


Figure 5. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, drawn at the 50% probability level.

The ^{1}H NMR spectrum of **6** prepared via eq 7 was fully consistent with the structure.



(7)

6

For comparison, the alternative metalation/CO_2 insertion product, the benzyl carboxylate $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, was synthesized similarly according to eq 8 and structurally characterized, Figure 6. Interestingly, the ^{1}H NMR spectrum of **7**

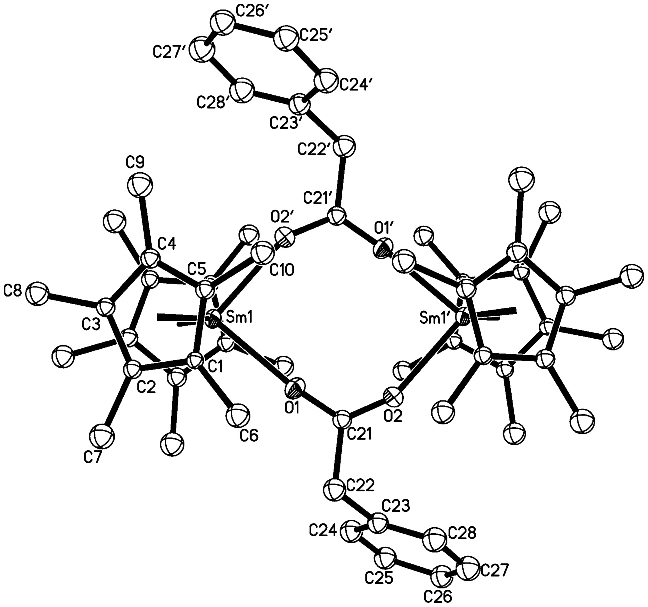
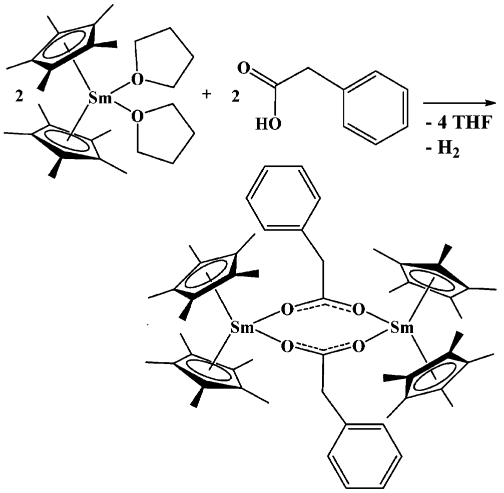


Figure 6. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, with ellipsoids shown at 50% probability.

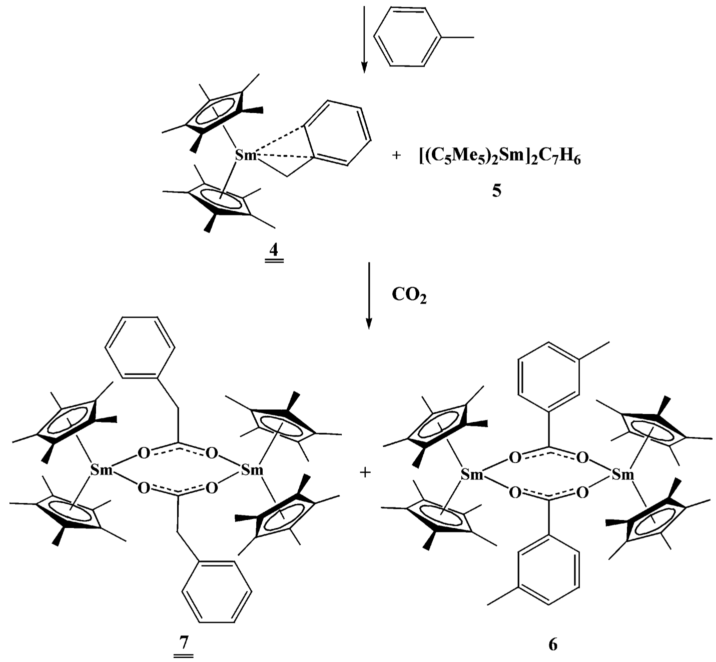


(8)

7

Scheme 4. $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/LiMe Reaction in Toluene Followed by CO_2 Derivatization[a]

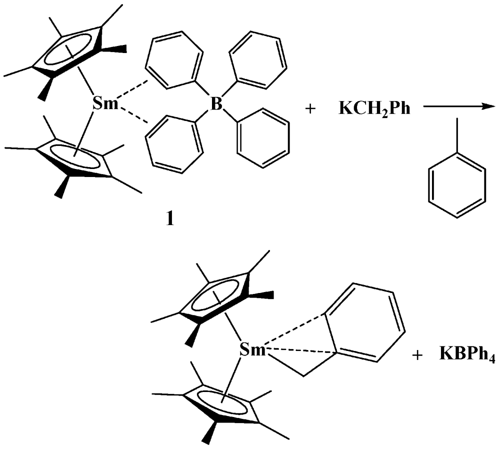
$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]} + LiMe \rightarrow \underset{\mathbf{2}}{1/3\ [(C_5Me_5)_2SmMe]_3} + LiBPh_4$$



