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Facile Insertion of CO_2 into Tetra- and Pentamethylcyclopentadienyl Lanthanide Moieties To Form $(C_5Me_4RCO_2)^-$ Carboxylate Ligands (R = H, Me)

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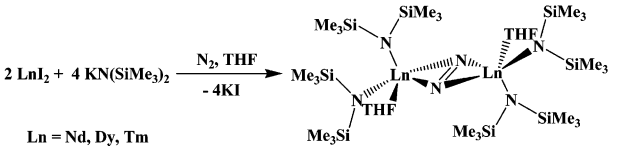
Recent efforts to extend the reduction chemistry of LnZ_3/M and LnZ_2Z'/M (Ln = lanthanide; Z = C_5Me_5, C_5Me_4H; Z′ = BPh_4, Cl; M = alkali metal) to substrates beyond N_2 have identified unexpectedly facile insertion of CO_2 into lanthanide cyclopentadienyl linkages to make carboxylate ligands. The insertion was initially identified in $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, **1**, a product of a $(C_5Me_4H)_3La/Na/CO_2$ reaction in the presence of chloride. In this case, both insertion and reduction of CO_2 to carbonate was observed. A $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]/KC_8/CO_2$ reaction also provided a CO_2 insertion product, $[(C_5Me_5)La(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CC_5Me_5)]_2$, **2**, but in this case a CO_2 reduction product was not identified. CO_2 insertion also occurs in the absence of an alkali metal. Hence, the $(C_5Me_4H)_3Ln$ complexes (Ln = La, Nd, Sm, Gd) react with CO_2 to form mixtures of tetramethylcyclopentadienyl carboxylate products. In the La complex, single crystals of $\{[(C_5Me_4H)_2La](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, **3**, could be isolated and structurally characterized. Crystallographic characterization of a rare example of a tetramethylcyclopentadienyl lanthanide ate salt, $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, **4**, was also obtained as part of this study, and it was found to have a chain structure in the solid state involving bridging methyl groups as well as bridging chloride ligands.

Introduction

Recent advances in the reduction chemistry of the lanthanides have included the use of the LnZ_3/M system, where Z is a monoanionic ligand such as $[N(SiMe_3)_2]^-$ or $(C_5Me_4H)^{1-}$ and M is an alkali metal,[1−11] to mimic the reductive chemistry of the divalent "LnZ_2" lanthanides, particularly in reducing dinitrogen. Hence, dinitrogen reduction using divalent Tm^{2+}, Dy^{2+}, and Nd^{2+} reagents,[8,12−14] eq 1, can be mimicked by the combination of trivalent $Ln[N(SiMe_3)_2]_3$ complexes with Na, K, or KC_8 for Ln = Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y, eq 2.[7,8] By extending the LnZ_3/M system to heteroleptic precursors LnZ_2Z'/M, e.g., eq 3, the formation of $(N_2)^{2-}$ complexes has been accomplished for La, Ce, and Pr as well.[9,11]



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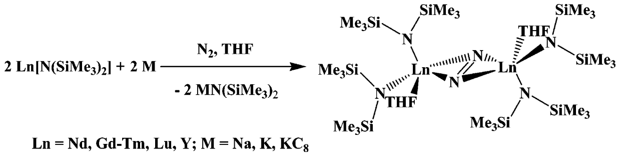

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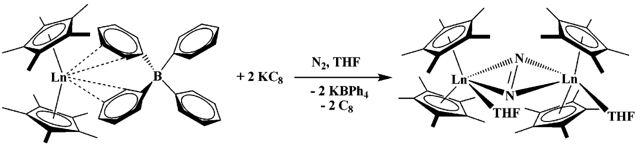
2 

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To determine if the LnZ_3/M and LnZ_2Z'/M reduction systems would lead to unusual chemistry with substrates other than dinitrogen, reactions with CO_2 were examined. Carbon dioxide is a more complicated substrate than dinitrogen for this system,

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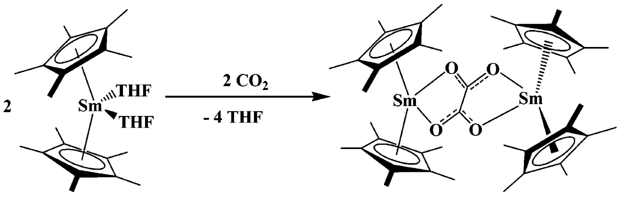
since there is independently reported chemistry between CO_2 and alkali metals.[15-17] For example, alkali and alkaline earth metal amalgams react with CO_2 at temperatures from 25 to 180 °C to make a variety of products including carbonates and oxalates.

Both of these products have been observed from CO_2 reduction by Sm^{2+}. With $(C_5Me_5)_2Sm(THF)_2$ the reductive coupling of CO_2 to oxalate, $[(C_5Me_5)_2Sm]_2(O_2CCO_2)$, was observed, eq 4.[18] Recently, a porphyrinogen complex of Sm^{2+}, $Sm(C_{38}N_4H_{54})(THF)_2$, has been found to reduce CO_2 to carbonate, eq 5 (*meso*-ethyl groups not shown for clarity).[19]



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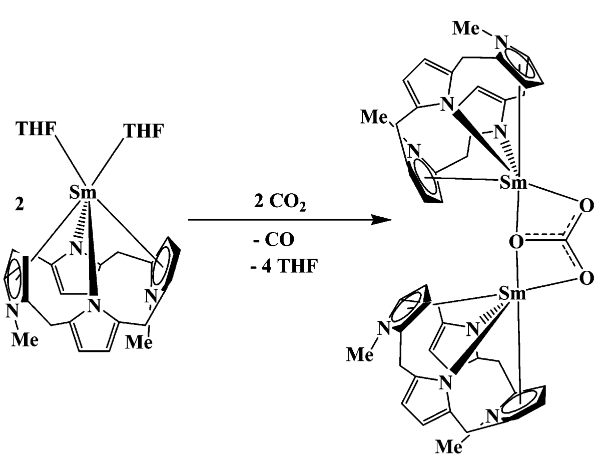

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To determine if this Sm^{2+} reductive chemistry could be extended to diamagnetic lanthanides and to see if new reaction products would be accessible, the *lanthanum* reduction systems $(C_5Me_4H)_3La/M$ and $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]/M$ were chosen. These were selected because both gave isolable diamagnetic products in good yield with N_2 as a substrate.[7,9]

Experimental Section

The manipulations described below were performed under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$[20] and KC_8[21] were prepared according to the literature. $(C_5Me_4H)_3Ln$ was prepared according to the literature (Ln = La,[22] Nd,[23] Sm[22]) or as described in the Supporting Information (Ln = Gd). C_5Me_5H was dried over molecular sieves and degassed by three freeze−pump−thaw cycles prior to use. $C_5Me_4H_2$ was distilled onto molecular sieves and degassed by three freeze−pump−thaw cycles prior to use. KC_5Me_4H and KC_5Me_5 were prepared by adding $C_5Me_4H_2$ and C_5Me_5H, respectively, to either excess potassium bis(trimethylsilyl)amide or excess potassium bis(dimethylphenylsilyl)amide[24] in toluene. Hydrated lanthanide trichlorides were desolvated with NH_4Cl.[25] Sodium was purchased from Strem and freshly shaved before use. Solvents were sparged with argon and dried as previously described.[24] NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred before use. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker GN 500 MHz or Bruker Cryo 500 MHz spectrometer. Infrared spectra were recorded as thin films obtained from benzene using an ASI ReactIR 1000 spectrometer.[26] Elemental analyses were performed by Desert Analytics (Tucson, AZ) or by complexometric titration.[27] Air/water-free ES-MS analyses were recorded on a Waters LCT Premier-MS set in the atmospheric pressure chemical ionization (APCI) mode;[28] masses reported are for the most abundant isotope.

