

## Reactivity of $(C_5Me_5)_3LaL_x$ Complexes: Synthesis of a Tris(pentamethylcyclopentadienyl) Complex with Two Additional Ligands, $(C_5Me_5)_3La(NCCMe_3)_2$

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**Abstract:** The limits of steric crowding in tris(pentamethylcyclopentadienyl) complexes have been expanded by isolation of the first compound with this ligand set and two additional ligands,  $(C_5Me_5)_3ML_2$ . This result was obtained in a study of the effect of added ligands on the reactivity of sterically crowded  $(C_5Me_5)_3La$ , **1**. Although neither THF nor  $Ph_3PO$  formed crystallographically characterizable  $(C_5Me_5)_3LaL_x$  complexes with **1**, these  $(C_5Me_5)_3La/L_x$  mixtures displayed enhanced reactivity compared to **1** with substrates such as  $C_8H_8$  and  $CO_2$ . Attempts to use adamantyl azide,  $AdN_3$ , to make  $(C_5Me_5)_3LaL_x$  complexes led to the first example of azide insertion into a metal cyclopentadienyl linkage to generate  $(C_5Me_5)_2La[\eta^2-(N,N')-(C_5Me_5)NN'N''Ad](N_3Ad)$ . Addition of  $Me_3CCN$  to **1** produced the first crystallographically characterized  $(C_5Me_5)_3ML_2$  complex,  $(C_5Me_5)_3La(NCCMe_3)_2$ .

### Introduction

Prior to the isolation of  $(C_5Me_5)_3Sm$ ,<sup>1</sup> it was believed that  $(C_5Me_5)_3M$  complexes were too sterically crowded to exist. This was reasonable since the cone angle of the  $(C_5Me_5)^{1-}$  ligand was estimated to be  $142^\circ$ .<sup>2</sup> Isolation of  $(\eta^5-C_5Me_5)_3M$  complexes ( $M = La$ ,<sup>3</sup>  $Ce$ ,<sup>4</sup>  $Pr$ ,<sup>4</sup>  $Nd$ ,<sup>5</sup>  $Sm$ ,<sup>1</sup>  $Gd$ ,<sup>6</sup>  $Y$ ,<sup>6</sup>  $U$ <sup>7</sup>) showed that the  $(C_5Me_5)^{1-}$  ligand could adopt a  $120^\circ$  cone angle by positioning the three rings further from the metal than had ever been observed before. These “long bond organometallics” showed that, under the proper synthetic conditions, it was possible to make an entire new series of  $(C_5Me_5)^{1-}$  complexes with longer than conventional bond lengths.

The  $(C_5Me_5)_3M$  complexes not only were structurally unusual but also displayed unexpected reactivity. The normally inert  $(C_5Me_5)^{1-}$  ligand was found to adopt three types of sterically induced reactivity. With some substrates, the  $(C_5Me_5)_3M$  complexes act as one-electron reductants where a  $(C_5Me_5)^{1-}$  ligand delivers an electron and forms  $(C_5Me_5)_2^{4,8-11}$  as a

byproduct in a process called sterically induced reduction (SIR). A second type of reaction involves  $\eta^1$ -like  $(C_5Me_5)^{1-}$  reactivity. These reactions include  $CO$  and  $CO_2$  insertion,<sup>4,12</sup> olefin polymerization,<sup>7</sup> and hydrogenolysis.<sup>11</sup> A third type of reaction, ligand displacement of one of the pentahapto  $(C_5Me_5)^{1-}$  ligands by the typically monohapto  $[N(SiMe_3)_2]^{1-}$ , has been observed with  $(C_5Me_5)_3U$ .<sup>13</sup>

Examination of the reactivity of  $(C_5Me_5)_3U$  showed that it was possible to synthesize tris(pentamethylcyclopentadienyl) complexes that contained a fourth ligand in the coordination sphere. Hence, it was possible to isolate and crystallographically characterize  $(C_5Me_5)_3UF$ ,<sup>14</sup>  $(C_5Me_5)_3UCl$ ,<sup>14</sup>  $(C_5Me_5)_3U(CO)$ ,<sup>15</sup>  $(C_5Me_5)_3U(N_2)$ ,<sup>16</sup>  $(C_5Me_5)_3UMe$ ,<sup>17</sup> and  $(C_5Me_5)_3ThH$ .<sup>18</sup> This showed that even more crowded tris(pentamethylcyclopentadienyl) metal complexes were accessible with actinides.

We report here that the limit of steric crowding does not stop with  $(C_5Me_5)_3ML$ . The structure of  $(C_5Me_5)_3La(NCCMe_3)_2$  reported here is the first example of a tris(pentamethylcyclopentadienyl) lanthanide complex with any extra ligation and the first example of a  $(C_5Me_5)_3ML_2$  complex of any kind. This complex was isolated while studying the effects of Lewis bases on sterically induced reactivity to better understand the correlation of steric crowding and reactivity in these crowded

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complexes. This study also revealed the first insertion of an organoazide into a metal cyclopentadienyl linkage.

## Experimental Section

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents were dried over a sodium–potassium alloy, degassed, and vacuum transferred prior to use.  $Ph_3PO$  and adamantyl azide were purchased from Aldrich and placed under vacuum ( $10^{-3}$  Torr) for 12 h prior to use.  $C_8H_8$ ,  $Me_3CCN$ , and  $CS_2$  were distilled onto 4A molecular sieves and degassed by three freeze–pump–thaw cycles before use.  $CO_2$  was purchased from Airgas and used as received.  $(C_5Me_5)_3La$ ,  $1^3 [(C_5Me_5)_2La][BPh_4]^5$  and  $(C_5Me_5)_2La[O(CH_2)_4C_5Me_5](THF)_2^4$  were prepared as previously described.  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectra were obtained on a Bruker DRX500 MHz spectrometer at 25 °C. IR samples were prepared as KBr pellets, and the spectra were obtained on a Varian 1000 FT-IR system. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer or by complexometric titration.<sup>19</sup>

$(C_5Me_5)_3La(C_8H_8)(THF)$ , **2**.  $C_8H_8$  (1.7  $\mu$ L, 0.015 mmol) was added *via* syringe to **1** (16 mg, 0.029 mmol) in 1 mL of  $C_6D_6$  and transferred to a J-Young tube. Tetrahydrofuran (2.5  $\mu$ L, 0.031 mmol) was added *via* syringe to the J-Young tube. The solution was degassed by three freeze–pump–thaw cycles. Over 24 h at 25 °C, the previously characterized  $(C_5Me_5)_3La(C_8H_8)(THF)^{20}$  was observed by  $^1H$  NMR spectroscopy (40%) along with **1** and unreacted  $C_8H_8$ . After heating the sample for 14 d at 60 °C, a 77% conversion from **1** to  $(C_5Me_5)_3La(C_8H_8)(THF)$  was observed by  $^1H$  NMR spectroscopy.

$[(C_5Me_5)_3La(OPPh_3)_2]_x$ , **3**.  $Ph_3PO$  (137 mg, 0.492 mmol) in 4 mL of toluene was added to a stirred solution of **1** (113 mg, 0.207 mmol) in 4 mL of toluene. The solution immediately turned from yellow to dark gray. After stirring for 2 h, the solution was centrifuged and the toluene solution was decanted. The remaining dark gray insoluble material was washed with hexane, and excess solvent was removed under reduced pressure to yield a dark gray powder (182 mg, 80%). IR: 2960m, 2901m, 2854m, 2814m, 2361w, 1588w, 1484w, 1438s, 1197w, 1138s, 1121s, 1067s, 1026w, 998w, 752m, 723s, 694s  $cm^{-1}$ . Anal. Calcd for  $[(C_5Me_5)_3La(OPPh_3)_2]_x$ : C, 71.79; H, 7.12; La, 12.6. Found: C, 71.20; H, 6.74; La, 12.4. Melting point: 178 °C.

$[(C_5Me_5)_2La(OPPh_3)_2][BPh_4]$ , **4**.  $Ph_3PO$  (78 mg, 0.28 mmol) in 5 mL of  $C_6H_6$  was added to a stirred solution of  $[(C_5Me_5)_2La][BPh_4]^5$  (103 mg, 0.14 mmol) in 5 mL of  $C_6H_6$ . After 12 h, a white precipitate had formed and was separated by centrifugation. The white powder was subsequently washed with  $C_6H_6$  and hexane to yield a white powder (180 mg, 99%). Colorless X-ray quality crystals were grown from a hot toluene solution slowly cooled to room temperature.  $^1H$  NMR ( $THF-d_8$ )  $\delta$  7.74 (m, 8 H,  $BPh_4$ ) 7.64 (m, 12 H,  $OPPh_3$ ), 7.54 (m, 12 H,  $OPPh_3$ ), 7.29 (m, 6 H,  $OPPh_3$ ), 6.81 (m, 8 H,  $BPh_4$ ), 6.67 (m, 4 H,  $BPh_4$ ), 1.74 (s, 30 H,  $C_5Me_5$ ).  $^{13}C$  NMR ( $THF-d_8$ )  $\delta$  137.39 ( $OPPh_3$ ), 134.96 ( $BPh_4$ ), 133.74 ( $OPPh_3$ ), 130.39 ( $OPPh_3$ ), 125.86 ( $BPh_4$ ), 121.93 ( $BPh_4$ ), 121.59 ( $C_5Me_5$ ), 11.92 ( $C_5Me_5$ ). IR: 3050m, 3035m, 2983m, 2906m, 2858m, 1818w, 1590m, 1580m, 1483m, 1438s, 1383w, 1313w, 1266w, 1186w, 1138s, 1121s, 1066s, 1028m, 999m, 845m, 748m, 726s, 704s, 613m, 541s  $cm^{-1}$ . Anal. Calcd for  $C_{80}H_{80}BLaO_2P_2$ : C, 74.77; H, 6.27. Found: C, 74.22; H, 6.28. Melting point: 260 °C (decomp).