[a] Double underlines indicate the major products identified by NMR spectroscopy, but **5** and **6** preferentially crystallized.

matched the NMR spectrum of the CO_2 reaction solution that produced crystals of **6**. This suggested that the CO_2 reaction with the $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/LiMe/toluene product mixture actually formed mainly **7** and that **6** was a less soluble minor product that crystallized preferentially.

To further define this system, $(C_5Me_5)_2Sm(CH_2Ph)$, **4**, was independently synthesized using the tetraphenylborate alkali metal alkyl reaction method of eq 3. Hence, reaction of $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$ with KCH_2Ph, prepared from a mixture of KO^tBu and ^nBuLi in toluene,[28] gave $(C_5Me_5)_2Sm(CH_2Ph)$ in 80% yield according to eq 9.



(9)

The synthesis in eq 9 is a better route to **4** than the earlier method[21] which involved metalation of toluene with $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.[34] In that case, a major byproduct was also formed, the tuckover complex derived from $(C_5Me_5)^{1-}$ metalation, $[(C_5Me_5)_2Sm(\mu\text{-}H)](\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$.[21] Previous studies also showed that $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ would metalate toluene in higher yield in the presence of cyclohexene, but this synthesis did not provide material suitable for crystallographic analysis.[21]

When compound **4** was prepared via eq 9, this compound finally yielded to structural analysis and was found to be the monomeric trihapto complex, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$, shown in Figure 7. This fully characterized $(C_5Me_5)_2Sm(CH_2Ph)$ complex reacts cleanly with CO_2 to form only the benzylcarboxylate, $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, as expected, eq 10.

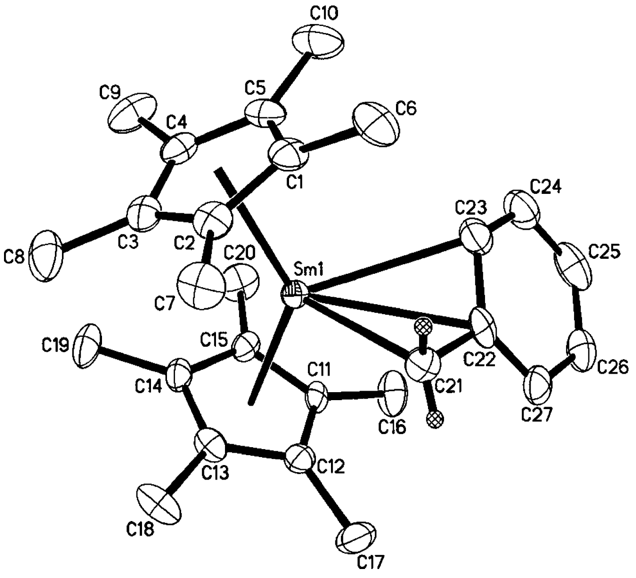
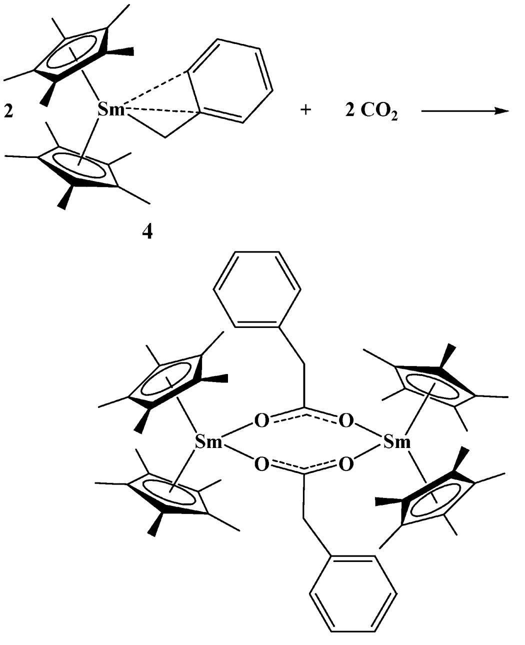


Figure 7. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$, **4**, drawn at the 50% probability level.