$[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, 1. Complex **1** was originally isolated from a reaction of $(C_5Me_4H)_3La$ and Na[8] that evidently contained chloride as a contaminant. Since a reduced carbonate product could not subsequently be crystallized in the absence of chloride, the following synthesis of **1** was developed. THF (ca. 15 mL) was degassed through three freeze−pump−thaw cycles and condensed onto $(C_5Me_4H)_3La$ (142 mg, 0.28 mmol), $LaCl_3$ (38 mg, 0.15 mmol), and sodium that had been smeared on the bottom of a sealable flask. CO_2 (1 atm) was introduced and the solution was allowed to stir overnight. The solvent was removed *in vacuo*, and solids were extracted with toluene. Toluene was removed *in vacuo*, and solids were dissolved in a minimal amount of diethyl ether and centrifuged to remove solids. At −35 °C over 1−3 weeks, a concentrated sample gave colorless, X-ray quality crystals of **1** (10 mg). **1** was also successfully obtained from $[(C_5Me_4H)_2La]Cl_2K(THF)_x$ and excess Na using a procedure like that above. ^1H NMR (C_6D_6): δ 1.41 (12H, *THF*), 1.70 (s, 18H, $O_2CC_5Me_4H$), 1.98 (s, 18H, $O_2CC_5Me_4H$), 2.34 (s, 18H, C_5Me_4H), 2.36 (s, 18H, C_5Me_4H), 3.47 (s, 3H, $O_2CC_5Me_4H$), 3.73 (br s, 12H, *THF*), 5.83 (s, 3H, C_5Me_4H). ^{13}C NMR (C_6D_6): δ 11.6 ($O_2CC_5Me_4H$), 11.7 (C_5Me_4H), 13.4 (C_5Me_4H), 13.7 ($O_2CC_5Me_4H$), 26.0 (*THF*), 68.5 (5-$O_2CC_5Me_4H$), 69.9 (*THF*), 113.3 (5-C_5Me_4H), 121.0 (C_5Me_4H), 121.7 (C_5Me_4H), 133.2 ($O_2CC_5Me_4H$), 138.1 ($O_2CC_5Me_4H$), 177.7 ($O_2CC_5Me_4H$). Elemental analyses were performed on single crystals of $\mathbf{1}\cdot Et_2O$ (see below). Anal. Calcd for $C_{70}H_{102}O_{12}ClLa_3\cdot C_4H_{10}O$ (i.e., $\mathbf{1}\cdot Et_2O$): C, 53.48; H, 6.79; Cl, 2.13; La, 25.08. Calcd for **1** without Et_2O in the crystal unit cell, $C_{70}H_{102}O_{12}ClLa_3$: C, 52.95; H, 6.42; Cl, 2.23; La, 26.25. Calcd for **1**−3THF, $C_{58}H_{78}O_9ClLa_3$: C, 50.79; H, 5.73; Cl, 2.58; La, 30.39. Found: C, 51.52; H, 6.26; Cl, 2.3; La, 24.4. IR: 2957m, 2926m, 2856m, 1644m, 1567m, 1513s, 1494, 1409vs, 1363s, 1328m, 1305m, 1189w, 1100w, 1069w, 850w, 815w, 776w, 714w, 676s, 656m cm^{-1}.

$\{[(C_5Me_4H)_2Ln](\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, 3. A THF (ca. 15 mL) solution of $(C_5Me_4H)_3La$ (146 mg, 0.3 mmol) was degassed through three freeze−pump−thaw cycles. CO_2 (1 atm) was introduced, and

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Table 1. Air-Free Anhydrous APCI-MS of $(C_5Me_4H)_3Ln/CO_2$ Reaction Products (Ln = La, Nd, Sm, Gd), *m/z*

fragment identification	La	Nd	Sm	Gd[a]
$[(C_5Me_4H)(O_2CC_5Me_4H)(\text{toluene})Ln]^+$	517	522	530	536
$[(C_5Me_4H)_2(O_2CC_5Me_4H)Ln]^+$	546	551	559	565
$[(C_5Me_4H)_3(O_2CC_5Me_4H)_2Ln_2]^+$	971	981	994	1009
$[(C_5Me_4H)_2(O_2CC_5Me_4H)_3Ln_2]^+$	1015	1025	1038	1053
$[(C_5Me_4H)(O_2CC_5Me_4H)_4Ln_2]^+$	1059	1069	1082	n/a

[a] The APCI mass spectrum of the $(C_5Me_4H)_3Gd/CO_2$ reaction products also showed a peak at 834.

the solution was allowed to stir overnight. The solvent was removed *in vacuo*, and solids were extracted with toluene. The toluene was then removed *in vacuo*, leaving a pale yellow solid. ^{1}H NMR (THF-d_8): δ 1.39, 1.73, 1.75, 1.79, 1.80, 1.84, 1.89, 1.91, 1.97, 1.99, 2.02, 5.41, 5.43, 5.45, 5.84. ^{13}C NMR (THF-d_8): δ 10.77, 10.79, 11.1, 11.5, 12.1, 12.9, 13.0, 13.1, 13.2, 13.36, 13.39, 13.4, 13.5, 13.6, 117.8, 118.0, 119.1, 120.2, 120.7, 121.1, 125.9, 126.1, 129.0, 129.7, 132.0, 132.6, 133.5, 136.56, 137.6, 138.3, 146.7, 148.0, 153.5, 168.7, 177.5, 183.0, 184.7. IR: 3613w, 2968m, 2910s, 2860m, 2729w, 1654w, 1552vs, 1478m, 1440s, 1393s, 1374s, 1355s, 1328m, 1239w, 1177w, 1146w, 1108m, 1073w, 1034m, 992w, 973w, 934w, 907w, 842m, 768m, 706w, 676m, 641w cm^{-1}. The Nd analogue was pale blue; the Sm and Gd analogues were yellow. IR data for Ln = Nd, Sm, and Gd can be found in the Supporting Information. APCI-MS (toluene) for Ln = La, Nd, Sm, and Gd are given in Table 1. At −26 °C over 1−3 weeks, a concentrated sample of **3** gave yellow X-ray quality crystals of $\{[(C_5Me_4H)_2La](\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$ (41 mg, 26%). ^{1}H NMR (C_6D_6): δ 1.6, 1.73, 1.75, 1.77, 20.6, 2.08, 2.11, 2.12, 2.13, 2.15, 2.18, 2.20, 2.33 (d), 5.77, 5.82, 5.83. ^{13}C NMR (C_6D_6): δ 11.0, 11.6, 11.7, 11.8, 11.9, 12.0, 12.6, 13.1, 13.2, 13.3, 15.6, 14.6, 15.6, 17.0, 51.1, 114.4, 119.8, 120.3, 121.1, 121.2, 121.6, 121.7, 122.0, 122.2, 132.0, 133.0, 135.2, 137.4, 138.4, 138.6, 149.0, 156.0, 174.3, 181.5, 181.5. Anal. Calcd for $La_2C_{56}H_{78}$: C, 61.53; H, 7.19; La, 25.42. Found: C, 50.56; H, 5.86; La, 22.1 (elemental ratio $La_2C_{53}H_{73}$).

