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Synthesis, X-ray Crystal Structures, and Reaction Chemistry of Homoleptic and Heteroleptic Organolanthanoid Complexes Incorporating the [(Dimethylamino)methyl]phenyl Ligand

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Full details are provided on the synthesis and characterization of the heteroleptic and homoleptic lanthanoid aryl complexes (η^8-C_8H_8)Ln[o-$C_6H_4CH_2N(CH_3)_2$](THF) [Ln = Er, Lu] and Ln[o-$C_6H_4CH_2N(CH_3)_2$]$_3$ [Ln = Er, Yb, Lu] incorporating the sterically demanding, internally chelating [(dimethylamino)methyl]phenyl ligand. The X-ray crystal structure of (η^8-C_8H_8)Lu[o-$C_6H_4CH_2N(CH_3)_2$](THF) has been determined and compared with other known structure types. (η^8-C_8H_8)Lu[o-$C_6H_4CH_2N(CH_3)_2$](OC_4H_8) crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions a = 11.867 (2) Å, b = 12.685 (3) Å, c = 12.749 (3) Å, β = 91.12 (2)°, and D_{calcd} = 1.68 g cm^{-3} for Z = 4. Least-squares refinement gave a final R value of 0.034 using 4103 independent observed reflections. The C_8H_8 ligand is planar and is η^8-coordinated to the lutetium atom at an average Lu–C bond distance of 2.55 (1) Å. The aryl moiety bonds lutetium with a Lu–C bond length of 2.395 (6) Å and a Lu–N separation of 2.479 (6) Å. The THF group completes the lutetium coordination with a Lu–O distance of 2.368 (5) Å. The reaction chemistry of both the heteroleptic and homoleptic complexes with typical small molecule substrates has been investigated. Reaction with sterically demanding terminal alkynes yields readily characterized alkynide derivatives. No reaction is observed for either complex with olefins or hydrogen. Reaction with carbon monoxide produces mixtures of uncharacterizable products.

Introduction

The synthesis of heteroleptic[1] and homoleptic[2] organolanthanoid complexes incorporating the sterically demanding internally chelating [(dimethylamino)methyl]phenyl ligand has been reported recently. We now communicate full synthetic details on the preparation of these compounds, the X-ray crystal structure of (η^8-C_8H_8)Lu[o-$C_6H_4CH_2N(CH_3)_2$](THF) and the chemical reactivity of these hydrocarbyls with a variety of small molecule substrates.

Experimental Section

General Data. The compounds described are extremely air and moisture sensitive. Therefore, the syntheses of these compounds and manipulations involving these materials are conducted by using standard Schlenk and high vacuum line techniques or are performed in the recirculated argon atmosphere of a Vacuum Atmospheres HE-43 Dri Lab.

Materials. Hydrated rare-earth chlorides, $LnCl_3·6H_2O$, were obtained from Research Chemicals, Phoenix, AZ, and were dehydrated by the method of Taylor and Carter.[3] THF and toluene (Aldrich Sure-Seal grade) were distilled from sodium benzophenone ketyl under argon. Pentane (Aldrich Sure-Seal grade) was distilled from $LiAlH_4$ under argon before use. *N*,*N*-Dimethylbenzylamine was refluxed over and distilled from sodium under argon. Li[o-$C_6H_4CH_2N(CH_3)_2$] was prepared by the method of Cope and Gourley.[4] Cyclooctatetraene (Aldrich) was degassed and freed from nonvolatile impurities by vacuum transfer. 3,3-Dimethyl-1-butyne, phenylacetylene, 3,3-dimethyl-1-butene, and 1-(trimethylsilyl)propyne (Aldrich) were dried over activated 4-Å molecular sieves (Linde) and vacuum transferred before use. Carbon monoxide, hydrogen, and ethylene were Matheson Research Grade and were used without further purification. Benzene-d_6 and THF-d_8 (Stohler Isotope Chemicals) were dried over sodium benzophenone ketyl.

Measurements. Infrared spectra were recorded on solid samples which had been mulled with dry, degassed Nujol and sandwiched between 25 × 4 mm NaCl plates protected from the atmosphere in an O-ring sealed Barnes Presslok holder. IR spectra were recorded with a Nicolet 5DX FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are referenced to the residual protons contained in each solvent for ^1H NMR and to the chemical shift of the solvent for ^{13}C NMR. Complexometric metal analyses were conducted as previously described.[5] Complete elemental analyses were obtained from Analytische Laboratorien, Postfach 1249, D-5250 Engelskirchen, West Germany.