These results suggest the sequence of reactions shown in Scheme 4. The **1**/LiMe/toluene reaction produces $[(C_5Me_5)_2$-

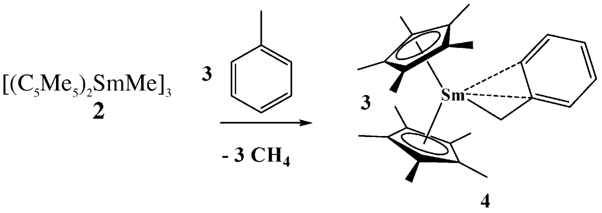


7

(10)

SmMe]$_3$, **2**, which metalates the toluene solvent to make $(C_5Me_5)_2Sm(CH_2Ph)$, **4**, as the major component (by NMR spectroscopy) which contains a small amount of another species which crystallizes as the disordered **5**. This mixture of **4** and **5** reacts with CO_2 to make primarily $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, according to eq 10, but the least soluble product that crystallizes first is the *meta*-carboxylate, $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, which presumably arises from the minor component (possibly related to **5**) in the **1**/LiMe/toluene reaction.

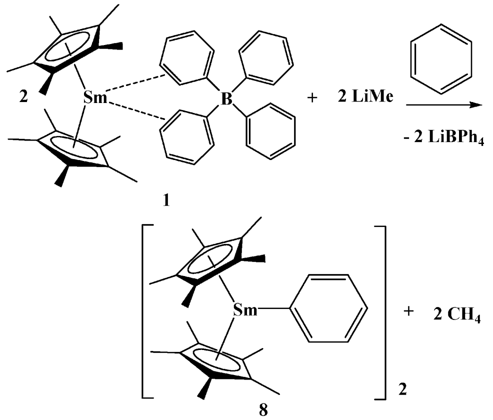
To add further credence to this interpretation, independently isolated $[(C_5Me_5)_2SmMe]_3$, **2**, was treated with toluene and found to make primarily $(C_5Me_5)_2Sm(CH_2Ph)$, **4**, eq 11.



(11)

However, as in the metalation of toluene by $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, the ^{1}H NMR spectrum of the reaction mixture contained other resonances in the C_5Me_5 region. In this case, two other resonances are found at δ 0.78 and 1.48 ppm, neither of which match fully characterized samarium metallocenes previously identified. The total integrated intensity of these peaks was one-third that of the C_5Me_5 resonance of $(C_5Me_5)_2Sm(CH_2Ph)$.

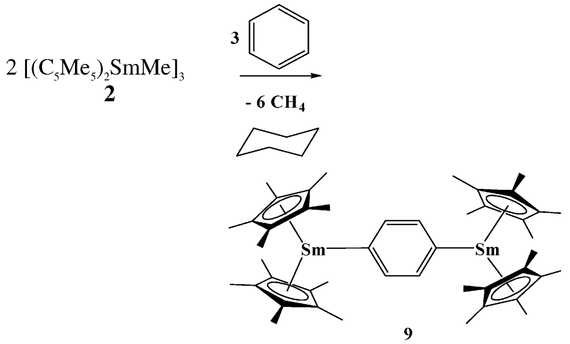
Benzene. Like toluene, benzene is also metalated by the **1**/LiMe system: reaction of LiMe with **1** in benzene gives an immediate reaction. The reaction product, $[(C_5Me_5)_2SmPh]_2$, **8**, eq 12, was identified by ^{1}H NMR spectroscopy in comparison with the samples previously prepared by other methods. These



(12)

include reduction of $BiPh_3$ with $(C_5Me_5)_2Sm$, which produces **8** as a byproduct[32,33] and the reaction of $(C_5Me_5)_2Sm$ and $HgPh_2$, a study which reported that **8** was a dimer by molecular weight studies.[31] Although crystallographic characterization of **8** was not obtained in these studies, its THF addition product, $(C_5Me_5)_2SmPh(THF)$, made from $(C_5Me_5)_2Sm(THF)_2$ and $HgPh_2$, was characterized by X-ray diffraction.[52]

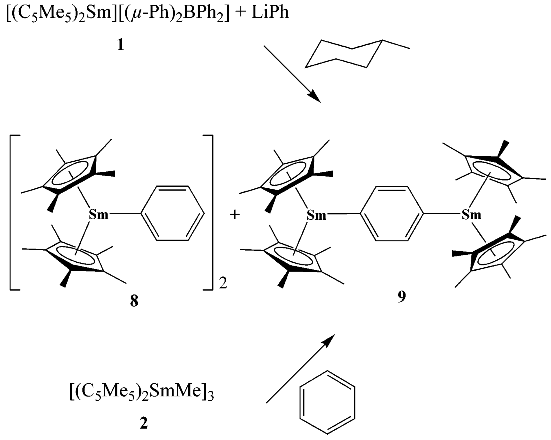
Although **8** did not yield to crystallization, crystals of the dimetalated product, $[(C_5Me_5)_2Sm]_2(C_6H_4)$, **9**, were obtained by reaction of **2** with benzene in cyclohexane according to eq 13.



(13)

This product was previously identified and crystallographically characterized in the $(C_5Me_5)_2Sm/HgPh_2$ reaction system.[31] Clearly, dimetalation of arenes is possible in this active methyl system (cf. **5** above).