Synthesis of $[(C_5Me_4H)_2La]Cl_2K(THF)_x$ and $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, 4. KC_5Me_4H (225 mg, 1.4 mmol) was added to a stirred suspension of $LaCl_3$ (162 mg, 0.7 mmol) in ca. 20 mL of THF, and the mixture was allowed to stir overnight. The solution was then centrifuged, and subsequent removal of solvent *in vacuo* gave $[(C_5Me_4H)_2LaCl_2K(THF)_x]$ as a flaky, yellow powder (188 mg, 45%). ^{1}H NMR (THF-d_8): δ 1.94 (s, 12H, $C_5\mathit{Me}_4H$), 2.00 (s, 12H, $C_5\mathit{Me}_4H$), 5.54 (s, 2H, $C_5Me_4\mathit{H}$). ^{13}C NMR (THF-d_8): δ 11.8 ($C_5\mathit{Me}_4H$), 13.4 ($C_5\mathit{Me}_4H$), 112.1 (C_5Me_4H), 119.0 (C_5Me_4H), 121.3 (C_5Me_4H). Anal. Calcd for $(C_5Me_4H)_2LaCl_2K$: La, 28.27. Found: La, 28.1. A solution of $[(C_5Me_4H)_2La]Cl_2K(THF)_x$ (92 mg, 0.14 mmol) and 18-crown-6 (45 mg, 0.16 mmol) in ca. 0.5 mL of THF at −35 °C over 1−3 weeks produced colorless crystals of $[(C_5Me_4H)_2LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, **4** (104 mg, 82%).

X-ray Data Collection, Structure Solution, and Refinement for 1·Et$_2$O and 2. X-ray crystallographic data were obtained by mounting a crystal on a glass fiber and transferring it to a Bruker CCD platform diffractometer. The SMART[29] 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[30] and SADABS[31] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[32] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[33] for neutral atoms were used throughout the analysis.

$[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)\cdot Et_2O$, 1·Et$_2$O. A colorless crystal of approximate dimensions 0.27 × 0.33 × 0.36 mm was handled as described above. 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 were included using a riding model. There was one molecule of diethyl ether solvent present. The tetramethylcyclopentadienyl ring defined by atoms C(19)−C(28) was disordered. Each methyl carbon was included with a site occupancy of 0.80 to account for an even distribution of those atoms over the five ring positions. The methyl carbons were also assigned the same isotropic thermal parameters. The $(C_5Me_4H)^-$ ring hydrogen atom was not included. At convergence, wR2 = 0.1051 and Goof = 1.059 for 777 variables refined against 16 715 data (0.78 Å). As a comparison for refinement on *F*, R1 = 0.0365 for those 14 267 data with $I > 2.0\sigma(I)$. Crystallographic data are presented in Table 1.

$[(C_5Me_5)La(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1{:}\ \eta^2\text{-}O_2CC_5Me_5)]_2$, 2. THF (10 mL) was degassed through three freeze−pump−thaw cycles and condensed onto $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$ (282 mg, 0.39 mmol) and KC_8 (57 mg, 0.42 mmol). CO_2 (1 atm) was introduced, and the solution was allowed to stir overnight. The solvent was removed *in vacuo*, and solids were extracted with toluene. Toluene was removed *in vacuo*, and solids were dissolved in a minimal amount of methylcyclohexane. At −26 °C over a period of months, a concentrated sample gave colorless, X-ray quality crystals of **2**. A colorless crystal of approximate dimensions 0.19 × 0.22 × 0.38 mm was handled as described above. 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 either were located from a difference Fourier map and refined (*x,y,z* and U_{iso}) or were included using a riding model. The molecule was located about an inversion center. There was one molecule of methylcyclohexane present per formula unit (also located about an inversion center). The solvent methyl group and associated hydrogen atoms were included at 1/2 site occupancy. The disordered hydrogen atom attached to C(35) was not included. At convergence, wR2 = 0.0467 and Goof = 1.064 for 570 variables refined against 8065 data (0.76 Å). As a comparison for refinement on *F*, R1 = 0.0185 for those 7693 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Solution, and Refinement for $\{[(C_5Me_4H)_2Ln](\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, 3. A light yellow block 0.12 × 0.10 × 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. The crystal-to-detector distance was 60 mm, and exposure time was 5 s per frame using a scan width of 0.3°. Data collection was 99.9% complete to 25.00° in θ. A total of 24 812 reflections were collected covering the indices $-22 \leq h \leq 21$, $-33 \leq k \leq 32$, $-18 \leq l \leq 17$; 6768 reflections were found to be symmetry-independent, with an R_{int} of 0.0311. Indexing and unit-cell refinement indicated a *C*-centered, monoclinic lattice. The space group was found to be *C*2/*c* (No. 15). The data were integrated using the Bruker SAINT software program and scaled using SADABS. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

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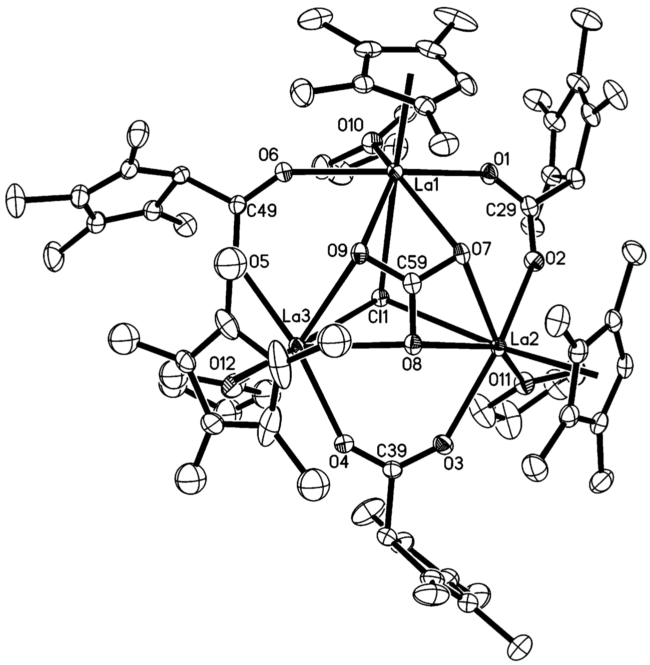


Figure 1. Thermal ellipsoid plot of $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, **1**, drawn at the 30% probability level. The disorder of the La(3) tetramethylcyclopentadienyl ring has been omitted for clarity.

X-ray Data Collection, Structure Solution, and Refinement for $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, 4. A colorless plate 0.15 × 0.10 × 0.04 mm in size was handled as described for **3**. A total of 41 555 reflections were collected covering the indices $-10 \leq h \leq 10$, $-23 \leq k \leq 23$, $-29 \leq l \leq 30$; 8058 reflections were found to be symmetry-independent, with an R_{int} of 0.0294. Indexing and unit-cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$ (No. 14). Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure.

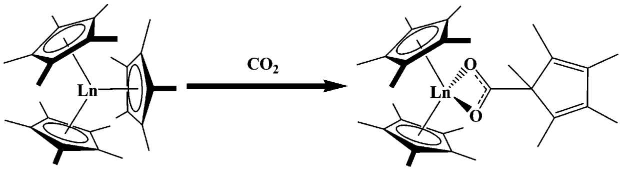
Results

$[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, 1. To test LnZ_3/M reduction of carbon dioxide, CO_2 at 1 atm was added to excess sodium and a sample of $(C_5Me_4H)_3La$. Unexpectedly, a chloride-containing product was obtained, $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, **1**, Figures 1 and 2. The $(C_5Me_4H)_3La$ starting material evidently contained residual chloride that originated from the $LaCl_3$ precursor. Retention of chloride in lanthanide syntheses often is a problem.[34]

Although complex **1** contained a chloride from an impurity in the starting material, it did reveal that this LnZ_2Z'/M contaminant could effect reduction of CO_2. In this case the product was not the oxalate of the Sm^{2+} metallocene reaction, eq 4, but a carbonate ligand, $(CO_3)^{2-}$, as observed in the Sm^{2+} porphyrinogen reaction, eq 5. The half reaction for this reduction is shown in eq 6.

$$2\,e^- + 2\,CO_2 \rightarrow CO_3^{\,2-} + CO \qquad (6)$$

The structure of **1** revealed that CO_2 also reacted in another way in this system. One $(C_5Me_4H)^-$ ligand per La had been converted to a tetramethylcyclopentadienyl-substituted carboxylate, $(O_2CC_5Me_4H)^-$. Insertion of CO_2 into metal ligand bonds is well-known[35−45] and includes insertion into Ln−C bonds.[40−45] However, insertion of CO_2 into lanthanide cyclopentadienyl ring linkages, to our knowledge, has been observed only with the sterically crowded $(C_5Me_5)_3Ln$ complexes, eq 7.[45] In these cases, the unusually long Ln−C(C_5Me_5) distances impart η^1-(C_5Me_5) alkyl-like reactivity and insertion reactivity to the rings in these complexes.