(η^8-C_8H_8)Ln[o-$C_6H_4CH_2N(CH_3)_2$](THF) (Ln = Er, Lu; a typical synthesis is described for Ln = Lu). In an argon-filled drybox, 0.6033 g (1.56 mmol) of (η^8-C_8H_8)LuCl·THF[1] was suspended in 50 mL of THF and placed in a 125-mL Erlenmeyer flask equipped with a Teflon stir bar. Li[o-$C_6H_4CH_2N(CH_3)_2$] (0.2204 g, 1.56 mmol) was dissolved in 20 mL of THF to yield a light gold solution. The latter solution was slowly dripped into the stirred suspension of (η^8-C_8H_8)LuCl·THF over a 15-min period. During addition, the suspension of (η^8-C_8H_8)LuCl·THF gradually disappeared until, at the end of addition, the solution contained no suspended solid and had assumed a murky yellow cast. The reaction was then allowed to stir overnight at room temperature. No further change in the appearance of the solution was noted. After 24 h solvent was removed by rotary evaporation to yield a clear yellow oil which could be triturated with pentane to produce an off-white powder. Exhaustive extraction of the crude product with toluene allowed the separation of insoluble byproduct LiCl by filtration. Removal of solvent by rotary evaporation gave microcrystalline (η^8-C_8H_8)Lu[o-$C_6H_4CH_2N(CH_3)_2$](THF) in 50% yield. Crystals suitable for analysis by X-ray diffraction were grown by maintaining a THF/pentane solution of the complex at −40 °C. The erbium analogue can be successfully synthesized in a similar manner. Attempts to extend the synthesis to early and middle lanthanoids failed. When Ln = La or Sm, workup

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of the final reaction solutions yielded sticky yellow and brown materials, respectively, whose ^1H NMR spectra were complex and suggestive of product decomposition. Anal. Calcd for $LuC_{21}H_{28}NO$: C, 51.96; H, 5.81; N, 2.88; Lu, 36.04; O, 3.29. Found: C, 51.62; H, 5.68; N, 2.78; Lu, 36.45; O, 3.47 (by difference). Anal. Calcd for $ErC_{21}H_{28}NO$: Er, 35.01. Found: Er, 33.80. IR (Nujol, cm^{-1}, identical for Ln = Er, Lu): 1420 m, 1380 m, 1360 m, 1305 m, 1235 m, 1170 s, 1095 m, 1040 m, 1010 m, 990 m, 940 m, 890 s, 855 s, 750 s, 700 s. ^1H NMR (benzene-d_6) δ 8.15, 7.01 (m, $C_6H_4CH_2N(CH_3)_2$), 6.71 (s, C_8H_8), 3.01, 1.00 (m, α- and β-THF, respectively), 2.79 (s, $C_6H_4CH_2N(CH_3)_2$), 1.82 (s, $C_6H_4CH_2N(CH_3)_2$). Integrated ratios are as expected.

$Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu; a typical synthesis is described for Ln = Lu). To a stirred suspension of anhydrous $LuCl_3$ in THF (1.3006 g, 4.62 mmol) was slowly added a light gold solution of $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$ in THF (1.9576 g, 13.87 mmol). As the lithium reagent was slowly added, the suspended $LuCl_3$ gradually disappeared until, at the end of addition, the reaction solution was a clear light ginger-ale color. The reaction solution was then allowed to stir overnight at ambient temperature in the drybox. No further change in the appearance of the solution was noted. After 24 h solvent was removed by rotary evaporation to yield a light yellow semisolid material. Trituration with pentane followed by filtration allowed the isolation of an off-white powder. Extraction of the crude product with toluene separated insoluble lithium chloride and produced a clear ginger-ale colored solution of the homoleptic aryl. Concentration of this solution followed by storage overnight at −40 °C afforded microcrystalline analytically pure white $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ which could be isolated by rapid filtration of the cooled solution in 75% yield. The bright pink and bright yellow erbium and ytterbium homologues were synthesized, purified, and isolated similarly (albeit in reduced yield (40–50%)). On occasion, recrystallization was necessary to remove all traces of chloride-containing byproducts (conveniently assayed by X-ray fluorescence). Unfortunately, corresponding stable complexes cannot be isolated for the early and middle lanthanoid elements (Ln = Pr, Nd, Sm, Tb). In these cases, reaction of $PrCl_3$, $NdCl_3$, $SmCl_3$, and $TbCl_3$ with 3 equiv of $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$ produced dark brown reaction solutions from which no characterizable products could be isolated. Anal. Calcd for $LuC_{27}H_{36}N_3$: Lu, 30.29; C, 56.15; H, 6.28; N, 7.27. Found: Lu, 30.40; C, 55.90; H, 6.24; N, 7.11. Anal. Calcd for $ErC_{27}H_{36}N_3$: Er, 29.35. Found: Er, 30.80. Anal. Calcd for $YbC_{27}H_{36}N_3$: Yb, 30.06. Found: Yb, 28.40. IR (Nujol, cm^{-1}, identical for Ln = Er, Yb, Lu): 1284 w, 1234 m, 1171 w, 1146 w, 1093 m, 1038 w, 1026 m, 1009 s, 976 w, 845 m, 743 s, 714 m. ^1H NMR (THF-d_8, Ln = Lu): δ 8.01, 7.96, 6.87 (m, $C_6H_4CH_2N(CH_3)_2$), 3.71 (s, $C_6H_4CH_2N(CH_3)_2$), 2.55 (s, $C_6H_4CH_2N(CH_3)_2$)]. Integrated ratios are as expected. ^{13}C NMR (benzene-d_6, Ln = Lu): δ 196.65, 147.19, 139.83, 125.65, 125.34, 124.96 ($C_6H_4CH_2N(CH_3)_2$), 69.51 ($C_6H_4CH_2N(CH_3)_2$), 46.22 ($C_6H_4CH_2N(CH_3)_2$).