Complex **8** can also be made from $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$ and LiPh in methylcyclohexane, but the product is a mixture of **8** and **9**. Similarly, reaction of isolated $[(C_5Me_5)_2SmMe]_3$, **2**, with neat benzene generates **8** and **9** by ^{1}H NMR spectroscopy, eq 14.



(14)

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(51) Evans, W. J.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **1998**, *17*, 2103.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, $[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, **11**, $[(C_5Me_5)_2Sm(O_2CPh)]_2$,[51] and $[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)]_2$[51]

compound	**6**	**7**	**11**	$[(C_5Me_5)_2Sm(O_2CPh)]_2$	$[(C_5Me_5)_2Sm(O_2CCH_2CH{=}CH_2)]_2$
Sm−C(ring) avg	2.725(4)	2.718(7)	2.73(2)	2.720(6)	2.729(3)
Sm−O(1)	2.328(3)	2.303(2)	2.330(2)	2.303(4)	2.327(2)
Sm−O(2)	2.311(3)	2.333(3)	2.317(3)	2.317(4)	2.307(2)
Sm−O(3)			2.309(3)		
Sm−O(4)			2.335(3)		
C−O	1.260(5) 1.256(5)	1.263(4) 1.256(4)	1.260(4) 1.261(4) 1.266(4) 1.266(4)	1.265(6) 1.252(6)	1.257(3) 1.252(3)
Cnt−Sm−Cnt	131.9	133.5	131.7	133.1	133.4
O−Sm−O	89.06(10)	88.95(9)	89.34(10)	87.36(13)	90.85(7)
O(1)−C(O_2C)−O(2′)	124.8(4)	124.7(3)	123.1(4)	124.4(5)	
C(O_2C)−C(R or Ar)	1.506(5)	1.515(5)	1.498(5) 1.499(5)	1.492(7)	

Structures of Arene Derived Products. The structures of the carboxylates, $[(C_5Me_5)_2Sm(O_2CC_6H_4Me\text{-}m)]_2$, **6**, and $[(C_5Me_5)_2Sm(O_2CCH_2Ph)]_2$, **7**, Figures 4 and 5, respectively, are structurally similar to those of $[(C_5Me_5)_2Sm(O_2CPh)]_2$ and $[(C_5Me_5)_2Sm(O_2CCH_2CHCH_2)]_2$,[51] prepared from reactions of CO_2 with **8** and $(C_5Me_5)_2Sm(CH_2CHCH_2)$. As shown in Table 3, the metrical parameters for the carboxylates do not vary extensively regardless of the substituent, i.e., phenyl, benzyl, or allyl. The eight atoms in the SmOCOSmOCO rings in **6** and **7** are coplanar to within 0.09 and 0.10 Å, respectively.

The structure of the benzyl complex,$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$ **4**, which has eluded us for many years, proved to be isomorphous with the cerium analogue obtained from metalating toluene with $(C_5Me_5)_2Ce[CH(SiMe_3)_2]$.[17] Evidently the small change in radial size from 1.143 Å for formally eight-coordinate Ce(III) to 1.079 Å for Sm(III),[47] made the samarium complex much more difficult to isolate in crystalline form. Complex **4** crystallizes in the solid state as a monometallic species in which the ligand adopts a η^3-arrangement. This is formally similar to the crystallographically characterized samarium allyl complexes $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2\text{-}Me)$.[22] Table 4 compares the metrical data on these three complexes as well as the cerium analogue. As expected, the bond distances in **4** are shorter than those in the cerium complex by the difference in their ionic radii, 0.07 Å.[47] Other structural features are similar to the cerium complex, whose structure has been thoroughly discussed previously.[18]

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$, **4**, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$,[22] $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$,[22] $[(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_2)]_2$,[22] and $(C_5Me_5)_2Ce(\eta^3\text{-}CH_2Ph)$[17]

complex	**4**	$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$	$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$	$[(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_2)]_2$	$(C_5Me_5)_2Ce(\eta^3\text{-}CH_2Ph)$
Ln−C(ring)-average	2.736(3), 2.703(3)	2.724(30)	2.727(20), 2.729(30)	2.725(27), 2.728(27)	2.76(3), 2.80(3)
Cn−Ln−Cn	136.4	140.3	138.9, 139.1	138.7, 137.8	137.5(2)
C(A)−Ln−C(C)[a]	55.63(14)	57.1(8)	55.6(5), 56.5(5)	54.2(6), 55.8(6)	53.6
Ln−C(A)	2.518(4)	2.630(15)	2.551(17), 2.579(17)	2.575(17), 2.560(17)	2.596(5)
Ln−C(B)	2.820(4)	2.668(18)	2.689(16), 2.659(15)	2.680(16), 2.686(15)	2.885(6)
Ln−C(C)	2.816(4)	2.643(18)	2.715(14), 2.674(16)	2.730(17), 2.721(16)	2.882(6)
C(A)−C(B)	1.470(6)	1.465(32)	1.401(22), 1.392(22)	1.377(24), 1.348(22)	1.451(7)
C(B)−C(C)	1.404(6)	1.369(32)	1.358(24), 1.380(25)	1.363(24), 1.348(22)	1.39(1)
C−C−C	121.1(4)	125.6(20)	126.3(15), 127.6(15)	124.2(18), 125.9(16)	121.8

[a] The allyl carbon atoms are labeled as follows: $\eta^3\text{-}C^AH_2C^BHC^CHR$.

