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No CIDNP effects can be observed which indicates that these insertions most likely proceed concertedly. It follows that singlet germylenes, like singlet carbenes,[9,10] are capable to use different mechanism pathways during an insertion reaction.

Acknowledgment. We thank Prof. Dr. W. P. Neumann for his continuous interest and for helpful discussions.

Registry No. 1, 76054-64-3; Me_2Ge:, 74963-95-4; $PhCH_2Br$, 100-39-0; $PhCH_2Me_2GeBr$, 90030-12-9; $BeMe_2Br_2$, 1730-66-1.

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(9) Closs G. L. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, London, Sidney, Toronto, 1975; p 159.
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Homoleptic Organolanthanoid Hydrocarbyls. The Synthesis and X-ray Crystal Structure of Tris[*o*-((dimethylamino)methyl)phenyl]lutetium

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Summary: The synthesis, characterization, and X-ray crystal structure (Ln = Lu) of stable homoleptic organolanthanoid aryl complexes $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu) incorporating the sterically demanding, internally chelating *o*-((dimethylamino)methyl)phenyl ligand are reported. $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ crystallizes in the *C*2/*c* space group with unit cell dimensions of a = 24.237 (6) Å, b = 9.388 (3) Å, c = 26.423 (6) Å, β = 123.95 (6)°, and D_{calcd} = 1.54 g cm^{-3} for Z = 8. Least-squares refinement resulted in a final R value of 0.023 based on 2607 independent observed reflections. The Lu–C distances range from 2.425 (7) to 2.455 (7) Å and average 2.435 (14) Å. The Lu–N distances fall into a two-short, one-long pattern: 2.468 (6), 2.478 (5), and 2.588 (5) Å. In the five-membered metallocyclic rings, the three carbon atoms and the lutetium atom are planar to 0.02 Å and the nitrogen atom resides 0.7 Å out of the plane. The torsion angles that involve the nitrogen and three carbon atoms of the rings are −25, 31, and −38°. Unfortunately, the synthesis is not general for all lanthanoids since analogous complexes cannot be isolated when Ln = Pr, Nd, Sm, or Tb.

The sterically demanding, chelating *o*-((dimethylamino)methyl)phenyl ligand has been used successfully in the synthesis and stabilization of early transition-metal aryl complexes such as $(\eta^5\text{-}C_5H_5)_2Ti[o\text{-}C_6H_4CH_2N(CH_3)_2]$ and $Cr[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$. The synthesis and characterization of the related group 3A metal scandium complexes have also been reported.[1] However, apart from a brief note in the patent literature reporting the synthesis of $Er[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$,[2] the utility of this ligand in stabilizing homoleptic organolanthanoid complexes has not been explored.[3] As part of our general synthetic program aimed at the synthesis of inclusive homologous series of organolanthanoid hydrocarbyls,[4] we have examined the ability of this ligand to yield stable neutral organolanthanoid aryl complexes as a function of lanthanoid element. We report at this time the synthesis, characterization, and X-ray crystal structure (Ln = Lu) of the late lanthanoid compounds $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Yb, Lu). Unfortunately, corresponding stable complexes cannot be isolated for the early and middle lanthanoid elements (e.g., Ln = Pr, Nd, Sm, Tb).

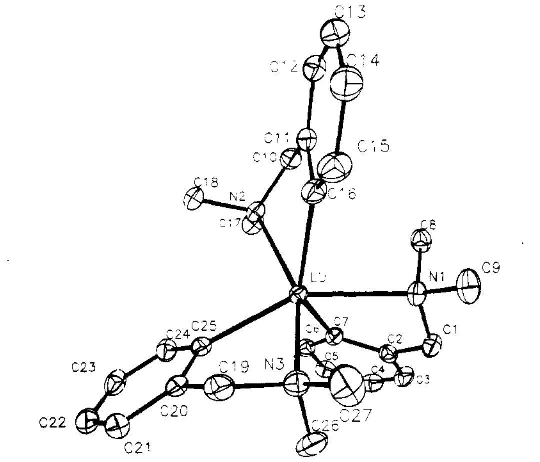

Figure 1. A perspective ORTEP diagram of $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$. Important parameters are listed in Table I and the text.