$(\eta^8\text{-}C_8H_8)Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)$. To a stirred solution of $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ (0.3455 g, 0.71 mmol) in THF was slowly added a 13-fold molar excess of 3,3-dimethyl-1-butyne (0.770 g, 9.37 mmol). No change in the appearance of the solution (clear, colorless) was noted after addition. However, over a period of several days of stirring at ambient temperature, the solution gradually became turbid and a fine white precipitate was deposited. Addition of fresh THF dissolved the precipitate. After 3 days of stirring, solvent was removed by rotary evaporation to produce a cream-colored tacky solid. Trituration with pentane and filtration allowed the isolation of cream-colored $(\eta^8\text{-}C_8H_8)Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)\cdot(THF)_x$ (x = 0–1) in 75% yield. Examination of the pentane extract by ^1H NMR) revealed only the presence of *N*,*N*-dimethylbenzylamine (the expected product in a straightforward metalation reaction). The initially isolated lanthanoid product is a nonstoichiometric tetrahydrofuranate, based upon its infrared spectrum (strong band at 1023 cm^{-1}) and ^1H NMR spectrum. However, the THF is apparently weakly bound since it is lost slowly upon standing (see elemental analysis) or during crystallization. Anal. Calcd for $LuC_{14}H_{17}$: Lu, 48.57; C, 46.67; H, 4.75. Found: Lu, 48.40; C, 46.32; H, 4.86. IR (Nujol, cm^{-1}): 2048 s, 1819 w, 1712 w, 1581 w, 1358 s, 1342 w, 1314 w, br, 1241 s, 1201 m, 1180 w, 1023 s, 891 s, 871 s, 751 s, 700 s. ^1H NMR (THF-d_8) δ 6.07 (s, C_8H_8), 3.72 (m, α-THF), 1.71 (m, β-THF), 1.29 (s, $C{\equiv}C{-}C(CH_3)_3$). Integrated ratios are as expected. No integrated values could be obtained for THF due to partial overlap with residual protons in the solvent. ^{13}C NMR (THF-d_8) δ 93.12 (s, C_8H_8), 31.21 (s, $C{\equiv}C{-}C(CH_3)_3$).

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]\cdot OC_4H_8$
mol wt	485.4
space group	$P2_1/n$
cell constants	
a, Å	11.867 (2)
b, Å	12.685 (3)
c, Å	12.749 (3)
β, deg	91.12 (2)
cell vol, $Å^3$	1919
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.68
μ(calcd), cm^{-1}	54.1
rel range of transmission factors	0.32–1.00
radiation	Mo Kα
max crystal dimens, mm	0.80 × 0.42 × 0.48 mm
scan width	0.80 + 0.20 tan θ
std reflctns	6
decay of std	±2%
reflctns measd	5704
2θ range	$3° \le 2\theta \le 60°$
independent reflctns collected [$I > 2.5\sigma(I)$]	4103
no. of parameters varied	217
GOF	2.45
R	0.034
R_w	0.043

$Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)_3$. To a stirred solution of $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (0.3088 g, 0.53 mmol) in THF was slowly added a 4-fold excess of 3,3-dimethyl-1-butyne in THF. No immediate reaction was observed, but after several hours of stirring at ambient temperature the solution became turbid and a white solid began to precipitate. After stirring for 1 day at ambient temperature, this white solid was removed by filtration and identified as the insoluble tris(alkynide), based upon complexometric metal analysis and infrared spectroscopy. After removal of THF, the filtrate was analyzed by ^1H NMR and ^{13}C NMR spectroscopy and found to consist of an approximately 60:40 ratio of *N*,*N*-dimethylbenzylamine and 2-β-(3,3-dimethylbutenyl)-*N*,*N*-dimethylbenzenemethanamine.[6] Anal. Calcd for $LuC_{18}H_{27}$: Lu, 41.82. Found: Lu, 41.80. IR (Nujol cm^{-1}): 2048 s, 1363 s, 1241 s, 1203 s.