The isolation of **4** allows a comparison of benzyl versus allyl coordination with the same metal. As is typical for metallocene derivatives of this type, **4** has C_5Me_5 metrical parameters similar to those of the related allyl complexes in Table 4. The samarium benzyl complex has a 121.1(4) Å C−C−C angle involving the three closest carbon atoms which is also similar to the analogous 124(2)°−127.6(15)° angles in the previously characterized $(C_5Me_5)_2Sm(CH_2CHCHR)$ complexes (R = H, Me, $CH_2CH_2CHCHCH_2$).[22] Complex **4** differs from the allyl complexes in that there is a greater discrepancy between the bond distances to the three closest carbons. Hence, the difference between the 2.518(4) Å Sm−C(21) length and the 2.820(4) and 2.816(4) Å distances to C(22) and C(23), respectively, is greater than that in the allyl compounds. The three Sm−C distances in $(C_5Me_5)_2Sm(CH_2CHCH_2)$ are quite similar, 2.630(15)−2.668(18) Å, and in the substituted allyls, $(C_5Me_5)_2Sm(CH_2CHCHR)$, one Sm−C distance is in the range 2.55(2)−2.58(2) Å and the others 2.659(15)−2.73(2) Å. Hence, the benzyl interaction appears to be more localized on one carbon than in the allyl complexes. In fact, the Sm−C(21) length is equivalent to the 2.528(8) Å Sm−C(CH_2Ph) single bond in $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2Ph)(THF)$.[21]

Metalation of Tetramethylsilane. $[(C_5Me_5)_2SmMe]_3$, **2**, metalates tetramethylsilane in methylcyclohexane to generate $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$, **10**, according to eq 15. This complex can be obtained more directly by the tetraphenylborate/alkyllithium route, eq 16.

$$\underset{\mathbf{2}}{[(C_5Me_5)_2SmMe]_3} + Me_4Si \rightarrow \underset{\mathbf{10}}{[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x} + CH_4 \quad (15)$$

$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]} + LiCH_2SiMe_3 \rightarrow \underset{\mathbf{10}}{[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x} + LiBPh_4 \quad (16)$$

The ^1H NMR spectrum of **10** showed a single C_5Me_5 resonance which was not nearly as broad as the analogous signal in **2**. Single CH_2SiMe_3 and CH_2SiMe_3 resonances could also be located, the latter shifted to 15.3 ppm due to the paramagnetism of Sm(III). Crystals suitable for X-ray diffraction studies were isolated, but a suitable refinement was not obtained possibly due to a twinning problem. However, a crystallographically charcterizable derivative of **10** was obtained by reaction with CO_2, namely $[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, **11**. As shown in eq 17 and Figure 8, **11** has a dimeric structure similar to those of **6** and **7**. As shown in Table 3, the metrical parameters of **11**

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(52) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood. J. L. *Organometallics* **1985,** *4*, 112.