(7)

Ln = La, Ce, Pr, Nd, Sm

Attempts to isolate a crystalline carbonate product from reduction of chloride-free $(C_5Me_4H)_3La$ were unsuccessful. However, the synthesis of **1** could be reproduced from mixtures of $(C_5Me_4H)_3La$ and $LaCl_3$ in a 2:1 ratio as well as from the "ate" salt, $(C_5Me_4H)_2LaCl_2K(THF)_x$, although the yield was low in all cases.

As shown in Figures 1 and 2, the structure of **1** contains three $[(C_5Me_4H)(THF)La]^+$ units that form a nearly equilateral triangle with La···La distances of 4.433, 4.457, and 4.491 Å. The three metals are connected on one side of the La_3 plane by a triply bridging chloride ligand and on the other by a triply bridging carbonate. All of the $(C_5Me_4H)^-$ ligands are located on the same side of the lanthanide plane as the $(CO_3)^{2-}$ moiety, while the THF ligands are all on the same side of the lanthanide plane as the chloride. The metals are also connected by the three μ-η^1:η^1-tetramethylcyclopentadienyl carboxylates. The tetramethylcyclopentadienyl carboxylates are oriented away from the $(C_5Me_4H)^-$ ligands and toward the THF side of the plane. The Cl···C(carbonate) vector is perpendicular to the plane of the three lanthanum atoms.

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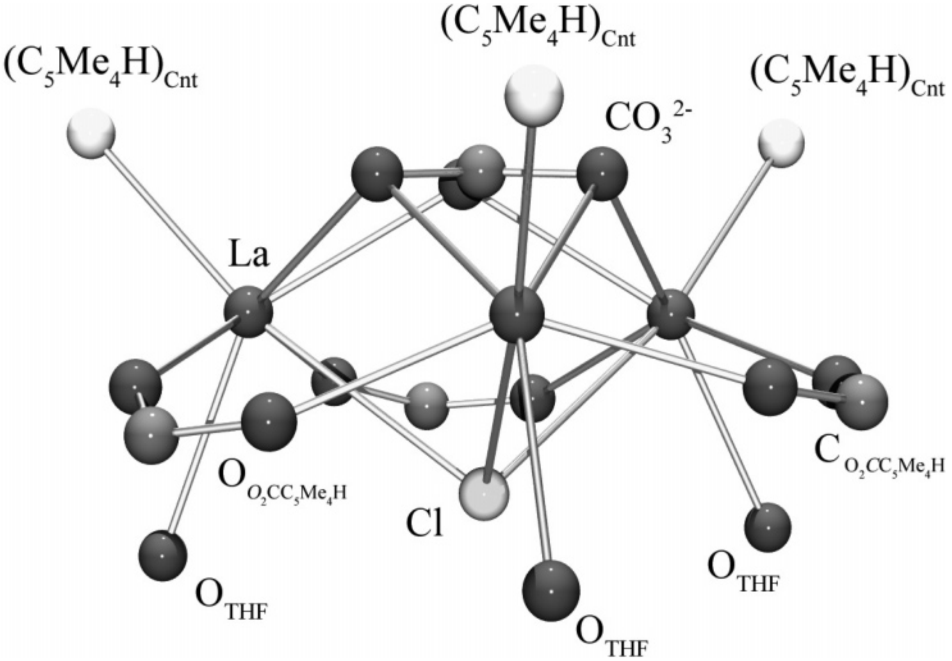

Figure 2. "Core" of $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, **1**, as seen along the edge of the lanthanide plane.

Table 2. X-ray Data Collection Parameters for $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, 1, $[(C_5Me_5)La(\mu\text{-}\eta^1{:}\eta^2\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_5)]_2$, 2, $\{[(C_5Me_4H)_2La](\mu\text{-}\eta^1{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, 3, and $[(C_5Me_4H)_2LaCl(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)]_n$, 4

empirical formula	$C_{70}H_{102}ClLa_3O_{12}\cdot C_4H_{10}O$ **1**	$C_{64}H_{90}O_8La_2\cdot C_7H_{14}$ **2**	$C_{56}H_{78}La_2O_4$ **3**	$C_{30}H_{50}O_6Cl_2KLa$ **4**
fw	1661.82	1363.36	1093.00	755.61
temp (K)	163(2)	163(2)	100(2)	100(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/n$
a (Å)	23.814(3)	12.0519(15)	17.136(3)	8.572(3)
b (Å)	12.5446(15)	12.3970(16)	25.010(4)	17.910(6)
c (Å)	26.514(3)	12.8787(16)	13.844(2)	22.612(7)
α (deg)	90	68.495(2)	90	90
β (deg)	106.749(2)	74.493(2)	100.998(3)	95.777(5)
γ (deg)	90	77.091(2)	90	90
volume $Å^3$	7584.6(16)	1708.1(4)	5824.3(17)	3454.1(19)
Z	4	1	4	4
ρ_{calcd} (Mg/m^3)	1.455	1.325	1.246	1.453
μ (mm^{-1})	1.752	1.285	1.485	1.549
R1^a [$I > 2.0\sigma(I)$]	0.0365	0.0185	0.0401	0.0256
wR2^b (all data)	0.1051	0.0467	0.1229	0.0613

^{a}R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 $= [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\ ]^{1/2}$.

The $(CO_3)^{2-}$ moiety is planar, with O−C−O angles of 119.7(3)°, 120.1(3)°, and 119.5(3)°. The C−O carbonate distances are equivalent within the error limits: 1.247(5)−1.261(5) Å. As shown in Figure 2, the plane of the $(CO_3)^{2-}$ ligand is parallel to the plane of the three lanthanide atoms. The La−O(carbonate) distances vary from 2.556(3) to 2.603(3) Å, Table 3, which are typical for La−O(carbonate) distances.[18,46]

The six La−O(carboxylate) distances vary from 2.435(3) Å for La(1)−O(1) to 2.480(3) Å for La(2)−O(3). These are within the broad range observed in La−O(carboxylate) distances, e.g., distances range from 2.403(2) Å for $La[O_2CC(CH_2)Me]_3(H_2O)_2$[47] to 2.738(3) Å for $\{La[O_2CC(CH_2)Me]_3(phen)(CH_2CMeCO_2H)\}_2$.[48] The 2.533 Å average La−(C_5Me_4H ring centroid) distance is close to other La−(C_5Me_4H ring centroid) distances such as 2.573 Å in $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[9] and $La(C_8H_8)(C_5Me_4H)(THF)_2$,[49] and 2.616 Å in $(C_5Me_4H)_3La$.[22,23] The 2.587(3) and 2.612(3) Å La−O(THF) distances are similar to the 2.636(3) Å La−O(THF) distance in $[(C_5Me_4H)_2(THF)La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$.[9] The lanthanide−chloride distances average 3.086 Å and are longer than the terminal nine-coordinate lanthanide chloride bond lengths of 2.789(2) and 2.893(2) Å for $\{LaCl_2(OH_2)[O(CH_2CH_2OCH_2CH_2OH)_2]\}Cl\cdot H_2O$[50] and 2.816(2) and 2.872(2) Å for $LaCl_3(N_6C_{18}H_{18})$[51]and are also longer then the μ_2-bridging distances of 2.781(1) and

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(46) For example, 2.409(3) to 2.608(3) Å for $[La_6(tpen)_4(CH_3CN)_2(H_2O)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CO_3)_4(\mu_3\text{-}\ \eta^1{:}\eta^1{:}\eta^2\text{-}CO_3)_2][OTf]_6\cdot 6CH_3CN$ (Natrajan, L.; Pécaut, J.; Mazzanti, M. *Dalton Trans.* **2006**, 1002). Additionally, the Sm−O(carbonate) distances in $[Co(NH_3)_6][Sm(CO_3)_3(H_2O)]$ vary from 2.408(3) to 2.565(6) Å, which when normalized to La, are 2.492 to 2.607 Å (Clark, D. L.; Donohoe, R. J.; Gordon, J. C.; Gorden, P. L.; Keogh, D. W.; Scott, B. L.; Tait, C. D.; Watkin, J. G. *J. Chem. Soc., Dalton Trans.* **2000**, 1975), and the Nd−O(carbonate) distances in $Nd(CO_3)_4^{5-}$ vary from 2.452(3) to 2.544(3) Å, which when normalized to La, are 2.505 and 2.597 Å (Runde, W.; Neu, M. P.; Van Pelt, G.; Scott, B. L. *Inorg. Chem.* **2000**, *39*, 1050).