$(C_5Me_5)_2La[O(CH_2)_4C_5Me_5](OPPh_3)_2$ , **5**. THF (15  $\mu$ L, 0.18 mmol) was added *via* syringe to a stirred solution of **3** (114 mg,

0.104 mmol) in 5 mL of toluene. An immediate color change from dark gray to colorless was observed, and the solvent was removed under reduced pressure to yield a colorless tacky solid (118 mg, 97%).  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.69 (m, 12 H,  $OPPh_3$ ), 7.07 (m, 18 H  $OPPh_3$ ), 4.30 (t, 2 H,  $OCH_2$ ), 2.13 (s, 30 H,  $C_5Me_5$ ), 1.82 (s, 6 H,  $C_5Me_5$ ), 1.79 (s, 6 H,  $C_5Me_5$ ), 1.74 (m, 2 H,  $CCH_2$ ), 1.67 (m, 5 H,  $CCH_2$ ), 1.01 (s, 3 H,  $C_5Me_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  140.95 ( $C_5Me_5$ ), 134.25 ( $C_5Me_5$ ), 132.97 ( $OPPh_3$ ), 129.10 ( $OPPh_3$ ), 129.01 ( $OPPh_3$ ), 117.13 ( $C_5Me_5$ ), 69.16 ( $O-CH_2CH_2$ ), 56.85 ( $O-CH_2CH_2$ ), 39.15 ( $CH_2CH_2CH_2$ ), 37.01 ( $CH_2CH_2C$ ), 23.11 ( $C_5Me_5$ ), 21.88 ( $C_5Me_5$ ), 11.77 ( $C_5Me_5$ ), 11.60 ( $C_5Me_5$ ), 10.40 ( $C_5Me_5$ ).  $^{31}P$  NMR ( $C_6D_6$ ):  $\delta$  35.7. IR: 2960m, 2918s, 2853s, 2800w, 1591w, 1485w, 1438s, 1377w, 1155s, 1120s, 1090m, 1073m, 1028w, 998w, 747w, 723s, 694s, 541s  $cm^{-1}$ . Anal. Calcd for  $C_{70}H_{83}LaO_3P_2$ : C, 71.66; H, 7.13. Found: C, 72.16; H, 7.28.

**5 from  $(C_5Me_5)_2La[O(CH_2)_4C_5Me_5](THF)_2$  and  $Ph_3PO$** .  $Ph_3PO$  (26 mg, 0.093 mmol) in 3 mL of toluene was added to a stirred solution of  $(C_5Me_5)_2La[O(CH_2)_4C_5Me_5](THF)_2$  (32 mg, 0.046 mmol) in 1 mL of toluene. After 30 min, the solvent was removed under reduced pressure to yield a colorless tacky solid (49 mg, 99%). The  $^1H$  NMR spectrum of the reaction product matched that of **5**.

$(C_5Me_5)_2La(O_2CC_5Me_5)(OPPh_3)$ , **6**. Complex **3** (46 mg, 0.042 mmol) was added to a flask with 3 mL of toluene, degassed *via* three freeze–pump–thaw cycles, and cooled to  $-78$  °C.  $CO_2$  (1 atm) was introduced into the vessel, and the dark gray mixture immediately turned colorless. After 1 min, the solution was degassed. The solvent was removed under reduced pressure to yield a colorless oil which was triturated with hexane to yield a white powder (43 mg, 89%).  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.83 (m, 6 H,  $OPPh_3$ ), 7.14 (m, 9 H,  $OPPh_3$ ), 2.24 (s, 6 H,  $C_5Me_5$ ), 2.03 (s, 30 H,  $C_5Me_5$ ), 1.87 (s, 6 H,  $C_5Me_5$ ), 1.63 (s, 3 H,  $C_5Me_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  139.31 ( $C_5Me_5$ ), 135.45 ( $C_5Me_5$ ), 133.22 ( $OPPh_3$ ), 129.66 ( $OPPh_3$ ), 129.15 ( $OPPh_3$ ), 129.05 ( $OPPh_3$ ), 118.01 ( $C_5Me_5$ ), 65.69 ( $O_2C$ ), 21.76 ( $C_5Me_5$ ), 20.02 ( $C_5Me_5$ ), 12.36 ( $C_5Me_5$ ), 11.81 ( $C_5Me_5$ ), 11.67 ( $C_5Me_5$ ).  $^{31}P$  NMR ( $C_6D_6$ ):  $\delta$  35.11. IR: 2964s, 2908s, 2855s, 2722w, 1987w, 1588w, 1522s, 1438s, 1403s, 1378m, 1351w, 1150s, 1120s, 1088m, 997m, 751m, 721s, 695s  $cm^{-1}$ . Anal. Calcd for  $C_{67}H_{75}LaO_4P_2$ : C, 70.27; H, 6.60. Found: C, 70.13; H, 6.53.

$(C_5Me_5)_2La(S_2CC_5Me_5)$ , **7**.  $CS_2$  (15  $\mu$ L, 0.25 mmol) was added *via* syringe to a stirred solution of **1** (81 mg, 0.15 mmol) in 5 mL of toluene. After 30 min, the solvent was removed under reduced pressure to yield a yellow powder (92 mg, 99%). Yellow X-ray quality crystals were grown from a concentrated toluene solution at  $-35$  °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  2.06 (s, 6 H,  $C_5Me_5$ ), 1.92 (s, 30 H,  $C_5Me_5$ ), 1.76 (s, 6 H,  $C_5Me_5$ ), 1.71 (s, 3 H,  $C_5Me_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  142.44 ( $C_5Me_5$ ), 138.02 ( $C_5Me_5$ ), 120.72 ( $C_5Me_5$ ), 80.51 ( $S_2C$ ), 23.39 ( $C_5Me_5$ ), 21.92 ( $C_5Me_5$ ), 11.86 ( $C_5Me_5$ ), 11.58 ( $C_5Me_5$ ), 11.07 ( $C_5Me_5$ ). IR: 2969s, 2907s, 2855s, 1657w, 1601w, 1494w, 1437s, 1379s, 1319w, 1129w, 1142m, 1066m, 978s, 954s, 825m, 803w, 744w, 729w, 712m, 694w  $cm^{-1}$ . Anal. Calcd for  $C_{31}H_{45}LaS_2$ : C, 59.98; H, 7.31. Found: C, 59.95; H, 7.83.

$(C_5Me_5)_2La(S_2CC_5Me_5)(OPPh_3)$ , **8**.  $CS_2$  (9  $\mu$ L, 0.15 mmol) was added *via* syringe to a stirred mixture of **3** (76 mg, 0.069 mmol) in 5 mL of toluene. An immediate color change from dark gray to yellow was observed, and the solvent was removed under reduced pressure. The resulting yellow oil was triturated with hexane to yield a tacky yellow solid (81 mg, 99%). Yellow X-ray quality crystals were grown from a concentrated toluene solution at  $-35$  °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.72 (m, 6 H,  $OPPh_3$ ), 7.03 (m, 9 H,  $OPPh_3$ ), 2.21 (s, 6 H,  $C_5Me_5$ ), 2.11 (s, 30 H,  $C_5Me_5$ ), 1.81 (s, 3 H,  $C_5Me_5$ ), 1.79 (s, 6 H,  $C_5Me_5$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  142.74 ( $C_5Me_5$ ), 136.70 ( $C_5Me_5$ ), 133.13 ( $OPPh_3$ ), 129.68 ( $OPPh_3$ ), 128.99 ( $OPPh_3$ ), 128.89 ( $OPPh_3$ ), 118.72 ( $C_5Me_5$ ), 79.51 ( $S_2C$ ), 22.62 ( $C_5Me_5$ ), 21.81 ( $C_5Me_5$ ), 12.39 ( $C_5Me_5$ ), 11.93 ( $C_5Me_5$ ), 11.77 ( $C_5Me_5$ ).  $^{31}P$  NMR ( $C_6D_6$ ):  $\delta$  36.23. IR: 2964s, 2905s, 2854s, 1484w, 1438s, 1378m, 1198m, 1147s, 1119s, 1086m, 1072w, 994m, 964m, 750m, 721s, 694s  $cm^{-1}$ . Anal. Calcd for  $C_{49}H_{60}LaOPS_2$ : C, 65.46; H, 6.73. Found: C, 66.03; H, 6.60.

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(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[N(SiMe<sub>3</sub>)<sub>2</sub>], **9**. KN(SiMe<sub>3</sub>)<sub>2</sub> (3 mg, 0.01 mmol) in 1 mL of C<sub>6</sub>H<sub>6</sub> was added to a stirred solution of **1** (7 mg, 0.01 mmol) in 3 mL of C<sub>6</sub>H<sub>6</sub>. The bright yellow solution immediately turned colorless. After 30 min, white insoluble material was removed by centrifugation and the solvent was removed under reduced pressure to yield a white powder (8 mg, 99%). <sup>1</sup>H NMR spectroscopy showed the product to be consistent with the previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[N(SiMe<sub>3</sub>)<sub>2</sub>].<sup>20</sup> Colorless X-ray quality crystals were grown *via* slow evaporation of a concentrated benzene solution at 25 °C.