The reactions of $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ *and* $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ *with 3,3-dimethyl-1-butene and 1-(trimethylsilyl)propyne* were conducted similarly. However, no reaction was observed in either case after stirring for several days at ambient temperature. Only starting material (identified by ^1H NMR) was recovered upon workup.

Reactions of $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ *and* $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ *with gases* were conducted in a closed vacuum manifold of calibrated volume equipped with a mercury manometer. Stoichiometries of gaseous reactions could therefore be precisely controlled by use of simple gas-law expressions. When the gaseous reactant was *ethylene or hydrogen*, no reaction was observed (toluene as reaction solvent). When the gaseous reactant was *carbon monoxide*, (stoichiometric amounts), intense color changes of the reaction solutions were observed in both cases (deep red-purple), but reaction workup yielded only mixtures of uncharacterizable products (complex IR spectra, broad featureless ^1H NMR spectra).

X-ray Data Collection, Structure Determination, and Refinement for $(\eta^8\text{-}C_5H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](OC_4H_8)$. Single crystals of the air-sensitive compound were sealed under nitrogen in thin-walled glass capillaries. Data collection was carried out by Crystalytics Co.[7] Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 12°$) accurately centered on the diffrac-

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(6) 2-β-(3,3-Dimethylbutenyl)-*N*,*N*-dimethylbenzenemethanamine was identified by its ^1H NMR and ^{13}C NMR spectra.

(7) Day, C. S., Crystalytics Co., P.O. Box 82286, Lincoln, NE 68501.

tometer are given in Table I. The systematic absences indicated the space group to be $P2_1/n$.

Data were collected on a Nicolet P$\bar{1}$ autodiffractometer using 1.0° ω scans and graphite-monochromated Mo Kα radiation. Each of these 1.0° wide scans was divided into 17 equal time intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for half the total time used for the net scan (13/17 of the total scan time), were measured at ω settings 1° above and below the calculated Kα doublet value for each reflection. A summary of data collection parameters is given in Table I. The entire data set was corrected empirically for absorption using ψ scans for seven close-to-axial reflections having 2θ between 8.8° and 34.7°. All absorption profile curves were mutually consistent, with maximum and minimum corrections at essentially identical values of ϕ. The data were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. The 002 reflection was deleted from the data set because of secondary extinction.

Calculations were carried out with the SHELX system of computer programs.[8] Neutral atom scattering factors for Lu, O, N, and C were taken from Cromer and Waber,[9] and the scattering for lutetium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[10] Scattering factors for H were from ref 11.

The position of the lutetium atom was located by inspection of a Patterson map. Subsequent difference Fourier maps phased on the lutetium atom revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic temperature factors led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.075$. The hydrogen atom positions which could be calculated were with hydrogens placed 1.08 Å from the bonded carbon atoms. The methyl hydrogens were located with the aid of a difference Fourier map. The hydrogen atom parameters were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.034$ and $R_w = 0.043$. A final difference Fourier map showed no feature greater than 0.4 e/Å.^{3} The maximum parameter shifts in the final least-squares refinement cycle was less than 0.01 of their estimated standard deviations. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.[12]

Table II. Final Fractional Coordinates for $(\eta^8\text{-}C_8H_8)Lu(o\text{-}C_6H_4CH_2N(CH_3)_2]\bullet OC_4H_8$