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_4H)La(THF)]_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}CO_3)(\mu_3\text{-}Cl)$, 1

La(1)−O(7)	2.563(3)	La(1)−O(10)	2.603(3)
La(1)−O(9)	2.557(3)	La(2)−O(11)	2.587(3)
La(2)−O(7)	2.564(3)	La(3)−O(12)	2.612(3)
La(2)−O(8)	2.591(3)	La(1)−Cnt1[a]	2.537
La(3)−O(8)	2.603(3)	La(2)−Cnt2[a]	2.528
La(3)−O(9)	2.556(3)	La(3)−Cnt3[a]	2.538
La(1)···C(59)	2.879(4)	La(1)−Cl(1)	3.1278(9)
La(2)···C(59)	2.907(4)	La(2)−Cl(1)	3.0720(9)
La(3)···C(59)	2.904(4)	La(3)−Cl(1)	3.0581
La(1)−O(1)	2.435(3)		
La(1)−O(6)	2.445(3)		
La(2)−O(2)	2.445(3)	O(7)−La(1)−O(9)	51.57(8)
La(2)−O(3)	2.480(3)	O(7)−La(1)−Cl(1)	68.80(6)
La(3)−O(4)	2.453(3)	O(9)−La(1)−Cl(1)	68.87(6)
La(3)−O(5)	2.460(3)	O(10)−La(1)−Cl(1)	79.58(7)
		O(1)−La(1)−O(10)	72.62(10)
C(59)−La(1)−Cl(1)	60.24(7)	O(6)−La(1)−O(10)	75.24(10)

[a] Cnt1 is C(1)−C(5), Cnt2 is C(10)−C(14), and Cnt3 is C(19)−C(23).

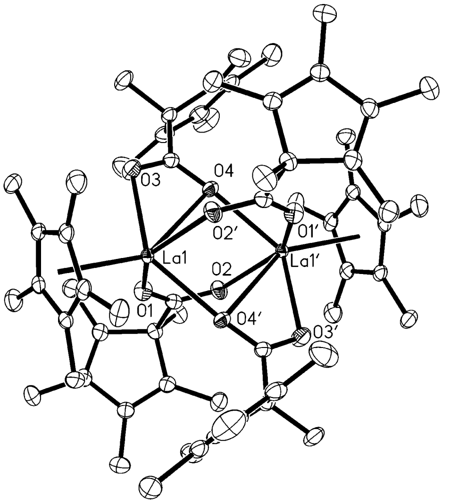

Figure 3. Thermal ellipsoid plot of $[(C_5Me_5)La(\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_5)]_2$, **2**, drawn at the 50% probability level.

2.86(3) Å for $[LaCl_2(NO_3)(12\text{-crown-}4)]_2$[52] and 2.85(1)−3.013(2) Å for $\{LaCl_3[O(CH_2CH_2OCH_2CH_2OH)_2]\}_2$.[53] Longer distances are expected for a triply bridging ligand.

$[(C_5Me_5)La(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CC_5Me_5)]_2$, 2. Attempts were also made to reduce CO_2 with a LnZ_2Z'/K reaction like that in eq 3. Addition of CO_2 to $[(C_5Me_5)_2La][(\mu\text{-}Ph)_2BPh_2]$ and KC_8 in THF gave a mixture of products with a complicated ^{1}H NMR spectrum indicative of numerous species. Although no single CO_2 reduction product was isolated, single crystals of a CO_2 insertion product were obtained in low yield that could be characterized by X-ray crystallography, $[(C_5Me_5)La(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CC_5Me_5)]_2$, **2**, Figure 3. Since each metal in complex **2** had three $(C_5Me_5)^-$ groups in the form of $(C_5Me_5)^-$ or $(O_2CC_5Me_5)^-$ and the starting material had only two, ligand redistribution must have occurred in this reaction.

Complex **2** contains two symmetry-related $[(C_5Me_5)La]^{2+}$ units bridged by two crystallographically independent $(\mu\text{-}O_2CC_5Me_5)^-$ carboxylates. One carboxylate adopts a $\mu\text{-}\eta^1\text{:}\eta^1$ bridging mode, and the other is $\mu\text{-}\eta^1\text{:}\eta^2$. Both of these have previously been observed in $La_2[O_2CC(CH_3)_2CH_2CH_3]_6(C_5H_5N)_4$.[54] A variety of carboxylate bridging modes have been observed in dimeric lanthanide complexes,[54,55] and variations in structure depending on the particular cyclopentadienyl ligand have been described.[56,57]

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)La(\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CC_5Me_5)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_5)]_2$, 2

La(1)−Cnt[a]	2.490	Cnt−La(1)−O(1)	109.4
La(1)−O(1)	2.4202(11)	Cnt−La(1)−O(2′)	110.0
La(1)−O(2′)	2.4363(11)	Cnt−La(1)−O(3)	100.8
La(1)−O(3)	2.4542(12)	Cnt−La(1)−O(4′)	123.4
La(1)−O(4′)	2.4715(11)	La(1)−O(4)−La(1′)	91.73(3)
La(1)−O(4)	2.9073(11)	O(3)−La(1)−O(4′)	99.90(4)
La(1)−La(1′)	3.8700(4)		

[a] Cnt is C(1)−C(5).

The three La−O(carboxylate) distances, Table 4, for the nonbridging oxygen atoms are similar to those in **1**: La(1)−O(1), La(1)−O(2′), and La(1)−O(3) are 2.420(1), 2.436(1), and 2.454(1) Å, respectively. The bridging oxygen has a distance of 2.471(1) Å for La(1)−O(4′) and a long-range interaction of 2.904(1) Å for La(1)−O(4). The La−(C_5Me_5) distance is 2.490 Å and can be compared to other mono-(C_5Me_5) complexes of lanthanum: 2.503 Å for $(C_5Me_5)La(AlMe_4)_2$,[58] 2.517, 2.537, and 2.541 Å for $\{[(C_5Me_5)La]_3(\mu\text{-}Cl)_3(thf)(\mu\text{-}\eta^2\text{:}\eta^6\text{:}\eta^6\text{-}C_{16}H_{10})\}$,[59] 2.528 and 2.534 Å for $(C_5Me_5)La[CH(SiMe_3)_2]_2$,[60,61] and 2.559 Å for $(C_5Me_5)La[CH(SiMe_3)_2]_2(THF)$.[61]

Reaction of $(C_5Me_4H)_3Ln$ with CO_2 (Ln = La, Nd, Sm, Gd). To determine if the CO_2 insertion chemistry could be observed without the alkali metal reagent, $(C_5Me_4H)_3La$ was treated with CO_2 without the presence of an external reductant. The ^{1}H NMR spectrum of the bulk product showed 11 peaks in the $(C_5Me_4H)^-/(O_2CC_5Me_4H)^-$ region. The ^{13}C NMR spectrum showed four distinct peaks in the carboxylate region, with the most prominent at 178 ppm, which is typical of metal carboxylates[38,62,63] and similar to that found in **1**. This suggested that insertion of CO_2 into La−(C_5Me_4H) units had occurred, but that multiple products were present.