**9 from 3 with KN(SiMe<sub>3</sub>)<sub>2</sub>**. KN(SiMe<sub>3</sub>)<sub>2</sub> (4 mg, 0.02 mmol) in 3 mL of toluene was added to a stirred slurry of **3** (22 mg, 0.019 mmol) in 2 mL of toluene. After 30 min, the dark gray slurry turned colorless. White insoluble material was removed by centrifugation, and the solvent was removed under reduced pressure to yield a white powder (22 mg, 98%). <sup>1</sup>H NMR and IR spectroscopy showed resonances consistent with free Ph<sub>3</sub>PO and the previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[N(SiMe<sub>3</sub>)<sub>2</sub>].<sup>20</sup>

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[η<sup>2</sup>-(N,N')-(C<sub>5</sub>Me<sub>5</sub>)NN'N'Ad](N<sub>3</sub>Ad), **10**. Adamantyl azide, (C<sub>10</sub>H<sub>15</sub>)N<sub>3</sub>, (19 mg, 0.11 mmol) in 2 mL of toluene was added to a stirred solution of **1** (30 mg, 0.055 mmol) in 3 mL of toluene. After 24 h, the solvent was removed under reduced pressure to yield a tacky, yellow solid (49 mg, 99%). Yellow X-ray quality crystals were grown from a concentrated toluene solution at -35 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.20 (s, 6 H, C<sub>5</sub>Me<sub>5</sub>), 2.10 (s, 3 H, C<sub>5</sub>Me<sub>5</sub>), 2.01 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.99 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.77 (s, 6 H, Ad-CH), 1.75 (s, 6 H, C<sub>5</sub>Me<sub>5</sub>), 1.64 (s, 12 H, Ad-CH<sub>2</sub>), 1.32 (s, 12 H, Ad-CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 141.05 (C<sub>5</sub>Me<sub>5</sub>), 134.28 (C<sub>5</sub>Me<sub>5</sub>), 120.65 (C<sub>5</sub>Me<sub>5</sub>), 120.48 (C<sub>5</sub>Me<sub>5</sub>), 44.28 (C<sub>5</sub>Me<sub>5</sub>), 42.07 (Ad-CH<sub>2</sub>), 37.60 (C<sub>5</sub>Me<sub>5</sub>), 36.22 (Ad-CH<sub>2</sub>), 30.43 (Ad-CH), 23.81 (C<sub>5</sub>Me<sub>5</sub>), 13.43 (Ad-C), 12.08 (C<sub>5</sub>Me<sub>5</sub>), 11.80 (C<sub>5</sub>Me<sub>5</sub>), 11.69 (C<sub>5</sub>Me<sub>5</sub>). IR: 2963s, 2911s, 2853s, 2124s, 2088m, 1451m, 1439m, 1377w, 1289m, 1186w, 1104w, 1049m, 1019w, 947w, 877w, 813w, 731w, 668m cm<sup>-1</sup>. Elemental analysis was consistent with the base-free adduct (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[η<sup>2</sup>-(N,N')-(C<sub>5</sub>Me<sub>5</sub>)NN'N'Ad]. Anal. Calcd for C<sub>40</sub>H<sub>60</sub>LaN<sub>3</sub>: C, 66.56; H, 8.38; N, 5.82. Found: C, 65.99; H, 8.94; N, 5.55.

(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La(NCCMe<sub>3</sub>)<sub>2</sub>, **11**. Me<sub>3</sub>CCN (35 μL, 0.32 mmol) was added *via* syringe to a stirred solution of **1** (85 mg, 0.16 mmol) in 5 mL of toluene. An immediate color change from yellow to colorless was observed, and after 30 min, the solvent was removed under reduced pressure to yield a white powder (110 mg, 99%). Colorless X-ray quality crystals were grown from a concentrated benzene solution at 25 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.13 (s, 45 H, C<sub>5</sub>Me<sub>5</sub>), 0.89 (s, 18 H, Me<sub>3</sub>CCN). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 119.45 (C<sub>5</sub>Me<sub>5</sub>), 27.68 (CCMe<sub>3</sub>), 13.24 (C<sub>5</sub>Me<sub>5</sub>). Neither the NCC nor CCMe<sub>3</sub> resonances were located. IR: 2976s, 2904s, 2855s, 2256s, 1476m, 1458s, 1439s, 1371s, 1238s, 1018m, 952m, 836w, 731w, 700w, 592m, 561m cm<sup>-1</sup>. Anal. Calcd for C<sub>40</sub>H<sub>63</sub>LaN<sub>2</sub>: C, 67.59; H, 8.93; N, 3.94. Found: C, 68.59; H, 9.41; N, 3.35.

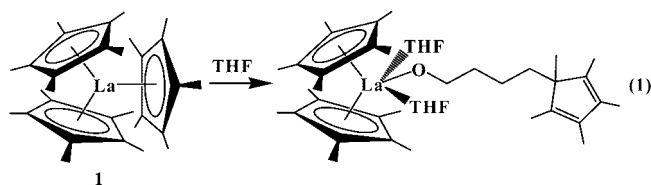
**X-ray Data Collection, Structure Determination, and Refinement for 4 and 7–11.** This information is available in the Supporting Information.

## Results

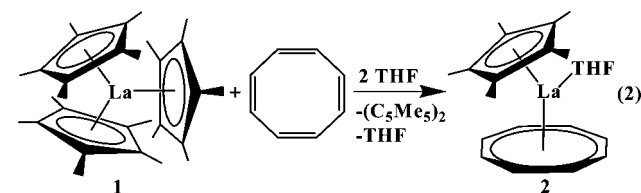
(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La, **1**, was selected to study the effects of Lewis bases on sterically induced reactivity since La<sup>3+</sup> is the largest metal ion known to make (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M complexes and **1** is consequently the least crowded, least reactive compound in this series. Complex **1** would be best able to accommodate additional ligands, and enhanced reactivity could be compared to that of the more sterically crowded complexes of smaller metals such as (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm.<sup>1</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La was also preferable since La<sup>3+</sup> is diamagnetic and the reactions could be monitored by <sup>1</sup>H NMR spectroscopy. The following sections are organized by added Lewis base and then by substrate.

**THF as the Lewis Base.** Although (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm readily reacts with trace amounts of THF to form the ring-opened product

(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm[O(CH<sub>2</sub>)<sub>4</sub>C<sub>5</sub>Me<sub>5</sub>](THF)<sub>2</sub>,<sup>4</sup> the less sterically crowded (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La does not readily react with stoichiometric amounts of THF in toluene solutions. (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La forms a ring-opened product only in neat THF, eq 1.<sup>4</sup>



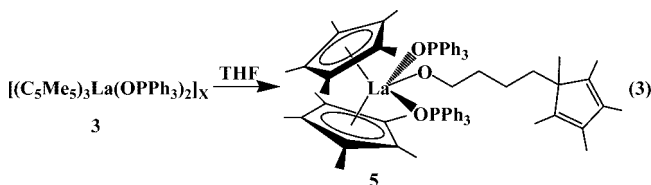
C<sub>8</sub>H<sub>8</sub>. To determine if small amounts of THF could affect the reactivity of **1** with other substrates, the reaction of **1** with C<sub>8</sub>H<sub>8</sub> was used. Complex **1** alone does not react with C<sub>8</sub>H<sub>8</sub>,<sup>4</sup> but in the presence of 2 equiv of THF, reduction occurs, eq 2. <sup>1</sup>H NMR spectroscopy showed that 40% conversion of **1** to



(C<sub>5</sub>Me<sub>5</sub>)La(C<sub>8</sub>H<sub>8</sub>)(THF), **2**, occurred over 24 h at room temperature. Hence, addition of a Lewis base such as THF enhances the reactivity of **1** with C<sub>8</sub>H<sub>8</sub>, although no specific (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La(THF)<sub>x</sub> was isolable.

**Ph<sub>3</sub>PO as the Lewis Base.** Complex **1** reacts with triphenylphosphine oxide, Ph<sub>3</sub>PO, to produce a dark gray solid with a composition determined by complete elemental analysis to be consistent with [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(OPPh<sub>3</sub>)<sub>2</sub>]<sub>x</sub>, **3**. Neither <sup>1</sup>H NMR nor <sup>13</sup>C NMR nor mass spectrometry data were obtainable since **3** is insoluble in alkane and arene solvents and reacts with polar solvents. DME, pyridine, and Et<sub>2</sub>O react with **3** to form multiple products as observed by <sup>1</sup>H NMR spectroscopy, and reactions with THF are described below. Attempts to prepare **3** from the reaction of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(OPPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>], **4**, with KC<sub>5</sub>Me<sub>5</sub> were unsuccessful as was observed with reactions of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>2</sub>][BPh<sub>4</sub>] with KC<sub>5</sub>Me<sub>5</sub>.<sup>21</sup> The relative reactivities of **1** and **3** were compared using THF, CO<sub>2</sub>, CS<sub>2</sub>, and KN(SiMe<sub>3</sub>)<sub>2</sub>.

**THF.** While the addition of 1–10 equiv of THF to **1** in benzene or toluene shows no reaction,<sup>4</sup> complex **3** reacts immediately with 1 equiv of THF to yield a single product, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[O(CH<sub>2</sub>)<sub>4</sub>C<sub>5</sub>Me<sub>5</sub>](OPPh<sub>3</sub>)<sub>2</sub>, **5**, eq 3. Therefore, as in



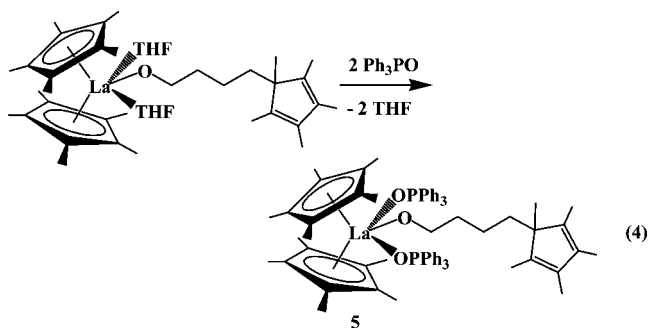
the case of THF as an added Lewis base, the presence of Ph<sub>3</sub>PO also enhanced reactivity toward ring-opening THF. With Ph<sub>3</sub>PO, only stoichiometric amounts of the Lewis base were necessary in contrast to eq 1 which required neat THF.