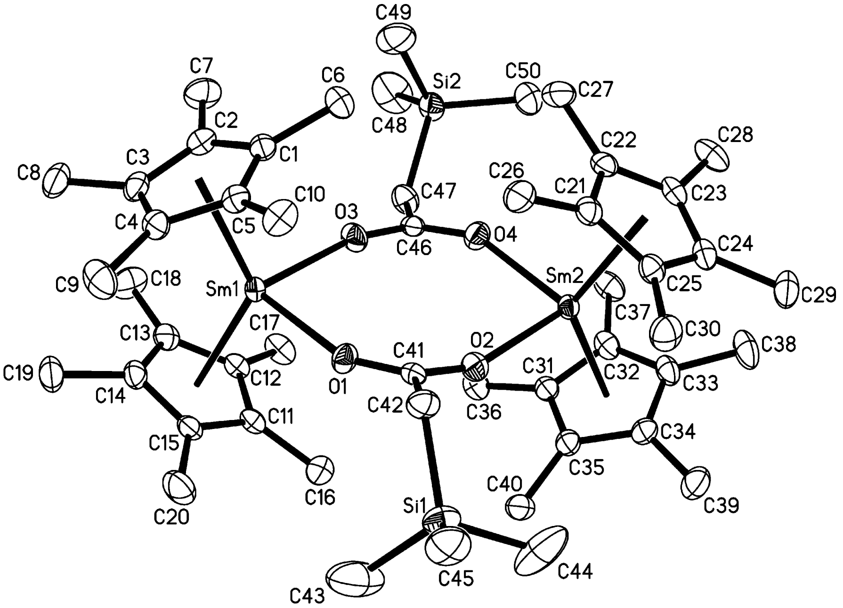
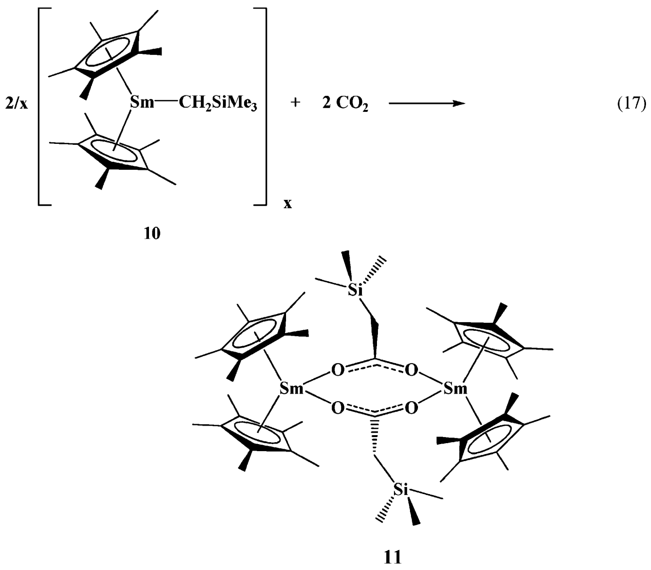


Figure 8. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(O_2CCH_2SiMe_3)]_2$, **11**, with ellipsoids shown at 50% probability.

are also similar to those of the other samarocene carboxylates.



Metalation of Pentamethylcyclopentadienide. In the course of these studies a highly metalated complex containing a doubly metalated pentamethylcyclopentadienide ion, i.e., the trianion, $[(C_5Me_3(CH_2)_2]^{3-}$ was also obtained. This complex, $(C_5Me_5)_6Sm_4[(C_5Me_3(CH_2)_2]_2$, **12**, is shown in Figure 9. Despite the complexity of this species, which might suggest it is just a rogue polymetallic that crystallized from solution,[53] an analogous cerium species was previously identified by Teuben et al. in their studies of the metalation chemistry of $(C_5Me_5)_2Ce[CH(SiMe_3)_2]$.[18] Hence, these tetrametallic species might be another general type of metalation product in the $[(C_5Me_5)_2LnR]_x$ system like the tuckover species, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$ (Ln = La,[54] Sm,[21] Y[55]) which involve monometalation of a $(C_5Me_5)^{1-}$ ring. The cerium complex is not isomorphous with **12** since it crystallized with cyclohexane in the lattice and **12** crystallized in an unsolvated form. Otherwise the two complexes are very similar. Although **12** was identified by X-ray crystallography, the quality of the data was not sufficient for a detailed discussion of bond distances.

Discussion

Synthesis. The reaction of the tetraphenylborate complexes, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, with alkali metal alkyls is a convenient route to unsolvated $[(C_5Me_5)_2LnR]_x$ complexes as shown by the syntheses of $[(C_5Me_5)_2SmMe]_3$, **2**, $[(C_5Me_5)_2LuMe]_2$, **3**, $[(C_5Me_5)_2LaMe]_x$, $(C_5Me_5)_2Sm(CH_2Ph)$, **4**, and $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$, **10**, in eqs 3, 5, 6, 9, and 16. The aryl

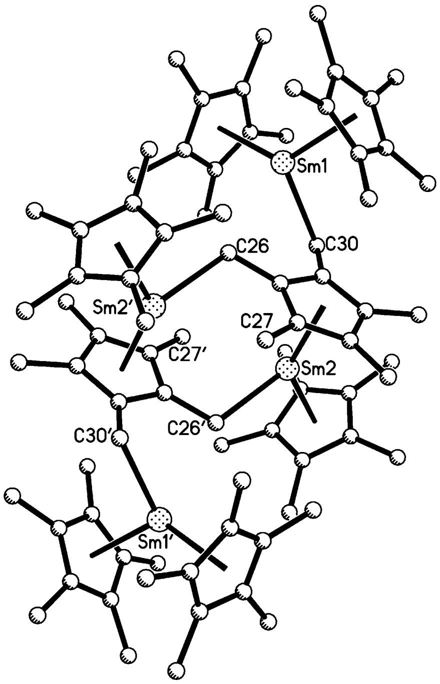


Figure 9. Ball-and-stick figure of $(C_5Me_5)_6Sm_4[(C_5Me_3(CH_2)_2]_2$, **12**.