A few crystals of the $(C_5Me_4H)_3La/CO_2$ reaction product were obtained along with a powdery byproduct. Unfortunately, the determination was complicated by a highly disordered structure. Data on a high-quality crystal, however, did allow for modeling of the disorder. The structure shows the insertion of CO_2 into one of the $(C_5Me_4H)^-$ rings to form a complex of composition $\{[(C_5Me_4H)_2La](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, **3**, Figure 4. The La and carboxylate moieties form an eight-membered ring in a structure similar to other lanthanide carboxylates.[42−44] However,

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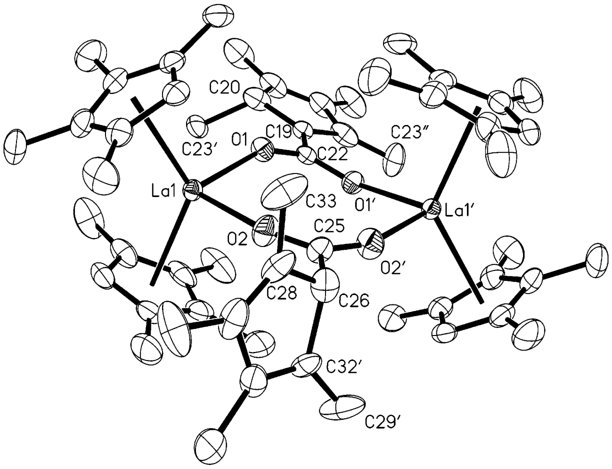

Figure 4. Thermal ellipsoid plot of $\{[(C_5Me_4H)_2La](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, **3**, drawn at the 50% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $\{[(C_5Me_4H)_2Ln](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_5Me_4H)\}_2$, 3

La(1)−Cnt1[a]	2.529	Cnt1−La(1)−Cnt2	129.85
La(1)−Cnt2[a]	2.548	C(20)−C(19)−C(20′)	109.2(5)
La(1)−O(1)	2.386(3)	C(19)−C(20)−C(23)	133.1(5)
La(1)−O(2)	2.387(3)	C(21)−C(20)−C(23)	120.8(5)
La(1)···La(1′)	5.219	C(19)−C(20)−C(21)	106.1(4)
C(19)−C(20)	1.424(5)	C(23)−C(20)−C(23′)	47.3(6)
C(20)−C(21)	1.488(6)	C(19)−C(20)−C(23′)	117.8(5)
C(21)−C(21′)	1.338(10)	C(21)−C(20)−C(23′)	111.0(5)
C(31)−C(32)	1.325(12)	C(20)−C(21)−C(21′)	109.3(3)
C(27)−C(28)	1.346(15)	C(24)−C(21)−C(24′)	127.5(3)
C(26)−C(28′)	1.374(9)	C(20)−C(21)−C24)	123.2(5)
C(27)−C(31′)	1.477(16)	C(28)−C(26)−C(25)	118.0(4)
C(26)−C(32′)	1.646(9)	C(28)−C(26)−C(32′)	102.3(6)
		C(25)−C(26)−C(32)	107.3(3)
C(32)−C(31)−C(27′)	109.5(9)	C(28)−C(27)−C(34)	134.7(11)
C(32)−C(31)−C(30)	137.0(10)	C(28)−C(27)−C(31′)	109.0(8)
C(27′)−C(31)−C(30)	113.3(9)	C(34)−C(27)−C(31′)	115.9(10)
C(31)−C(32)−C(29)	129.7(10)	C(27)−C(28)−C(26)	113.4(8)
C(31)−C(32)−C(26)	105.8(7)	C(27)−C(28)−C(33)	130.6(10)
C(29)−C(32)−C(26)	124.5(8)	C(26)−C(28)−C(33)	116.0(10)

[a] Cnt1 is C(1)−C(5) and Cnt2 is C(10)−C(14).

in contrast to the $[(C_5Me_5)_2Sm(O_2CR)]_2$ structures (R = phenyl,[42] allyl,[43] EPh[44]), which have planar eight-membered $(SmO_2C)_2$ rings, the structure of **3** has a kinked arrangement, similar to that seen in $\{[(C_5MeH_4)Yb](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_6H_5)\}_2$.[57] In contrast with **2**, only $\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CR$ bridging of the carboxylate is seen. This is consistent with the more sterically crowded environment of $[(C_5Me_4H)_2La]^+$ compared to $[(C_5Me_5)La]^{2+}$ and the propensity of bridging to increase with decreasing steric crowding.[56] Differences in the Ln−O−C angles have been ascribed to a coordination approaching $\mu\text{-}\eta^1\text{:}\eta^2\text{-}O_2CR$ rather than $\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CR$. In the case of **3**, the two angles are 151.2(2)° and 157.0(3)° for La(1)−O(1)−C(22) and La(1)−O(2)−C(25), respectively, which give a difference of about 5°, which is in contrast to 10−12° in $\{[(C_5MeH_4)Yb](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_6H_5)\}_2$[57] or 14−34° in $\{[(C_5H_5)Yb](\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CC_6F_5)\}_2$.[64]

The La(1)−(C_5Me_4H ring centroid) average, 2.539 Å, Table 5, is comparable to that found in **1**. The La(1)−O(1) and La(1)−O(2) distances of 2.386(3) and 2.387(3) Å, respectively, are equivalent to those found in **1**. The La(1)···La(1′) distance is 5.219 Å, which is much longer that the La···La distances of 4.433, 4.457, and 4.491 Å in **1**.

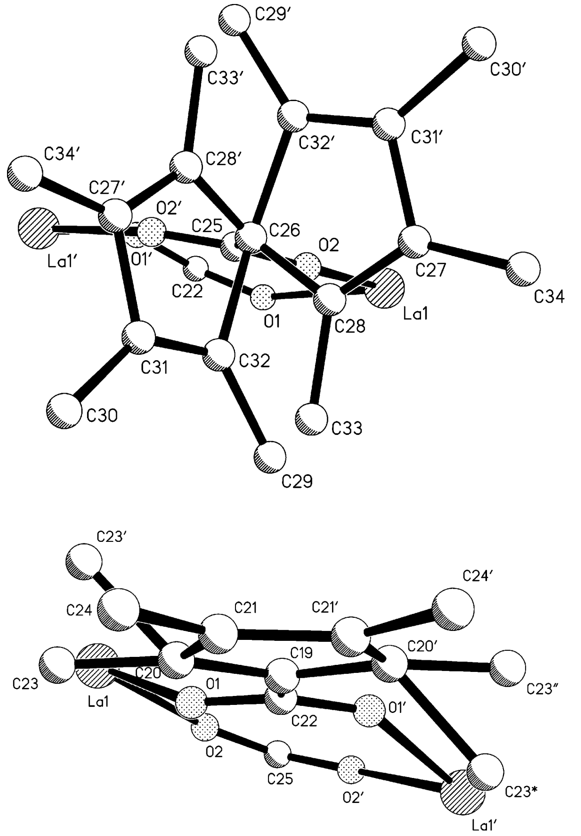

Figure 5. Ball-and-stick diagrams of the disordered $(O_2CC_5Me_4H)^-$ moieties. (Top) The $(O_2CC_5Me_4H)^-$ moiety associated with the C(25) carbonyl; (bottom) the $(O_2CC_5Me_4H)^-$ moiety associated with the C(22) carbon. Both $(O_2CC_5Me_4H)^-$ moieties are shown in the context of the $La_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}O_2CR)_2$ ring.