Complex **5** has a <sup>1</sup>H NMR spectrum similar to the distinctive spectrum of the THF ring-opened product in eq 1. This suggested that **5** was an analogue with Ph<sub>3</sub>PO replacing THF as the coordinating ligand. In support of this assignment, reaction

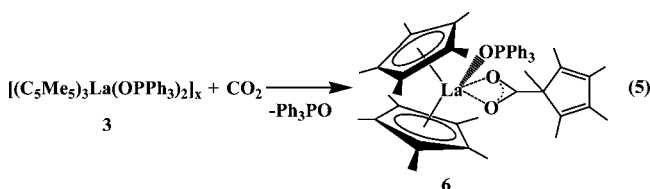
(21) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124.



of 2 equiv of  $Ph_3PO$  with  $(C_5Me_5)_2La[O(CH_2)_4C_5Me_5](THF)_2$  formed **5** and free THF according to eq 4.

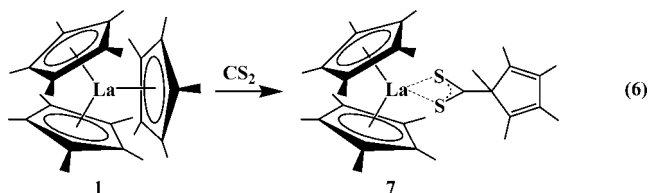


$CO_2$ . The reaction of **1** with  $CO_2$  yielded a product mixture that displayed at least 10 resonances in the  $(C_5Me_5)^{1-}$  region of the  $^1H$  NMR spectrum. However the reaction of **3** with  $CO_2$  yielded a single product, **6**. In this case, the presence of  $Ph_3PO$  led to a less complicated reaction mixture. Elemental analysis of **6** was consistent with  $(C_5Me_5)_2La(O_2CC_5Me_5)(OPPh_3)$ , and its  $^1H$  NMR spectrum displayed resonances at 2.24, 1.87, and 1.63 ppm that are similar to those observed in the crystallographically characterized  $CS_2$  analogue,  $(C_5Me_5)_2La(S_2CC_5Me_5)(OPPh_3)$ , described below. Hence, it appears that  $CO_2$  has inserted into one of the  $La-C(C_5Me_5)$  bonds to yield a pentamethylcyclopentadienyl-substituted carboxylate complex, eq 5. The phenyl region of the  $^1H$  NMR spectrum of the  $3/CO_2$

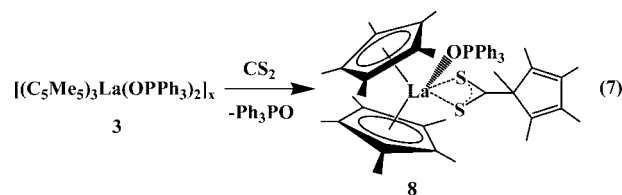


reaction mixture showed two unique  $Ph_3PO$  environments, one of which matched free  $Ph_3PO$ . This was consistent with the stoichiometry of eq 5. The infrared spectrum of the  $3/CO_2$  reaction mixture displayed strong absorptions at 1522 and 1438  $cm^{-1}$ , which are in the frequency range for OCO asymmetric and symmetric stretches, respectively, of metal carboxylate complexes.<sup>22–24</sup>

$CS_2$ . While **1** and **3** displayed different reactivity with  $CO_2$ , they both reacted in a similar manner with the congener,  $CS_2$ , to yield  $(C_5Me_5)_2La(S_2CC_5Me_5)$ , **7**, eq 6, and  $(C_5Me_5)_2La(S_2CC_5Me_5)(OPPh_3)$ , **8**, eq 7, respectively. In each case,  $CS_2$

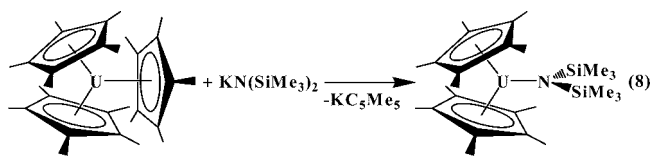


has inserted into one of the  $La-C(C_5Me_5)$  bonds to yield a pentamethylcyclopentadienyl-substituted dithiocarboxylate com-

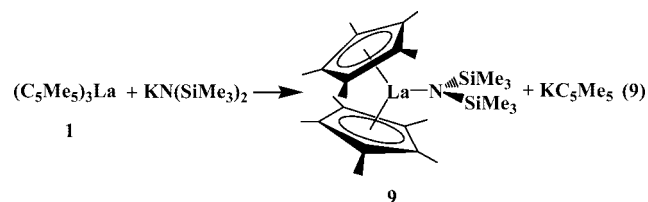


plex. Complexes **7** and **8** were characterized by  $^1H$ ,  $^{13}C$ , and  $^{31}P$  (**8**) NMR and IR spectroscopy as well as by X-ray crystallography, Figures 1 and 2. The infrared spectra of these complexes display absorptions at 978 and 954  $cm^{-1}$  for **7** and 994 and 964  $cm^{-1}$  for **8** that are similar to those previously observed in lanthanide metallocene dithiocarboxylate complexes.<sup>23</sup>

$KN(SiMe_3)_2$ . Complexes **1** and **3** were also treated with  $KN(SiMe_3)_2$  to determine if an  $\eta^1$ -ligand could displace an  $\eta^5$ -ligand in an unusual reaction of the type observed for  $(C_5Me_5)_3U$ , eq 8.<sup>13</sup> Such transformations are not usually

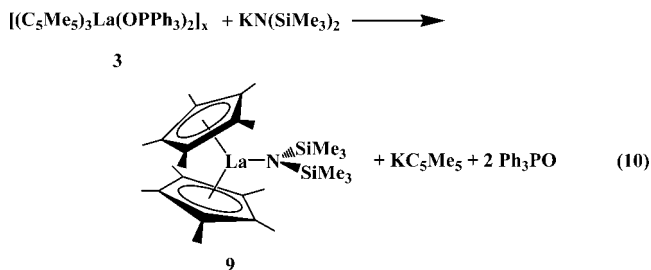


observed with conventional f element metallocenes. Complex **1** reacts with  $KN(SiMe_3)_2$  to produce the previously reported  $(C_5Me_5)_2La[N(SiMe_3)_2]$ ,<sup>20</sup> **9**, eq 9, which was characterized by



$^1H$  NMR spectroscopy and X-ray crystallography, Figure 3. Hence,  $\eta^1$ - for  $\eta^5$ -substitution reactions are possible with the least crowded  $(C_5Me_5)_3Ln$  lanthanide complex as well as with the actinide compound  $(C_5Me_5)_3U$ .

Complex **3** also reacts with  $KN(SiMe_3)_2$  to yield **9** along with free  $Ph_3PO$ , as observed by  $^1H$  NMR spectroscopy, eq 10. This



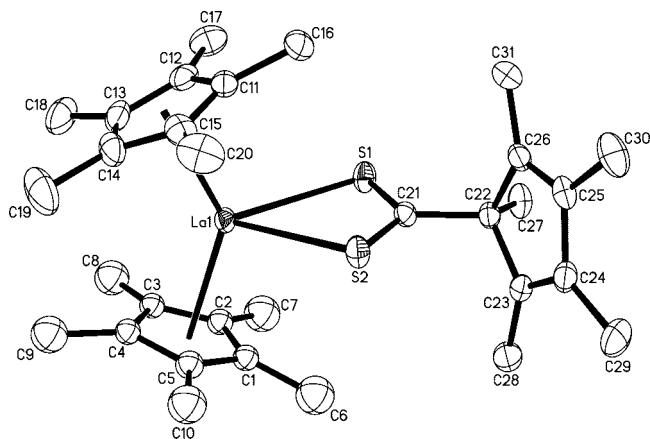
shows that  $Ph_3PO$  displacement as well as  $\eta^1$ - for  $\eta^5$ -substitution can occur in these crowded molecules.

**Adamantyl Azide as the Lewis Base.** Addition of 2 equiv of adamantyl azide,  $AdN_3$ , to  $(C_5Me_5)_3La$  did not produce a complex of the type  $(C_5Me_5)_3ML_x$ . Instead the insertion product

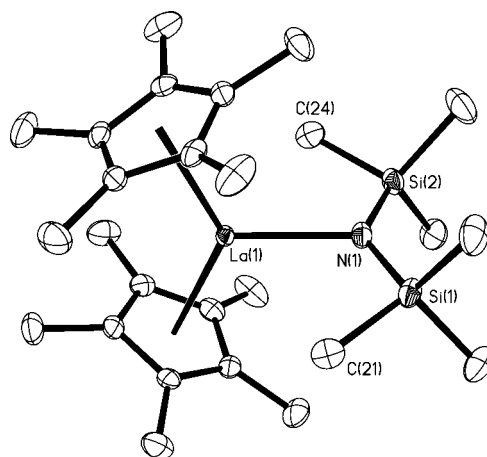
(22) (a) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. (b) Deacon, G.; Huber, F. *Inorg. Chim. Acta* **1985**, *104*, 41. (c) Grigor'ev, A. *Russ. J. Inorg. Chem.* **1963**, *8*, 409. (d) Patel, K.; Faniran, J.; Earnshaw, A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 352. (e) Alcock, N.; Tracy, V.; Waddington, T. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2243. (f) Karraker, D. J. *Inorg. Nucl. Chem.* **1969**, *31*, 2815. (g) Karraker, D.; Patel, K. *Spectrochim. Acta, Part A* **1976**, *32*, 1351.