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(53) Anwander, R. *Angew. Chem., Int. Ed.* **1998**, *37,* 599.
(54) Evans, W. J.; Perotti, J. M.; Ziller, J. W. Unpublished results.
(55) Booji, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.

complex $[(C_5Me_5)_2SmPh]_2$, **8**, can also be made in this way, eq 14. This synthetic approach is convenient, since the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ precursors can be readily made in large scale by the sequence of reactions shown in Scheme 2[23] and since the alkyllithium reagents are commercially available. The successful synthetic results with the largest and smallest lanthanides, La and Lu, and with intermediate-sized Sm suggest that the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/RLi reaction is general and should overcome the synthetic barriers to these complexes that may have previously inhibited study of their chemistry.

To the extent that other alkali metal reagents, MX (X = a small anion), are conveniently available, the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/MX route to *unsolvated* $[(C_5Me_5)_2LnX]_x$ complexes should be quite general for a variety of X, eq 18.

$$\underset{\mathbf{1}}{[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]} + MX \rightarrow [(C_5Me_5)_2SmX]_x + MBPh_4 \quad (18)$$

For example, this route should work well for formation of unsolvated metallocene derivatives of small amides, $[(C_5Me_5)_2Ln(NR_2)]_x$, alkoxides, and aryloxides, $[(C_5Me_5)_2Ln(OR)]_x$, chalcogenides, $[(C_5Me_5)_2Ln(SR)]_x$, silyls, $[(C_5Me_5)_2Ln(SiR_3)]_x$, etc.

The high metalation reactivity of the pentamethylmetallocene methyls provides another synthetic pathway to $[(C_5Me_5)_2LnR]_x$ complexes when alkyllithium reagents are *not* available for $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/LiR reactions. In these cases, it is possible to use the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/LiMe reaction product in situ to metalate a wide variety of organic compounds, RH, to make $[(C_5Me_5)_2LnR]_x$ complexes by C−H activation, eq 19.

$$[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2] + LiMe + RH \rightarrow [(C_5Me_5)_2LnR]_x + LiBPh_4 + CH_4 \quad (19)$$

Given the low acidity of the methane byproduct of this reaction, this approach is thermodynamically favorable for numerous classes of organic substrates. This means that unsolvated $[(C_5Me_5)_2LnR]_x$ complexes should be accessible even if the RLi precursors are not readily available. Equations 11−15 demonstrate this metalation approach to $[(C_5Me_5)_2LnR]_x$ complexes derived from benzene, toluene, and tetramethylsilane. The isolation of $(C_5Me_5)_6Sm_4[C_5Me_3(CH_2)_2]_2$, **12**, formed by dimetalation of $(C_5Me_5)^{1-}$ provides another example.

This metalation-based synthetic approach is also available with substrates other than hydrocarbons, eq 20.

$$[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2] + LiMe + XH \rightarrow [(C_5Me_5)_2LnX]_x + LiBPh_4 + CH_4 \quad (20)$$

Again, any HX more acidic than methane should be reactive. This provides an approach complementary to eq 18 for unsolvated $[(C_5Me_5)_2LnX]_x$ complexes when alkali metal MX reagents are not available. It should be applicable to amines, alcohols, phenols, thiols, silanes, etc. Note that when MX reagents are used for formation of $[(C_5Me_5)_2LnX]_x$ complexes, the solvent is generally an ether and the product is solvated, $(C_5Me_5)_2LnX$(ether) or an alkali metal adduct is formed, e.g., $(C_5Me_5)_2LnX_2M$(ether)$_2$. Only when the X is very large, like $[N(SiMe_3)_2]^{1-}$, can unsolvated $(C_5Me_5)_2LnX$ complexes be obtained from MX and $(C_5Me_5)_2LnCl_2M$(ether)$_2$.[17,56] The chemistry of unsolvated $[(C_5Me_5)_2LnX]_x$ complexes in which X is small is relatively unexplored.

C−H Activation Reactivity. As anticipated based on past results,[4−10,12,18] the unsolvated $[(C_5Me_5)_2SmMe]_3$, **2**, exhibits high C−H activation behavior. This causes cycloalkane solvents to be required for the $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/LiMe reaction but provides the opportunity to use **2** to generate a variety of other $[(C_5Me_5)_2SmR]_x$ complexes. The Sm−Me-based metalations of toluene, benzene, tetramethylsilane, and even the pentamethylcyclopentadienide anion, eqs 11−15, demonstrate how the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/LiMe reaction can provide a synthetic entry to unsolvated metallocene alkyls high in C−H activation reactivity. Since $[(C_5Me_5)_2LuMe]_2$, **3**, is now more readily accessible by this route, further development of its chemistry is not inhibited by synthetic barriers. Although the analogous lanthanum complex has so far proven to be too reactive to allow crystallographic characterization, the $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$/LiMe reaction still allows lanthanum-based C−H activation chemistry to be studied.