Both $(O_2CC_5Me_4H)^-$ ligands are disordered, each in a different way. The $(O_2CC_5Me_4H)^-$ unit involving C(25) is disordered over two positions, with C(26) being common for both, Figure 5. The model suggests insertion of CO_2 at the H-substituted carbon of the $(C_5Me_4H)^-$ ring. In the case of the other ring, disorder occurs in the methyl groups attached to the C(20) atoms adjacent to the carbon at which the CO_2 inserted. The data suggest that this latter carbon atom, C(19), is sp^2 hybridized and that a hydrogen shift has occurred such that the C(20) atom is substituted with both a methyl group and hydrogen. This would be consistent with the very complicated NMR spectra observed in these systems.[65]

Attempts to find an ordered system were made with other lanthanides, but this led to even more complexity. $(C_5Me_4H)_3Ln$ complexes of Nd, Sm, and Gd also react with CO_2, as evidenced by rapid color changes upon CO_2 addition in each case. X-ray diffraction on crystals obtained from the Nd reaction[66] gave a unit cell isomorphous with that of **3**, and those data similarly gave a highly disordered structure. Sm gave crystals in a different space group[67] from that of La and Nd, but also showed a similar extensive disorder. In this case, the limited data indicated that insertion occurred at the methyl-substituted carbon atoms *without* hydrogen migration. No X-ray quality crystals were obtained from the Gd reaction.

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[66] Space group $C2/c$; $a = 16.97$ Å, $b = 25.00$ Å, $c = 13.86$ Å, $\alpha = 90°$, $\beta = 101.70°$, $\gamma = 90°$, $V = 5755.8$ Å^3.

[67] Space group $P\bar{1}$; $a = 11.09$ Å, $b = 11.65$ Å, $c = 12.55$ Å, $\alpha = 72.68°$, $\beta = 66.67°$, $\gamma = 80.24°$, $V = 1419.17$ Å^3.

The infrared spectra of these $(C_5Me_4H)_3Ln/CO_2$ reaction products (Ln = La, Nd, Sm, Gd) are virtually identical. Absorptions in the 1300 to 1700 cm^{-1} region were characteristic of symmetric and asymmetric stretching of the carboxylate moieties[68] suggested by X-ray crystallography, but multiple peaks in this region, as well as in the lower wavelength region, characteristic of the OCO bending/rocking region, suggest that more than a single product is present.[44] This is consistent with the complicated ^1H and ^{13}C NMR spectra.

To obtain additional data on insertion of CO_2 into the $(C_5Me_4H)^-$ rings, the $(C_5Me_4H)_3Ln/CO_2$ reaction products were investigated by anhydrous/water-free atmospheric pressure chemical ionization mass spectrometry (APCI-MS).[28] Spectra for the products of all four reactions were similar, Table 1. The major peaks were due to $[(C_5Me_4H)(O_2CC_5Me_4H)(toluene)Ln]^+$ and $[(C_5Me_4H)_2(O_2CC_5Me_4H)Ln]^+$ fragments. The next most prominent ions were $[(C_5Me_4H)_3(O_2CC_5Me_4H)_2Ln_2]^+$, $[(C_5Me_4H)_2(O_2CC_5Me_4H)_3Ln_2]^+$, and $[(C_5Me_4H)(O_2CC_5Me_4H)_4Ln_2]^+$.

$[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, 4. In the course of these studies, it was of interest to obtain more information about the chloride intermediates formed from $LaCl_3$ and KC_5Me_4H. Although this type of information is well-known in the $(C_5Me_5)^-$ system, in which "ate" salts of formula $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2K(\text{donor solvent})_2$ are common,[69] only one structurally characterized $(C_5Me_4H)^-$ analogue had ever been reported to our knowledge, $(C_5Me_4H)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$.[70] This was obtained as a byproduct of a carborane metallocene reaction. Attempts to obtain an "ate" salt of $(C_5Me_4H)_2LnCl_2K$ were aided by the addition of 18-crown-6, and an unusual structure was obtained, $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, **4**, Figure 6, which contains a bridging $(C_5Me_4H)^-$ ligand.

The structure of **4** differs from $(C_5Me_4H)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$[70] in that the alkali metal is not coordinated by both halide ligands. The presence of a terminal Cl cannot be attributed solely to the presence of the crown ether, since an "ate" salt containing a K(18-crown-6) moiety is known in which both halides are bridging: $[C_5H_2(^tBu)_3]_2Dy(\mu\text{-}Cl)_2K(18\text{-crown-}6)$.[71] In **4**, Cl(1) is a terminal ligand with a Cl(1)−La(1) distance of 2.732(1) Å, Table 6. There are no long-distance interactions with other lanthanum ions: the closest La is 5.857 Å away and the closest distance between Cl(1) and another unit of **4** is a 3.901 Å distance to a methyl group of a $(C_5Me_4H)^-$ group. Cl(2) bridges between La(1) and K(1) with a La(1)−Cl(2) distance of 2.770(1) Å and a K(1)−Cl(2) distance of 3.022(1) Å. The Cl−La−Cl angle and the Cl−La−Cnt angles are all within the narrow range 102.6−105.9°. This is in contrast to $(C_5Me_4H)_2Yb(\mu\text{-}Cl)_2Li(THF)_2$, which has a Cl−Yb−Cl angle of 86.7°. All the K(1)−O(18-crown-6) distances are typical[24,72] and fall in the range 2.736(3)−2.895(3) Å.

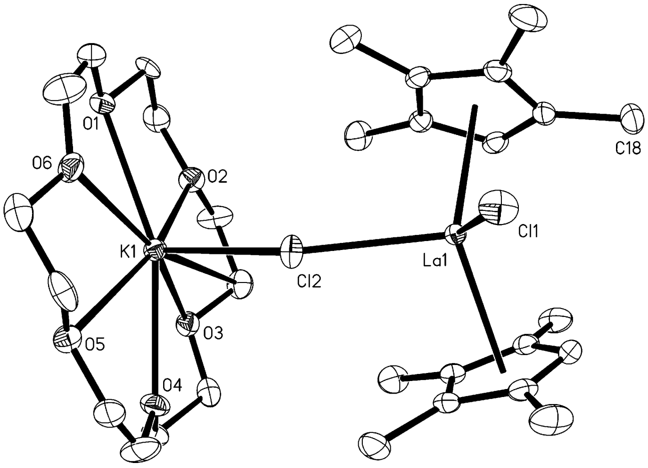

Figure 6. Thermal ellipsoid plot of a monomer of $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, **4**, drawn at the 50% probability level.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, 4

La(1)−Cl(1)	2.7322(10)	Cl(1)−La(1)−Cl(2)	102.637(18)
La(1)−Cl(2)	2.7695(10)	Cnt1−La(1)−Cnt2	132.4(5)
La(1)−Cnt1^a	2.551(2)	Cnt(1)−La(1)−Cl(1)	105.1(4)
La(1)−Cnt2^a	2.553(2)	Cnt(1)−La(1)−Cl(2)	103.3(4)
K(1A)−Cl(2)	3.0222(9)	Cnt(2)−La(1)−Cl(1)	105.9(5)
K(1)−O(1)	2.849(3)	Cnt(2)−La(1)−Cl(2)	104.1(4)
K(1)−O(2)	2.736(3)	La(1)−Cl(1)−K(1)	146.61(2)
K(1)−O(3)	2.850(3)	C(13)−C(18)−K(1′)	171(1)
K(1)−O(4)	2.776(3)		
K(1)−O(5)	2.895(3)	H(18A)−K(1′)	2.982
K(1)−O(6)	2.815(3)	H(18C)−K(1′)	2.915
C(18)−K(1′)	3.201(2)	H(18B)−K(1′)	3.167

^{a} Cnt1 is C(1)−C(5) and Cnt2 is C(10)−C(14).