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

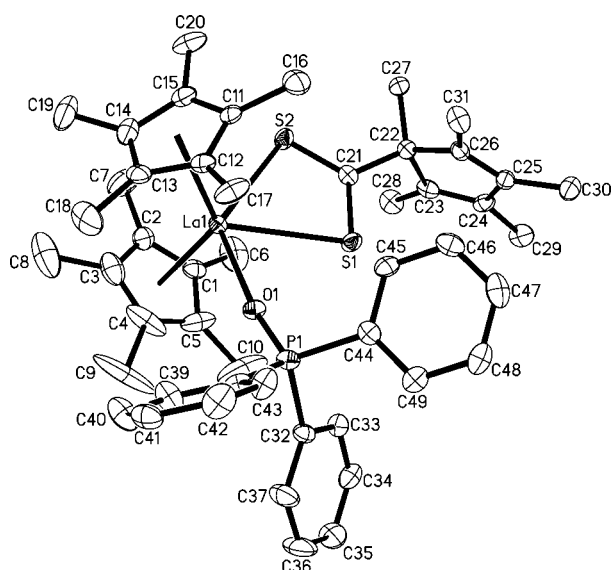
(24) Evans, W. J.; Rego, D. B.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4737.



**Figure 1.** Thermal ellipsoid plot of  $(C_5Me_5)_2La(S_2CC_5Me_5)$ , **7**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

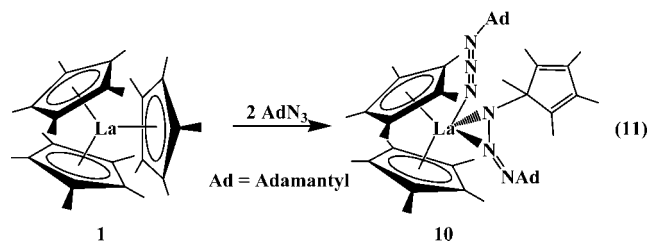


**Figure 3.** Thermal ellipsoid plot of  $(C_5Me_5)_2La[N(SiMe_3)_2]$ , **9**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.



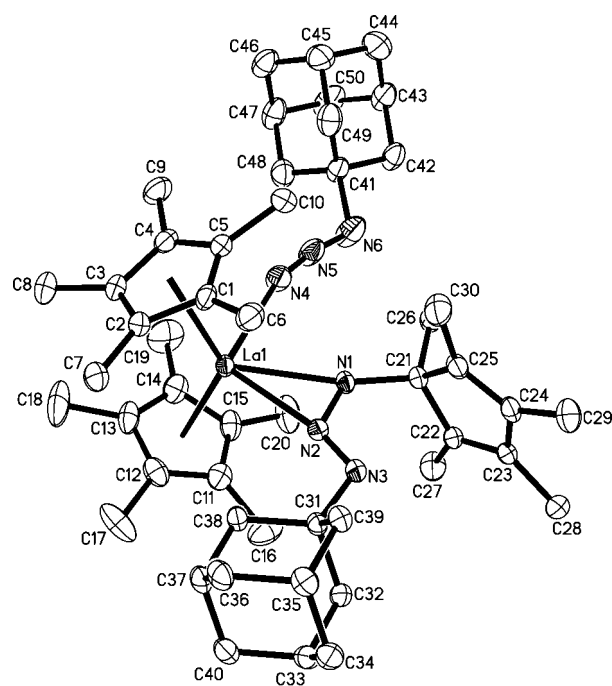
**Figure 2.** Thermal ellipsoid plot of  $(C_5Me_5)_2La(S_2CC_5Me_5)(OPPh_3)$ , **8**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

$(C_5Me_5)_2La[\eta^2-(N,N')-(C_5Me_5)NN''Ad](N_3Ad)$ , **10**, formed, eq 11. Complex **10** was characterized by  $^1H$ ,  $^{13}C$  NMR, and IR



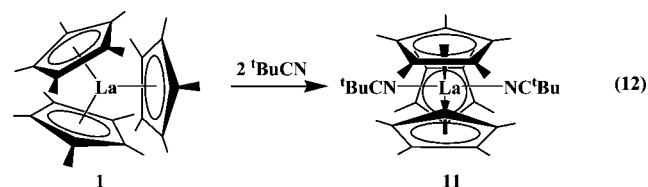
spectroscopy as well as by X-ray crystallography, Figure 4. To the best of our knowledge, this is the first example of an azide moiety inserting into an  $M-C(C_5Me_5)$  bond.  $^1H$  NMR analysis of the evolution of products in the reaction of **1** with adamantyl azide suggested that  $AdN_3$  first coordinates to the lanthanum metal center and insertion into the  $La-C(C_5Me_5)$  bond subsequently occurs (see Supporting Information).

**RC≡N as the Lewis Base.** The reaction of **1** with acetonitrile produced multiple products by  $^1H$  NMR spectroscopy. However,



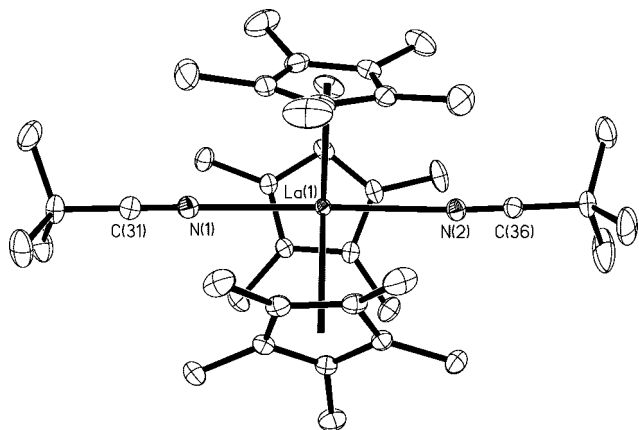
**Figure 4.** Thermal ellipsoid plot of  $(C_5Me_5)_2La[\eta^2-(N,N')-(C_5Me_5)NN''Ad](N_3Ad)$ , **10**, drawn at the 50% probability level. Hydrogen atoms and toluene solvent molecule have been omitted for clarity.

the reaction of **1** with 2 equiv of *tert*-butyl nitrile yielded  $(C_5Me_5)_3La(NCCMe_3)_2$ , **11**, eq 12, in quantitative yield. Com-



plex **11** was characterized by  $^1H$ ,  $^{13}C$  NMR, and IR spectroscopy as well as by elemental analysis and X-ray crystallography, Figure 5. Complex **11** is the first crystallographically characterized  $(C_5Me_5)_3ML_2$  complex.

**Structural Comparisons.** Complexes **4**, **7**, **8**, **9**, and **10**. The complexes in this subsection display normal bonding parameters



**Figure 5.** Thermal ellipsoid plot of  $(C_5Me_5)_3La(NCCMe_3)_2$ , **11**, drawn at the 50% probability level. Hydrogen atoms and benzene solvent molecule have been omitted for clarity.

for lanthanide metallocene complexes. Only brief descriptions of unusual features of the non-cyclopentadienyl ligands and atypical ligand sets will be presented.

$(C_5Me_5)_2La(OPPh_3)_2[BPh_4]$ , **4**. Complex **4** was crystallographically characterized to establish structural parameters for a  $[(C_5Me_5)_2La]^+$  lanthanum metallocene complex of  $Ph_3PO$ , Figure 6, Table 2. The  $89.5(1)^\circ O(1)-La(1)-O(1A)$  angle in **4** can be compared to the  $92.9(4)^\circ$  and  $92.2(1)^\circ O(1)-Ln(1)-O(1A)$  angles in the THF analogues  $[(C_5Me_5)_2Ln(THF)_2][BPh_4]$  ( $Ln = Sm^{21}, Yb^{25}$ ). Although the  $O(1)-Ln(1)-O(1A)$  angles are similar, the  $2.398(2) \text{ \AA}$   $La-O(OPPh_3)$  distances are shorter than the  $2.46(1) \text{ \AA}$   $Sm-O(THF)$  distances in  $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ ,<sup>21</sup> even though eight-coordinate  $La^{3+}$  is  $0.08 \text{ \AA}$  larger than the eight-coordinate  $Sm^{3+}$ .<sup>26</sup> This is consistent with previous comparisons of lanthanide complexes of  $Ph_3PO$  and THF.<sup>27,28</sup> Interestingly, the  $2.398(2) \text{ \AA}$   $La-O(OPPh_3)$  distances in **4** are the same as the  $2.398(3) \text{ \AA}$   $La-O(OPPh_3)$  bond length in  $(C_5H_5)_3La(OPPh_3)$ .<sup>28</sup>

$(C_5Me_5)_2La(S_2CC_5Me_5)$ , **7**, and  $(C_5Me_5)_2La(S_2CC_5Me_5)(OPPh_3)$ , **8**. Complexes **7** and **8**, Figures 1 and 2, are unusual in that both  $n$  and  $n+1$  coordinate complexes crystallize with the  $(C_5Me_5)_2La(S_2CC_5Me_5)$  ligand set. Ordinarily for trivalent lanthanide complexes, a ligand set gives a crystallographically characterizable complex either with or without added base, but not with both.<sup>29</sup> Table 2 shows that the  $La-C(C_5Me_5)$  and  $La-S$  distances differ as expected for  $n$  and  $n+1$  coordinate complexes, while the distances within the  $(S_2CC_5Me_5)^{1-}$  ligand are nearly identical. The  $(C_5Me_5 \text{ ring centroid})-La(1)-(C_5Me_5 \text{ ring centroid})$  angle in **8**,  $129.5^\circ$ , is smaller than that in **7**,  $137.5^\circ$ , which is consistent with the presence of an additional ligand in **8**. This shows the flexibility of the  $[(C_5Me_5)_2La]^{1+}$  unit in accommodating variable coordination. The  $La(1)-O(1)$  distance of  $2.483(3) \text{ \AA}$  in **8** is similar to the  $2.47(2) \text{ \AA}$   $La-OPPh_3$  bond distance in  $[(Me_3Si)_2N]_3La(OPPh_3)$ <sup>30</sup> but longer than the  $2.398(2) \text{ \AA}$   $La-OPPh_3$  bond distances in the cationic complex **4**.