atom	x/a	y/b	z/c
Lu	0.56908 (2)	0.32604 (2)	0.71868 (2)
O	0.5862 (4)	0.2014 (4)	0.5816 (4)
N	0.4988 (5)	0.1707 (5)	0.8157 (5)
C(1)	0.5628 (8)	0.5263 (7)	0.7153 (8)
C(2)	0.6252 (8)	0.4963 (7)	0.6288 (8)
C(3)	0.7152 (7)	0.4265 (8)	0.6130 (7)
C(4)	0.7777 (7)	0.3557 (8)	0.6774 (9)
C(5)	0.7761 (7)	0.3245 (8)	0.7818 (8)
C(6)	0.7111 (9)	0.3547 (8)	0.8664 (8)
C(7)	0.6228 (9)	0.4275 (9)	0.8838 (7)
C(8)	0.5619 (8)	0.4986 (8)	0.8209 (9)
C(9)	0.3712 (5)	0.3075 (6)	0.6828 (5)
C(10)	0.3274 (6)	0.2069 (6)	0.7071 (5)
C(11)	0.2148 (6)	0.1790 (8)	0.6946 (6)
C(12)	0.1402 (6)	0.2529 (8)	0.6545 (6)
C(13)	0.1766 (6)	0.3520 (7)	0.6284 (6)
C(14)	0.2907 (6)	0.3785 (6)	0.6433 (6)
C(15)	0.4089 (6)	0.1222 (6)	0.7484 (7)
C(16)	0.5853 (7)	0.0889 (8)	0.8414 (8)
C(17)	0.4490 (7)	0.2066 (9)	0.9155 (6)
C(18)	0.6775 (9)	0.126 (1)	0.5628 (9)
C(19)	0.688 (1)	0.093 (1)	0.4540 (9)
C(20)	0.561 (1)	0.138 (1)	0.4115 (8)
C(21)	0.524 (1)	0.2165 (9)	0.4821 (7)
H(1)	0.499	0.587	0.696
H(2)	0.599	0.537	0.557
H(3)	0.743	0.426	0.531
H(4)	0.844	0.317	0.634
H(5)	0.838	0.263	0.801
H(6)	0.732	0.311	0.939
H(7)	0.597	0.430	0.965
H(8)	0.499	0.542	0.866
H(9)	0.186	0.100	0.717
H(10)	0.052	0.232	0.643
H(11)	0.117	0.409	0.596
H(12)	0.318	0.459	0.623
H(13)	0.448	0.083	0.682
H(14)	0.363	0.063	0.792
H(15)	0.648	0.100	0.895
H(16)	0.546	0.034	0.879
H(17)	0.618	0.061	0.782
H(18)	0.404	0.158	0.956
H(19)	0.518	0.217	0.955
H(20)	0.374	0.268	0.923
H(21)	0.761	0.162	0.580
H(22)	0.672	0.058	0.617
H(23)	0.739	0.121	0.408
H(24)	0.668	0.006	0.447
H(25)	0.496	0.075	0.405
H(26)	0.571	0.170	0.333
H(27)	0.541	0.295	0.450
H(28)	0.433	0.212	0.494

Results and Discussion

Standard metathetical syntheses have resulted in the synthesis of heteroleptic and homoleptic organolanthanoids incorporating the sterically demanding, internally chelating [(dimethylamino)methyl]phenyl ligand. The new complexes $(\eta^8\text{-}C_8H_8)Ln[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ (Ln = Er, Lu) and $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu) can be isolated in good yield and purity and are easily characterized by standard analytical and spectroscopic techniques. Unfortunately, the [(dimethylamino)methyl]phenyl ligand is not capable of stabilizing early and middle lanthanoid derivatives of these complexes. All attempts to prepare such complexes have resulted in uncharacterizable mixtures of products. The failure to synthesize inclusive homologous series of hydrocarbyl complexes incorporating this ligand has precluded our original objective, namely, the study of organolanthanoid hydrocarbyl reactivity as a function of lanthanoid element. However, the synthesis of heteroleptic and homoleptic complexes of the same lanthanoid (lutetium) does provide an excellent opportunity to compare structural differences between the two related compound classes. In addition, an investigation of the chemical reactivity of the complexes[13] as compared to that now well documented for other organolanthanoid compound classes (notably the bis(cyclopentadienyl)lanthanoid alkyls) can readily be conducted. Accordingly, the X-ray crystal structures of the heteroleptic and homoleptic lutetium aryls have been determined. The solutions of these structures permit ready comparison with other crystallographically characterized cyclooctatetraenides and with other complexes containing the [(dimethylamino)methyl]phenyl ligand.

The molecular structure and atom labeling scheme for $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ are given in Figure 1. The π-bonded COT dianion with its five-electron pairs

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(8) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

(9) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(10) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(12) See paragraph at end of paper regarding supplementary material.

(13) The homoleptic and heteroleptic lutetium aryl complexes are the probe molecules of choice. Lu(III) is a $4f^{14}$ diamagnetic metal. Hence, ^1H NMR and ^{13}C NMR spectra of its complexes are readily obtainable facilitating investigation of their reaction chemistry.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen.* **1976**, *A32*, 751.