The isolation of the doubly metalated pentamethylcyclopentadienide ligand, $[C_5Me_3(CH_2)_2]^{3-}$, in $(C_5Me_5)_6Sm_4[C_5Me_3(CH_2)_2]_2$, **12**, suggests that the analogous cerium complex, discovered earlier, is not just an unusual lanthanide polymetallic.[18] It now seems likely that $(C_5Me_5)_6Ln_4[C_5Me_3(CH_2)_2]_2$ complexes are possible byproducts in any lanthanide metallocene reaction that could have a $[(C_5Me_5)_2LnR]_x$ intermediate. Hence, these tetrametallic species join the tuckover species, $(C_5Me_5)_2Ln(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Ln(C_5Me_5)$,[21,54,55] generated by single metalation of a pentamethylcyclopentadienide, as alternative products which may result in alkylmetallocene reactions. Ironically, $(C_5Me_5)^{1-}$ was initially introduced to lanthanide chemistry to avoid the unfavorable metalation chemistry which limited the use of lanthanide complexes of simple C_5H_4R cyclopentadienyl ligands (R = H, Me).[57,58] Clearly, if the activity of the Ln−Me unit can be increased enough, even the $(C_5Me_5)^{1-}$ anion is not immune to metalation. The fact that the $(C_5Me_5)_6Ln_4[C_5Me_3(CH_2)_2]_2$ complexes were isolated with larger metals earlier in the lanthanide series, rather than the sterically more limited smaller metals (e.g., with small scandium $[(C_5Me_5)Sc(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)]_2$ forms[59]), reflects the higher reactivity expected from the sterically less saturated $[(C_5Me_5)_2LnR]_x$ complexes.

Structural Aspects. The reactions in Scheme 4 provide a clear reminder of the well-known but sometimes overlooked problem that the material that crystallizes may not be representative of the bulk product in solution. In this case, the crystalline materials isolated *both* from the $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/LiMe/toluene reaction and the subsequent reaction with CO_2 (that was used to get better structural information!) were misleading in terms of the bulk species in solution. Fortunately, despite the paramagnetism of this system, fingerprint ^1H NMR data could be obtained for all of the main components by independent synthetic routes. This allowed the bulk chemistry occurring in solution to be differentiated from

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the chemistry implied by the structures of the least soluble byproducts which crystallized from solution.

The structures of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2Ph)$, **4**, and the $[(C_5Me_5)_2LnMe]_x$, complexes, **2** (Sm) and **3** (Lu), constitute good examples of how the large electrophilic lanthanides consistently seek additional electron density to alleviate steric unsaturation. Since the benzyl group is well-known to form η^3-structures, the structure of **4** is not unexpected, although it could have adopted an oligomeric variation that ostensibly would be as sterically saturated. Since the $Sm-C(CH_2)$ bond in **4** is equivalent to the single bond in $(C_5Me_5)_2Sm(\eta^1\text{-}CH_2Ph)(THF)$, the η^3-structure in **4** is not as delocalized as that found with three coordinating carbon atoms in the allyl complexes $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ (R = H, Me, $CH_2CH_2CHCHCH_2$).[22] Instead, the tipped nature of the phenyl substitutent in **4** is acting more like an agostic interaction from another part of an η^1-bound ligand or the bridging methyl groups in the $[(C_5Me_5)_2LnMe]_x$ complexes.

The differences between trimeric **2** and dimeric **3** diminish when the extended structures of these complexes are examined, Figure 3. The extended structures suggest that each seven-coordinate metal center in these structures attempts to increase its steric saturation by coordinating to another methyl. In **3**, the intermolecular bridging methyl may be located so far away because of steric constraints caused by small lutetium. This steric limitation is alleviated to some extent with the larger samarium in **2** and the central $[(C_5Me_5)_2Sm]^{1+}$ metallocene can accommodate two bridging methyl groups. Nevertheless, a seven-coordinate samarium is still preserved in **2**, and it attempts to gain more electron density via intermolecular orientation toward a terminal methyl of another molecule.

Conclusion

The reaction of $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ with alkyllithium reagents provides facile access to unsolvated alkyl lanthanide metallocenes, $[(C_5Me_5)_2LnR]_x$, which display high C−H activation reactivity. In the cases in which alkyllithium reagents are not easily available, the high metalation reactivity of $[(C_5Me_5)_2LnMe]_x$ complexes obtainable in situ from LiMe and $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ can provide unsolvated $[(C_5Me_5)_2LnR]_x$ products. The isolation of doubly metalated toluene, benzene, and pentamethylcyclopentadienide derivatives in this study emphasizes the high C−H activation reactivity available via unsolvated alkyls. The facile synthetic pathways now available to these alkyls may provide better opportunities to explore the productive use of this C−H activation reactivity.

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Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles; listing of observed and calculated structure factor amplitudes for compounds **2**−**4**, **6**, **7**, and **11** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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