$(C_5Me_5)_2La[N(SiMe_3)_2]$ , **9**. The structure of **9**, Figure 3, provides comparative data on another example of a  $(C_5Me_5)_2M[N(SiMe_3)_2]$  complex ( $M = U$ ,<sup>31</sup>  $Sm$ ,<sup>32</sup>  $Y$ <sup>33</sup>). As shown in Table 3, **9** has the largest metal radius of examples structurally characterized. Surprisingly, complexes of the smallest and largest metals, yttrium and lanthanum, respectively, both contain agostic interactions between the metal center and one of the carbon-hydrogen bonds from the  $[N(SiMe_3)_2]^{1-}$  ligand, while the intermediate sized metals, uranium and samarium, do not display similar agostic interactions.<sup>31,32</sup> In **9**, the  $3.120(2) \text{ \AA}$   $La(1)-C(24)$  distance is significantly shorter than the  $3.285(2) \text{ \AA}$   $La(1)-C(21)$  distance. Consistent with this, the  $111.64(9)^\circ$   $La(1)-N(1)-Si(2)$  angle is smaller than the  $116.34(9)^\circ$   $La(1)-N(1)-Si(1)$  angle. The  $3.120(2) \text{ \AA}$   $La(1)-C(24)$  bond distance is equivalent to the  $2.970(6) \text{ \AA}$   $Y(1)-C(24)$  bond distance in the yttrium analogue when the  $0.14 \text{ \AA}$  difference in ionic radii between lanthanum and yttrium<sup>26</sup> is taken into account. Since **9** is the least sterically saturated of the  $(C_5Me_5)_2M[N(SiMe_3)_2]$  complexes presented here, the agostic interaction may occur to achieve greater steric saturation at the metal center. In the yttrium complex, the agostic interaction could be rationalized because the metal center has the highest Lewis acidity of the metals presented here.

$(C_5Me_5)_2La[\eta^2-(N,N')-(C_5Me_5)NN'N''Ad](N_3Ad)$ , **10**. The  $[\eta^2-(N,N')-(C_5Me_5)NN'N''Ad]^{1-}$  ligand in **10**, Figure 4, is the first of its kind. The  $1.333(2) \text{ \AA}$   $N(1)-N(2)$  and  $1.272(2) \text{ \AA}$   $N(2)-N(3)$  distances are intermediate between the usual ranges for  $N-N$  single and double bonds<sup>34</sup> and indicate some delocalization of charge in the ligand. These distances, as well as the  $2.492(2) \text{ \AA}$   $La(1)-N(1)$  and  $2.546(2) \text{ \AA}$   $La(1)-N(2)$  distances in **10**, (Table 4) can be compared with analogues in other lanthanum metallocenes attached to two adjacent nitrogen atoms. In the hydrazonato complex,  $(C_5Me_5)_2La[\eta^2-(N,N')-CH_2=CHCH_2NN=CHSiMe_3]$ ,<sup>35</sup> the  $N-N'$  distance is  $1.343(3) \text{ \AA}$ , i.e., equivalent to  $N(1)-N(2)$  in **10**, and the  $La-N$  distances are  $2.397(2)$  and  $2.476(2) \text{ \AA}$ . In  $[(C_5Me_5)_2La(THF)]_2(\mu-\eta^2-N_2)$ ,<sup>36</sup> the  $(N_2)^{2-}$  ligand has a  $1.233(5) \text{ \AA}$   $N-N$  bond distance in the double bond region and the  $La-N$  distances are  $2.478(4)$  and  $2.537(4) \text{ \AA}$ . Hence, there is some variation of metrical parameters in complexes with this  $LnN_2$  bonding mode. The angles around  $N(1)$  and  $N(2)$  in **10** each sum to  $360^\circ$ , and  $C(31)$  is out of the  $N(1), N(2), N(3)$  plane by only  $0.0035 \text{ \AA}$ . The  $2.664(2) \text{ \AA}$   $La(1)-N(4)$  bond distance is within the range observed for neutral nitrogen donor ligands coordinated to a  $La^{3+}$  metal center.<sup>37-39</sup>

**Structure of  $(C_5Me_5)_3La(NCCMe_3)_2$ , **11**.** Complex **11**, Figure 5, has a trigonal bipyramidal geometry with the  $(C_5Me_5)^{1-}$  ring centroids occupying the equatorial positions and the two

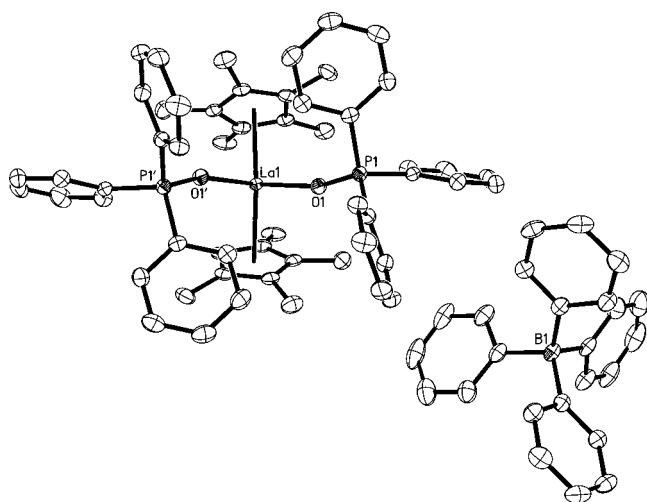
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**Table 1.** X-ray Data Collection Parameters for [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(OPPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>], **4**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>), **7**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>)(OPPh<sub>3</sub>), **8**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>M[N(SiMe<sub>3</sub>)<sub>2</sub>], **9**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[γ<sup>2</sup>-(N,N')-(C<sub>5</sub>Me<sub>5</sub>)NN'N''Ad](N<sub>3</sub>Ad), **10**, and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La(NCCMe<sub>3</sub>)<sub>2</sub>, **11**

	4	7	8	9	10	11
formula	C <sub>80</sub> H <sub>80</sub> BLaO <sub>2</sub> P <sub>2</sub> ·2(C <sub>7</sub> H <sub>8</sub> )	C <sub>31</sub> H <sub>45</sub> LaS <sub>2</sub>	C <sub>49</sub> H <sub>60</sub> LaOPS <sub>2</sub>	C <sub>26</sub> H <sub>48</sub> LaNSi <sub>2</sub>	C <sub>50</sub> H <sub>75</sub> LaN <sub>6</sub> ·(C <sub>7</sub> H <sub>8</sub> )	C <sub>40</sub> H <sub>63</sub> LaN <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>
fw	1469.37	620.70	898.97	569.74	991.20	788.94
space group	C2/c	P $\bar{1}$	P2 <sub>1</sub> /c	P $\bar{3}$	P $\bar{1}$	P2 <sub>1</sub> /c
crystal system	monoclinic	triclinic	monoclinic	trigonal	triclinic	monoclinic
a (Å)	13.463(2)	9.9376(6)	12.096(2)	17.791(1)	13.2291(8)	19.1633(6)
b (Å)	41.393(5)	11.3390(7)	12.075(2)	17.791(1)	14.6728(9)	17.5365(5)
c (Å)	14.208(2)	14.4297(9)	31.142(5)	15.625(2)	15.558(1)	12.9886(4)
V (Å <sup>3</sup> )	7868.2(2)	1476.0(2)	4546.7(1)	4282.7(6)	2595.5(3)	4271.7(2)
α (deg)	90	74.182(1)	90	90	76.555(1)	90
β (deg)	96.432(2)	83.380(1)	91.606(2)	90	76.062(1)	101.860(1)
γ (deg)	90	70.704(1)	90	120	63.486(1)	90
Z	4	2	4	6	2	4
ρ <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.240	1.397	1.313	1.325	1.268	1.227
μ (mm <sup>-1</sup> )	0.632	1.606	1.100	1.593	0.865	1.031
temp (K)	143(2)	163(2)	103(2)	155(2)	103(2)	103(2)
R1 [I > 2σ(I)] <sup>a</sup>	0.0405	0.0298	0.0503	0.0289	0.0315	0.0200
wR2 (all data) <sup>a</sup>	0.0968	0.0756	0.1243	0.0763	0.0843	0.0527

<sup>a</sup> Definitions: wR2 = [Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)]/Σ[w(F<sub>o</sub><sup>2</sup>)]]<sup>1/2</sup>, R1 = Σ|F<sub>o</sub> - |F<sub>d</sub>||/Σ|F<sub>o</sub>||.