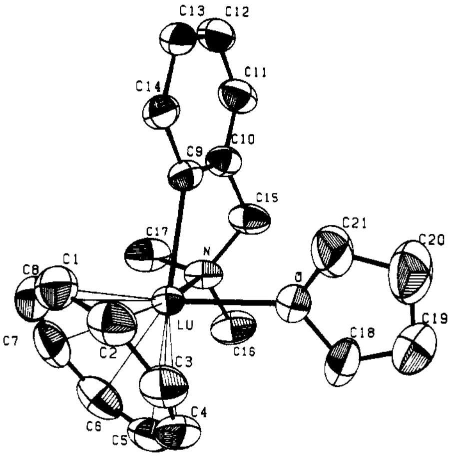

Figure 1. Molecular structure and atom labeling scheme for $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]\cdot OC_4H_8$.

occupies five lutetium coordination sites.[15] The formal eight-coordination found for the lutetium is completed by the phenyl carbon and the nitrogen of the [(dimethylamino)methyl]phenyl ligand and the oxygen atom of the THF.

The aromaticity of the COT ring can be established from the bond distances and angles in Table III. The C–C distances range from 1.39 (1) to 1.42 (1) Å and average 1.40 (1) Å. The internal C–C–C bond angles average 135 (1)° (the value for an internal angle of an octagon), and the ring is planar to within 0.02 Å. The lutetium atom is symmetrically coordinated to the COT ring with an average Lu–C distance of 2.55 (1) Å. The individual Lu–C distances range from 2.529 (8) to 2.570 (8) Å. Using the effective ionic radius for eight-coordinate Lu(III) as tabulated by Shannon[14] of 0.977 Å, an effective ionic radius of 1.57 Å can be calculated for the COT ring. The same type of calculation using the structure of $[Ce(\eta^8\text{-}C_8H_8)Cl\cdot 2THF]_2$[15] results in a value of 1.51 Å.

The coordination of the [(dimethylamino)methyl]phenyl ligand is similar to that observed in $(\eta^5\text{-}C_5H_5)_2Y[o\text{-}C_6H_4CH_2N(CH_3)_2]$[16] and in $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$.[2] The six phenyl carbon atoms are planar to within 0.005 Å, with the lutetium atom 0.03 Å out of this plane. The Lu–C distance of 2.395 (6) Å compares well with the average Y–C distance of 2.41 (2) Å in $(\eta^5\text{-}C_5H_5)_2Y[o\text{-}C_6H_4CH_2N(CH_3)_2]$[16] after a correction of 0.042 Å for the difference in effective ionic radius between yttrium and lutetium. This value is only slightly shorter than the average Lu–C distance of 2.44 (1) Å observed for the homoleptic aryl $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$.[2] The Lu–N separation of 2.479 (6) Å and the C(9)–C(10)–C(15)–N torsion angle of 35° agree well with the observed average values in $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$.[2]

The coordination sphere of lutetium is completed by the oxygen of a THF moiety with an observed Lu–O separation of 2.368 (5) Å. This value is longer than Lu–O distances observed in other eight-coordinate Lu(III) complexes including the 2.31 (2) Å found for the Lu–O separation in $(\eta^5\text{-}C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$.[17] It is consistent, however, with a more sterically crowded metal atom environment. The effects of a sterically demanding environment can be observed in the structure of $(\eta^5\text{-}C_5H_5)_3Y(THF)$.[18] Here, the ten-coordinate Y(III)–O separation is 2.451 (4) Å. After a 0.042-Å correction for the difference in the effective ionic radius of Y(III) and Lu(III), this would correspond to a Lu–O distance of 2.409 Å.

Table III. Bond Distances (Å) and Angles (deg) for $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]\bullet OC_4H_8$