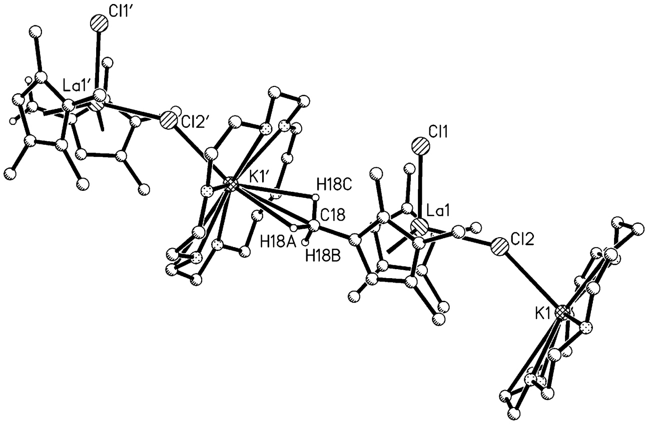

Figure 7. Ball-and-stick representation of the polymer chain of $[(\mu\text{-}C_5Me_4H)(C_5Me_4H)LaCl(\mu\text{-}Cl)K(18\text{-crown-}6)]_n$, **4**.

Unexpectedly, a methyl group on one of the $(C_5Me_4H)^-$ rings in **4**, C(18), is oriented toward a potassium of another molecule of **4**, resulting in the formation of a polymeric network, Figure 7. The K(1′)−C(18) distance is 3.201(2) Å, which is within the range of methyl−potassium agostic bonding: 3.082 to 3.357 Å.[73] This methyl bridging produces the chain structure in the solid state.

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Discussion

Attempts to use the LnZ_3/M and LnZ_2Z'/M reduction systems with CO_2 have revealed a much more general reaction of carbon dioxide with lanthanide metallocenes, namely, insertion. Although CO_2 can be reduced to carbonate by these systems as observed in **1**, the more general and pervasive reaction is insertion of CO_2 to make cyclopentadienyl carboxylates. This complicates the reduction chemistry of CO_2 with $(C_5Me_4H)^-$. With CO_2, the Sm^{2+} reductions in eqs 4 and 5 are more selective, higher yield reactions than the LnZ_3/M and LnZ_2Z'/M reductions. The obervation of two reaction pathways, insertion and reduction, in the synthesis of **1** has parallels in the complicated CO_2 reaction chemistry of $Yb(C_6F_5)_2$ reported by Deacon et al., in which CO_2 insertion is accompanied by C−F activation.[45]

The propensity of CO_2 insertion with these metallocenes was unexpected. CO_2 insertion reactions with $(C_5Me_5)_3Ln$ complexes to make $(C_5Me_5)_2Ln(O_2CC_5Me_5)$ products has been rationalized to occur due to the extreme steric crowding in the $(C_5Me_5)_3Ln$ starting materials.[45,74] The starting materials that insert CO_2 in this study have no obvious steric crowding. Their M−C bond distances are quite normal, yet CO_2 insertion is facile. Observation of CO_2 insertion in the formation of **1** and in the reactions with the $(C_5Me_4H)_3Ln$ complexes could be rationalized as a special reaction for the tetramethylcyclopentadienyl ligand with CO_2. However, formation of the $(C_5Me_5)^-$ product, **2**, from a $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ precursor shows that this is not limited to $(C_5Me_4H)^-$.

The complexity of the product mixtures found in this study suggests that CO_2 insertion into cyclopentadienyl ligands can occur in a variety of ways. Given the disorder in **3** and the ligand redistribution in **2**, it is quite possible that these reactions would form intractable mixtures. Perhaps this is why crystallographic data on this type of reaction have not been reported earlier. This type of reactivity must be kept in mind in any reactions of $(C_5Me_4H)^-$ complexes with CO_2 and related reagents. Formation of a variety of insertion products could complicate any other type of reactivity being pursued with these reagents.

Conclusion

Evaluation of the reduction chemistry of CO_2 with the LnZ_3/M and LnZ_2Z'/M reduction systems has revealed that CO_2 insertion into both $(C_5Me_4H)^-$ and $(C_5Me_5)^-$ ligands attached to lanthanides is much more facile than previously thought. Complicated mixtures of cyclopentadienyl carboxylates can be readily generated in these reactions.

Acknowledgment. We thank the National Science Foundation for support and Dr. John Greaves for assistance with the anhydrous/air-free APCI-MS.

Supporting Information Available: X-ray diffraction details (CIF), synthesis and X-ray crystal structure of $(C_5Me_4H)_3Gd$ (PDF), IR data for $(C_5Me_4H)_3Ln/CO_2$ (Ln = Nd, Sm, Gd) reaction products (PDF), APCI-MS of the $(C_5Me_4H)_3Ln/CO_2$ (Ln = La, Nd, Sm, Gd) reaction products (PDF), ball-and-stick diagram of $[(C_5Me_4H)_2Sm(O_2CC_5Me_4H)]_2$ (PDF), and X-ray data collection, structure solution, and refinement of compounds **1**, **2**, **3**, and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(73) Typical K−C(methyl) distances in these complexes are 3.082 and 3.089 Å for $\{KZn[N(SiMe_3)_2]_2(CH_2Ph)\}_\infty$ (Clegg, W.; Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Liddle, S. T. *Chem. Commun.* **2003**, 406); 3.14 and 3.30 Å for $\{\eta^1\text{-}[(PN^tBu)_2(N^tBu)_2]\}Zr{=}N^tBu[N(^tBu)_2PPN^tBu]\text{-}[K(C_6H_6)]_\infty$ (Bai, G.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Chem. Soc., Dalton Trans.* **2002**, 2437); 3.187(3) and 3.223(4) Å for $\{La\text{-}[(\eta^3\text{-}C_3H_3SiMe_3)_2SiMe_2]_2[\mu\text{-}K(THF)]_n{\cdot}THF\}_\infty$ (Woodman, T. J.; Schormann, M.; Bochmann, M. *Organometallics* **2003**, *22*, 2938); 3.245(2) Å for $[KN(SiMe_2Ph)_2(C_7H_8)]_2$;[24] 3.247(8) Å for $\{Yb[N(SiMe_3)_2]_3\}K_2[Zr_2(O^iPr)_9]$ (Evans, W. J.; Johnston, M. A.; Clark, R. D.; Anwander, R.; Ziller, J. W. *Polyhedron* **2001**, *20*, 2483); 3.261 Å for $[K(THF)_3]\{Si[NCH_2CHMe_2)_2C_6H_4\text{-}1,2]\}_4$ (Gehrus, B.; Hitchcock, P. B.; Pongtavornpinyo, R.; Zhang, L. *Dalton Trans.* **2006**, 1847); 3.327(5) Å for K(carbazole)$\{NMe[C_2H_4(NMe_2)]\}$ (Gregory, K.; Bremer, M.; von Rague Schleyer, P.; Klusener, P. A. A.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1224); 3.328(10) Å for $[K_2(C_5H_5)]\{Zn[N(SiMe_3)_2]_3\}$ (Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115); 3.290(3) Å for $K[C(Ph)(SiMe_3)_2]$ (Feil, F.; Harder, S. *Organometallics* **2000**, *19*, 5010); 3.349(3) Å for (18-crown-6)$K[Si(OMe)(SiMe_3)_2]$ (Likhar, P. R.; Zirngast, M.; Baumgartner, J.; Marchner, C. *Chem. Commun.* **2004**, 1764); 3.357 Å for [(DME)K(18-crown-6)]$_2[(MeSiC_{12}H_8)_2C_2H_4]$ (Liu, Y.; Stringfellow, T. C.; Ballweg, D.; Guzei, I. A.; West, R. *J. Am. Chem. Soc.* **2002**, *124*, 49).

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