**Figure 6.** Thermal ellipsoid plot of [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(OPPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>], **4**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.**Table 2.** Selected Bond Distances (Å) and Angles (deg) for [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(OPPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>], **4**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>), **7**, and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>)(OPPh<sub>3</sub>), **8**

	4	7	8
La-C(C <sub>5</sub> Me <sub>5</sub> ) range	2.791(3)– 2.852(3)	2.752(3)– 2.819(5)	2.797(6)– 2.912(6)
La-C(C <sub>5</sub> Me <sub>5</sub> ) avg	2.824(3)	2.793(6)	2.865(6)
La(1)–Cnt(1)	2.554	2.542	2.575
La(1)–Cnt(2)	2.554	2.512	2.627
La(1)–S(1)	-	2.9291(6)	3.026(1)
La(1)–S(2)	-	2.9587(6)	2.998(1)
C(21)–S(1)	-	1.697(2)	1.700(5)
C(21)–S(2)	-	1.688(2)	1.675(5)
La(1)–O(1)	2.398(2)	-	2.483(3)
O(1)–P(1)	1.514(2)	-	1.515(4)
Cnt(1)–La(1)–Cnt(2)	130.9	137.5	129.2
O(1)–La(1)–O(1')	89.5(1)	-	-
S(1)–C(21)–S(2)	-	122.6(1)	122.1(3)

Me<sub>3</sub>CCN ligands in the axial positions. In contrast to all previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ML complexes that have P6<sub>3</sub>/m symmetry, the three (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> in **11** are not equivalent by crystallographic symmetry. The three (C<sub>5</sub>Me<sub>5</sub> ring centroid)–M–(C<sub>5</sub>Me<sub>5</sub> ring centroid) angles, 118.9°,

120.4°, and 120.7°, Table 5, are not rigorously 120° as found in all previous examples, although they are close to 120° and sum to 360° to give a trigonal planar geometry of ring centroids. The lanthanum metal center is 0.005 Å out of the plane of the three ring centroids. The N(1)–La(1)–N(2) angle of 178.77(3)° shows the near linearity of the coordinated Me<sub>3</sub>CCN ligands in the axial positions of complex **11**. In the (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>UL and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>UX complexes,<sup>14–17</sup> the L ligand makes a rigorously 90° angle with the plane of the three (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> ring centroids, Figure 7.

The La–(C<sub>5</sub>Me<sub>5</sub> ring centroid) distances in **11**, 2.752, 2.734, 2.715 Å, are almost 0.2 Å longer than those described above for **4**, **7**, **8**, **9**, and **10**, namely 2.551, 2.540, 2.618, 2.589, and 2.586 Å, respectively. It was expected that the long bond organometallic **11** would have metrical parameters longer than those of conventional complexes. However, the La–(C<sub>5</sub>Me<sub>5</sub> ring centroid) distances in **11** are also 0.1 Å longer than those previously observed for the sterically crowded parent complex, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La, **1**, which had a 2.642 Å distance.<sup>3</sup> The range of La–C(C<sub>5</sub>Me<sub>5</sub>) distances in **11** is 2.869(1)–3.138(1) Å compared to 2.873(2)–2.975(3) Å in **1**. These are the longest La–C(C<sub>5</sub>Me<sub>5</sub>) bond distances observed to date and show that M–C(C<sub>5</sub>Me<sub>5</sub>) distances can be extremely long and still maintain ligation.

In contrast, the 2.681(1) La(1)–N(1) and 2.656(1) La(1)–N(2) bond distances are *not* unusually long. In all previously characterized (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>UL and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>UX complexes, the U–L and U–X distances are much longer than analogues in conventional complexes. The same was expected in **11**, but the La–N distances are similar to those in sterically “normal” {[1,3-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>La(NCMe)(DME)}[BPh<sub>4</sub>], 2.60(2) Å,<sup>37</sup> and (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>La(NCet), 2.657(5) Å.<sup>38</sup> They are 0.1 Å *shorter* than the analogous La–N bonds in (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>La(NCMe)<sub>2</sub>, 2.785(8) Å,<sup>40</sup> and (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>La(NCet)<sub>2</sub>, 2.759(9) Å.<sup>38</sup>

Another characteristic of long bond organometallic complexes is that one methyl per ring is significantly out of the (C<sub>5</sub>Me<sub>5</sub>)<sup>1-</sup> plane, specifically 0.48–0.54 Å from the plane.<sup>41</sup> As shown in

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**Table 3.** Selected Bond Distances (Å) and Angles (deg) for the (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>M[N(SiMe<sub>3</sub>)<sub>2</sub>] Complexes (M = La, U,<sup>31</sup> Sm,<sup>32</sup> Y<sup>33</sup>) Along with Their Seven-Coordinate M<sup>3+</sup> Ionic Shannon Radii<sup>26</sup>

(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> M[N(SiMe <sub>3</sub> ) <sub>2</sub> ]	La	U	Sm	Y
M <sup>3+</sup> ionic radius	1.24	1.22	1.16	1.10
La–C(C <sub>5</sub> Me <sub>5</sub> ) range	2.822(2)–2.878(2)	2.781(3)–> 2.826(3)	2.733(4)–2.769(6)	2.632(7)–2.737(7)
La–C(C <sub>5</sub> Me <sub>5</sub> ) avg	2.850(2)	2.799(3)	2.750(6)	2.682(4)
M(1)–Cnt1	2.589	2.532	2.479	2.400
M(1)–Cnt2	2.577	2.524	2.470	2.391
M(1)–N(1)	2.392(2)	2.352(2)	2.301(3)	2.274(5)
M(1)–C(21)	3.285(2)	3.222(4)	3.282	3.800
M(1)–C(24)	3.120(2)	3.197(4)	3.216	2.970(6)
N(1)–Si(1)–C(21)	105.5(1)	106.1(1)	106.4(2)	110.0(3)
N(1)–Si(2)–C(24)	105.5(1)	105.8(1)	106.3(2)	107.2(3)
M(1)–N(1)–Si(1)	116.34(9)	114.5(1)	116.5	129.7(3)
M(1)–N(1)–Si(2)	111.64(9)	114.1(1)	115.0	107.1(3)
Σ N(1) angles	359.9	360.0	359.9	360.0

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La[η<sup>2</sup>-(N,N')-(C<sub>5</sub>Me<sub>5</sub>)NN'N'Ad](N<sub>3</sub>Ad), **10**

La–C(C <sub>5</sub> Me <sub>5</sub> ) range	2.817(2)–2.897(2)	La–C(C <sub>5</sub> Me <sub>5</sub> ) avg	2.851(2)
La(1)–Cnt(1)	2.583	N(1)–N(2)	1.333(2)
La(1)–Cnt(2)	2.586	N(2)–N(3)	1.272(2)
La(1)–N(1)	2.492(2)	N(4)–N(5)	1.136(3)
La(1)–N(2)	2.546(2)	N(5)–N(6)	1.223(3)
La(1)–N(4)	2.664(2)	Σ N(1) angles	360.0
Cnt(1)–La(1)–Cnt(2)	133.8	Σ N(2) angles	360.0

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La(NCCMe<sub>3</sub>)<sub>2</sub>, **11**

La–C(C <sub>5</sub> Me <sub>5</sub> ) range	2.869(1)–3.138(1)	C(36)–N(2)	1.143(2)
La–C(C <sub>5</sub> Me <sub>5</sub> ) avg	2.986(1)	Cnt(1)–La(1)–Cnt(2)	118.9
La(1)–Cnt(1)	2.715	Cnt(2)–La(1)–Cnt(3)	120.4
La(1)–Cnt(2)	2.734	Cnt(1)–La(1)–Cnt(3)	120.7
La(1)–Cnt(3)	2.752	N(1)–La(1)–N(2)	178.77(3)
La(1)–N(1)	2.681(1)	N(1)–C(31)–C(32)	179.6(2)
La(1)–N(2)	2.656(1)	N(2)–C(36)–C(37)	179.4(2)
C(31)–N(1)	1.145(2)		

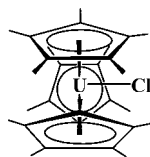
**Figure 7.** Rigorously trigonal planar (C<sub>5</sub>Me<sub>5</sub>)<sup>1−</sup> ring centroids in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>UCl<sup>14</sup> and the U–Cl bond perpendicular to this plane.

Table 6, complex **11** has a maximum methyl displacement of 0.43 Å that is below this expected range.

## Discussion

This study shows that the reactivity of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>La, **1**, can be enhanced with certain substrates by the addition of Lewis bases but that this is highly dependent on the specific Lewis base and substrate. For example, the sterically induced reduction reactivity of **1** with C<sub>8</sub>H<sub>8</sub> and the ring opening reactivity of **1** with THF are increased by addition of THF and Ph<sub>3</sub>PO, respectively. This is consistent with the observation that, for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Ln complexes, increased crowding increases reactivity: the more crowded complexes of the smaller lanthanide metals in the (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Ln series display greater reactivity.<sup>4,9,10</sup>

In contrast, CS<sub>2</sub> insertion into La–C(C<sub>5</sub>Me<sub>5</sub>) units to form [S<sub>2</sub>C(C<sub>5</sub>Me<sub>5</sub>)]<sup>1−</sup> ligands occurs readily with and without addition

**Table 6.** Methyl Displacement out of the Cyclopentadienyl Plane (Å) for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ML, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>MX, and (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ML<sub>2</sub> Complexes

	methyl displacement		
	max.	median	min.
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> UCl <sup>14</sup>	0.54	0.36	0.20
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> UF <sup>14</sup>	0.54	0.34	0.16
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> U(CO) <sup>15</sup>	0.53	0.34	0.25
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> U(N <sub>2</sub> ) <sup>16</sup>	0.53	0.34	0.24
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> U <sup>17</sup>	0.52	0.35	0.21
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> U <sup>7</sup>	0.52	0.34	0.18
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> ThH <sup>18</sup>	0.51	0.32	0.17
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> La, <b>1</b> <sup>3</sup>	0.50	0.31	0.16
(C <sub>5</sub> Me <sub>5</sub> ) <sub>3</sub> La(NCCMe <sub>3</sub> ) <sub>2</sub> , <b>11</b>	0.43	0.29	0.22

of bases to **1**. However, the reaction of **1** with CO<sub>2</sub> is greatly affected by Lewis base addition. In the absence of base, the CO<sub>2</sub> reaction produces multiple products, whereas addition of Ph<sub>3</sub>PO allows for the isolation of a single product. In this case, the added base seems to channel reactivity into one favorable pathway perhaps by stabilizing an initially formed intermediate.