	Bond Distances		
Lu–O	2.368 (5)	Lu–N	2.479 (6)
Lu–C(1)	2.542 (9)	Lu–C(2)	2.540 (8)
Lu–C(3)	2.556 (7)	Lu–C(4)	2.569 (8)
Lu–C(5)	2.570 (8)	Lu–C(6)	2.529 (8)
Lu–C(7)	2.538 (8)	Lu–C(8)	2.549 (9)
Lu–C(9)	2.395 (6)	O–C(18)	1.47 (1)
O–C(21)	1.47 (1)	N–C(15)	1.489 (9)
N–C(16)	1.49 (1)	N–C(17)	1.49 (1)
C(1)–C(2)	1.39 (1)	C(1)–C(8)	1.39 (1)
C(2)–C(3)	1.40 (1)	C(3)–C(4)	1.42 (1)
C(4)–C(5)	1.39 (1)	C(5)–C(6)	1.39 (1)
C(6)–C(7)	1.42 (1)	C(7)–C(8)	1.40 (1)
C(9)–C(10)	1.41 (1)	C(9)–C(14)	1.400 (9)
C(10)–C(11)	1.388 (9)	C(10)–C(15)	1.53 (1)
C(11)–C(12)	1.38 (1)	C(12)–C(13)	1.37 (1)
C(13)–C(14)	1.40 (1)	C(18)–C(19)	1.45 (1)
C(19)–C(20)	1.48 (2)	C(20)–C(21)	1.42 (1)
Lu–Cent[a]	1.775 (9)		
	Bond Angles		
C–Lu–N	82.7 (2)	O–Lu–C(9)	83.8 (2)
N–Lu–C(9)	71.3 (2)	Lu–O–C(18)	129.0 (5)
Lu–O–C(21)	120.0 (5)	C(18)–O–C(21)	107.8 (7)
Lu–N–C(15)	106.6 (4)	Lu–N–C(16)	115.2 (5)
C(15)–N–C(16)	108.7 (7)	Lu–N–C(17)	109.1 (5)
C(15)–N–C(17)	109.1 (6)	C(16)–N–C(17)	108.0 (6)
C(2)–C(1)–C(8)	135.3 (9)	C(1)–C(2)–C(3)	134.7 (9)
C(2)–C(3)–C(4)	135.0 (9)	C(3)–C(4)–C(5)	136.0 (9)
C(4)–C(5)–C(6)	133.0 (9)	C(5)–C(6)–C(7)	136.3 (9)
C(6)–C(7)–C(8)	134.9 (9)	C(1)–C(8)–C(7)	134.8 (9)
Lu–C(9)–C(10)	114.2 (5)	Lu–C(9)–C(14)	131.7 (5)
C(10)–C(9)–C(14)	114.0 (6)	C(9)–C(10)–C(11)	124.2 (7)
C(9)–C(10)–C(15)	118.4 (6)	C(11)–C(10)–C(15)	117.4 (7)
C(10)–C(11)–C(12)	118.6 (8)	C(11)–C(12)–C(13)	120.6 (7)
C(12)–C(13)–C(14)	119.6 (7)	C(9)–C(14)–C(13)	123.0 (7)
N–C(15)–C(10)	110.4 (6)	O–C(18)–C(19)	107.7 (9)
C(18)–C(19)–C(20)	106.5 (9)	C(19)–C(20)–C(21)	108 (1)
O–C(21)–C(20)	107.1 (9)	Cent–Lu–O	125 (1)
Cent–Lu–N	134 (1)	Cent–Lu–C(19)	139 (1)

[a] Cent is the centroid of the plane defined by the eight carbon atoms of the COT ring.

The C–C bond lengths and C–O separations in the THF ring average 1.45 (3) and 1.47 (1) Å, respectively. Although the thermal motion associated with the carbon atoms is somewhat large, no evidence for disorder of the THF ligand was observed. Large thermal motion and disorder of room-temperature structures having THF ligands are not uncommon.

The most extensively studied class of organolanthanoid complexes, the bis(cyclopentadienyl)lanthanoid alkyls, have been demonstrated to have a varied and important reaction chemistry. These complexes will react with molecular hydrogen to yield hydrides,[19] insert olefins to function as Ziegler–Natta polymerization catalysts,[20] react with CO to yield η^2-acyl complexes and unusual multiple CO insertion compounds[21] and metalate acidic hydrocarbon substrates.[22] Activation of the C–H bond in

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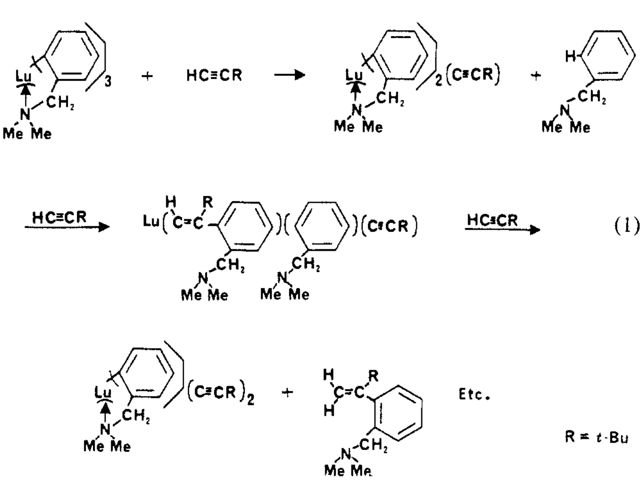
unactivated hydrocarbons such as tetramethylsilane and methane has also recently been reported.[23] In contrast, the reaction chemistry observed for $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$ and $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ is quite limited. The complexes are inert to hydrogenolysis with molecular hydrogen, although they will react with carbon monoxide to generate uncharacterizable reaction products. Simple olefins (ethylene) do not insert nor do internal alkynes, such as 1-(trimethylsilyl)propyne. Only in their metalation chemistry with terminal alkynes (to yield $(\eta^8\text{-}C_8H_8)Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)$ and $Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)_3$, respectively) do they follow a reactivity trend observed for the bis(cyclopentadienyl)lanthanoid alkyls.[22] Even in this case, the reaction chemistry is not clear-cut. In the case of the metalation of 3,3-dimethyl-1-butyne by $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, in addition to the expected organic byproduct *N,N*-dimethylbenzylamine, the insertion product 2-β-(3,3-dimethylbutenyl)-*N,N*-dimethylbenzenemethanamine is also isolated. This compound presumably arises from insertion of alkyne into a Lu–aryl bond prior to complete metalation.[24] A possible scheme is illustrated in reaction 1. However, since no insertion chemistry is observed for either compound with the sterically similar 3,3-dimethyl-1-butene or the sterically unhindered molecule ethylene, it is likely that insertion of the alkyne occurs after the loss of one or more aryl moieties (through metalation) has generated a coordinatively unsaturated intermediate. This order of reactivity is also supported by the complete lack of organic insertion byproduct in the metalation of the heteroleptic $(\eta^8\text{-}C_8H_8)Lu[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$. (Only *N,N*-dimethylbenzylamine is observed.)



The observed reactivity (or lack of it) with small molecule substrates (such as olefins and hydrogen) suggests that the complexes are too sterically saturated to react facilely (cf. the reactivity of $(C_5H_5)_3U\text{–}R$ vs. that of $(C_5Me_5)_2UR_2$).[25] In those cases where reaction is observed (with terminal alkynes and carbon monoxide), the product complex must exhibit sufficient steric bulk to ensure stability. For example, in the reaction of $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ with 3,3-dimethyl-1-butyne, a stable tris(alkynide) (albeit insoluble) is isolated. However, if the reaction is conducted with phenylacetylene, the reactant solution immediately turns a homogeneous dark brown upon addition, and no simple characterizable homoleptic alkynides can be isolated. Similarly, in the observed initial reaction of both the homoleptic and heteroleptic aryls with carbon monoxide, one molecule may insert into a lutetium–aryl bond, but the resulting complex (or intermediate complex) is apparently insufficiently sterically crowded (either by tight internal chelation or by steric bulk) to afford a product complex stable enough to isolate.

These reactivity patterns demonstrate that lanthanoid–carbon bond reactivity is critically dependent upon the coordination environment around the metal (both in determining whether initial reaction will occur and in determining whether intermediate products or final products will exhibit sufficient stability for isolation and characterization). Although the reactivity observed for these homoleptic and heteroleptic lutetium aryl complexes is disappointingly limited, the decidely distinct reactivity observed serves to illustrate that much is yet to be learned concerning the "fine-tuning" of lanthanoid coordination environments for optimal and/or specific reactivity. Our general studies in this area are under continued investigation.

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Registry No. $(\eta^8\text{-}C_8H_8)LuCl{\cdot}THF$, 96504-50-6; $(\eta^8\text{-}C_8H_8)ErCl{\cdot}THF$, 96504-51-7; $(\eta\text{-}C_8H_8)Lu(o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$, 84582-81-0; $(\eta^8\text{-}C_8H_8)Er(o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$, 96504-52-8; $Er[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 65521-48-4; $Yb[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 96612-36-1; $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 96612-37-2; $(\eta^8\text{-}C_8H_8)Lu(C{\equiv}C\text{-}t\text{-}C_4H_9)$, 96504-53-9; $Lu(C{\equiv}\text{-}t\text{-}C_4H_9)_3$, 96504-54-0; $LuCl_3$, 10099-66-8; $YbCl_3$, 10361-91-8; $ErCl_3$, 10138-41-7; $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$, 60528-57-6; 3,3-dimethyl-1-butyne, 917-92-0; *N,N*-dimethylbenzylamine, 103-83-3; 2-β-(3,3-dimethylbutenyl)-*N,N*-dimethylbenzenemethanamine, 96504-55-1; 3,3-dimethylbutene, 558-37-2; 1-(trimethylsilyl)propyne, 6224-91-5; ethylene, 74-85-1; hydrogen, 1333-74-0; carbon monoxide, 630-08-0.

Supplementary Material Available: Tables of thermal parameters, best planes results, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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