Since the stability of organometallic lanthanide complexes often depends upon steric saturation around the metal center, the difference in CS<sub>2</sub> and CO<sub>2</sub> reactivity can be explained using a steric argument. The reaction of **1** with CO<sub>2</sub> may yield multiple products due to the fact that a complex of the type “(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(O<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>)” would not be sterically saturated and thus unstable with respect to formation of other products. In this case, the addition of a coordinating base like Ph<sub>3</sub>PO to the reaction would stabilize the initial CO<sub>2</sub> insertion product to form **6**, as observed in eq 5. Due to the larger size of sulfur, the initial CS<sub>2</sub> insertion product could be sterically saturated enough to form a stable complex, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>), **7**, without added base, eq 6. The isolation of formally 9-coordinate (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>La(S<sub>2</sub>CC<sub>5</sub>Me<sub>5</sub>)(OPPh<sub>3</sub>), **8**, as well as 8-coordinate **7** is an unusual example in which *n* and *n*+1 coordinate trivalent lanthanide complexes both can be crystallographically characterized. Overall, the effect on reactivity of adding a Lewis base appears to be highly dependent on the specific substrate.

The reactions of **1** and **3** with KN(SiMe<sub>3</sub>)<sub>2</sub> constitute another example in which the presence of added base did not affect the outcome. These reactions, eqs 9 and 10, are independently important in that they demonstrate another general type of reaction for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M complexes along with sterically induced reduction and η<sup>1</sup>-(C<sub>5</sub>Me<sub>5</sub>)-like reaction chemistry.<sup>4</sup> Previously, the observation that an η<sup>5</sup>-(C<sub>5</sub>Me<sub>5</sub>) ligand could be displaced by an η<sup>1</sup>-N(SiMe<sub>3</sub>)<sub>2</sub> ligand had only been observed in uranium reactions, e.g., with (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>U, eq 8.<sup>13</sup> It was unknown if this

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reaction was general or if it only applied to actinides. Substitution of  $(C_5Me_5)^{1-}$  by  $[N(SiMe_3)_2]^{1-}$  now appears to be a general reaction for long bond organometallic complexes. It is another example of the power of steric crowding to change ligand reactivity patterns in these complexes.

The specific Lewis base selected to alter  $(C_5Me_5)_3M$  reactivity must be chosen carefully since some will go on to react with the initially formed  $(C_5Me_5)_3ML$  adduct complexes. In this study, both THF and organic azides fall in this category. These bases appear to coordinate and then enhance further reactivity with the base.

The insertion of  $AdN_3$  into the  $La-C(C_5Me_5)$  unit to make the  $[\eta^2-(N,N')-(C_5Me_5)NN'N''Ad]^{1-}$  ligand is, to our knowledge, a unique type of reaction for organic azides and metal cyclopentadienyl complexes. Until other examples are identified, this reaction could be attributed to steric crowding. In this sense, it is similar to the unique insertion of CO into  $M-C(C_5Me_5)$  linkages in  $(C_5Me_5)_3Ln$  complexes which forms the nonclassical carbonium ion products,  $(C_5Me_5)_3Ln[O_2C_2(C_5Me_5)]$ .<sup>4,12</sup>

The isolation of  $(C_5Me_5)_3La(NCCMe_3)_2$ , **11**, provided the first example of a  $(C_5Me_5)_3ML_2$  complex. The previously isolated  $(C_5Me_5)_3UL$  ( $L = CO$ ,<sup>15</sup>  $N_2$ <sup>16</sup>) and  $(C_5Me_5)_3AnX$  ( $X = F$ ,<sup>14</sup>  $Cl$ ,<sup>14</sup>  $Me$ ,<sup>17</sup>  $H$ <sup>18</sup>) complexes all crystallized in space group  $P6_3/m$  with rigorously trigonal planar  $(C_5Me_5)^{1-}$  ring centroids and  $U-L$  and  $An-X$  bonds perpendicular to this plane, Figure 7. In each case,  $L$  and  $X$  ligands were disordered on each side of the trigonal plane and it appeared that there would be room to accommodate a second  $L$  or  $X$  ligand. However, despite numerous synthetic attempts, no example was isolated until now. Furthermore, no examples of  $(C_5Me_5)_3LnL$  of any kind had been isolated for lanthanides. The synthesis of **11** showed that the limits of steric crowding in  $(C_5Me_5)_3M$  complexes are still expanding. The structure of **11** also reveals some new structural features for  $(C_5Me_5)_3M$  complexes as described in the following paragraphs.

The previously reported  $(C_5Me_5)_3UL$  ( $L = CO$ ,<sup>15</sup>  $N_2$ <sup>16</sup>) complexes are distinguished by elongated  $U-C(C_5Me_5)$  bond distances, Table 7, along with greater displacements of the methyl substituent out of the cyclopentadienyl plane compared to  $(C_5Me_5)_3U$ , Table 6. In the  $(C_5Me_5)_3UX$  ( $X = F$ ,<sup>14</sup>  $Cl$ ,<sup>14</sup>  $Me$ <sup>17</sup>) complexes, accounting for the 0.135 Å change in ionic radius from  $U^{3+}$  to  $U^{4+}$ ,<sup>26</sup> the  $U-(C_5Me_5)$  ring centroid) distances increased 0.10–0.12 Å upon addition of  $X$ . There was also a slight increase in the maximum methyl displacement from the cyclopentadienyl plane in all cases except  $(C_5Me_5)_3UMe$ , which displayed no change.

Complex **11** differs from these other examples in that it does not crystallize with  $P6_3/m$  symmetry and three equivalent  $(C_5Me_5)^{1-}$  rings. Complex **11** does display a significant increase in the  $La-C(C_5Me_5)$  bond distances compared to  $(C_5Me_5)_3La$  by as much as 0.155 Å, Table 7. However, the maximum methyl displacements are less than those found in  $(C_5Me_5)_3La$ . This

**Table 7.** Selected Bond Distances (Å) for  $(C_5Me_5)_3M$ ,  $(C_5Me_5)_3ML$ ,  $(C_5Me_5)_3MX$ , and  $(C_5Me_5)_3ML_2$  Complexes.

	M–Cnt	M–C( $C_5Me_5$ )		
		max.	median	min.
$(C_5Me_5)_3UCl$ <sup>14</sup>	2.551	2.899(9)	2.818(8)	2.780(6)
$(C_5Me_5)_3UF$ <sup>14</sup>	2.562	2.907(7)	2.830(5)	2.790(5)
$(C_5Me_5)_3U(CO)$ <sup>15</sup>	2.587	2.927(3)	2.847(2)	2.821(2)
$(C_5Me_5)_3U(N_2)$ <sup>16</sup>	2.587	2.927(4)	2.848(2)	2.823(3)
$(C_5Me_5)_3UMe$ <sup>17</sup>	2.570	2.904(6)	2.832(4)	2.802(4)
$(C_5Me_5)_3U$ <sup>7</sup>	2.582	2.920(3)	2.840(3)	2.813(3)
$(C_5Me_5)_3ThH$ <sup>18</sup>	2.614	2.946(3)	2.872(2)	2.845(2)
$(C_5Me_5)_3La$ , <b>1</b> <sup>3</sup>	2.643	2.975(3)	2.896(2)	2.873(2)
$(C_5Me_5)_3La(NCCMe_3)_2$ , <b>11</b>	2.752	3.138(1)	3.003(1)	2.898(1)
	2.734	3.122(1)	2.987(1)	2.869(1)
	2.715	3.072(1)	2.968(1)	2.884(1)

may be related to the fact that the  $(C_5Me_5)^{1-}$  ligands are located a greater distance from the metal center than in **1**. In the case of **11**, the  $(C_5Me_5)^{1-}$  ligands may be far enough away from the metal center that they do not mutually force their methyl groups out of the plane to the extent observed in **1**.

The long  $La-C(C_5Me_5)$  distances may also provide a rationale for the unexpectedly short  $La-N(RCN)$  distances. Electrostatic stabilization of  $La^{3+}$  may be reduced with the  $(C_5Me_5)^{1-}$  ligands so far away. To make up for this electrostatic deficiency and the corresponding enhanced electrophilicity, the  $La^{3+}$  ion may pull the RCN ligands closer. This sets up a new structural motif for  $(C_5Me_5)_3M$  complexes in which some ligands have unusually long  $M-L$  bond distances and others do not. This suggests a type of push–pull tension within the molecule that could have interesting implications in reactivity.

## Conclusion

The reactivity of  $(C_5Me_5)_3M$  complexes<sup>1-</sup> can be enhanced by addition of Lewis bases in reactions that are highly dependent on the specific substrate involved. Hence, reactivity is modified with  $C_8H_8$ , THF, and  $CO_2$ , but no effect is seen with  $CS_2$  and  $KN(SiMe_3)_2$ . With some substrates, e.g., THF and  $AdN_3$ , the Lewis base can become the substrate. With the appropriate base,  $(C_5Me_5)_3ML_2$  complexes can be isolated with  $M-C(C_5Me_5)$  distances even longer than those previously observed with  $(C_5Me_5)_3M$ ,  $(C_5Me_5)_3ML$ , and  $(C_5Me_5)_3MX$  compounds.

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**Supporting Information Available:** <sup>1</sup>H NMR data and X-ray data collection, structure solution, and refinement (PDF) and X-ray diffraction details of compounds **4**, **7**, **8**, **9**, **10**, **11** (CIF, CCDC Nos. 704809–704814). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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