The title complexes are synthesized by the slow, ambient-temperature addition of a THF solution of 3 equiv of $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$[5] to a magnetically stirred suspension of the respective anhydrous metal chlorides in THF.[6] After a reaction time of 24 h, solvent is removed from the characteristically colored, slightly cloudy solutions (pink-orange for erbium, bright orange for ytterbium, and light yellow for lutetium) to yield sticky, semisolid residues. Trituration of the crude products with pentane produces free-flowing powders that are extracted with toluene to remove insoluble byproduct lithium chloride. Concentration of the toluene extracts followed by cooling at −40 °C allows the separation of microcrystalline products in 75% yield. The complexes are then recrystallized in order to separate all traces of chloride-containing byproducts.[7]

The bright pink, yellow, and white complexes (Ln = Er, Yb, and Lu, respectively) are extremely air and moisture sensitive. They are marginally soluble in alkane solvents and soluble in aromatic and ethereal solvents. They are characterized by infrared,[8] ^1H NMR, and ^{13}C NMR

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(1) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068 and references therein.

(2) Manzer, L. E. U.S. Patent 4 057 565, 1977; *Chem. Abstr.* **1978**, *88*, 62468.

(3) Homoleptic organolanthanoid hydrocarbyls are not an unknown compound class. Several types of neutral and anionic hydrocarbyl complexes have been synthesized and crystallographically characterized (see references cited in: Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press. New York, 1982; Vol. 3, Chapter 21 pp 197–201.). However, these complexes owe their stability to the steric bulk of the ligand utilized. The present study (taken with the work described in ref 4) represents the first systematic attempt to synthesize stable organolanthanoid hydrocarbyls by exploiting the stability conferred by internally chelating ligands.

(4) Wayda, A. L. *Organometallics* **1983**, *2*, 565.

(5) Cope, A. C.; Gourley, R. N. *J. Organomet. Chem.* **1967**, *8*, 527.

(6) All manipulations are conducted with rigorous exclusion of air and moisture. Anhydrous metal chlorides are prepared by the method of Taylor and Carter (Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387).

(7) Complexes are assayed for absence of chloride-containing contaminants by X-ray fluorescence.

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Table I. Bond Lengths (Å) and Angles (deg) for $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$

		Bond Distances			
Lu-N(1)	2.588 (5)	C(11)-C(16)	1.42 (1)	N(3)-C(26)	1.46 (1)
Lu-N(3)	2.468 (6)	C(13)-C(14)	1.36 (1)	C(1)-C(2)	1.50 (1)
Lu-C(16)	2.455 (7)	C(15)-C(16)	1.42 (1)	C(2)-C(7)	1.418 (9)
N(1)-C(1)	1.481 (9)	C(20)-C(21)	1.38 (1)	C(4)-C(5)	1.38 (1)
N(1)-C(9)	1.481 (8)	C(21)-C(22)	1.38 (1)	C(6)-C(7)	1.407 (9)
N(2)-C(17)	1.480 (9)	C(23)-C(24)	1.37 (1)	C(11)-C(12)	1.39 (1)
N(3)-C(19)	1.484 (9)	Lu-N(2)	2.478 (5)	C(12)-C(13)	1.38 (1)
N(3)-C(27)	1.50 (1)	Lu-C(7)	2.426 (7)	C(14)-C(15)	1.39 (1)
C(2)-C(3)	1.41 (1)	Lu-C(25)	2.425 (7)	C(19)-C(20)	1.50 (1)
C(3)-C(4)	1.37 (1)	N(1)-C(8)	1.477 (9)	C(20)-C(25)	1.40 (1)
C(5)-C(6)	1.39 (1)	N(2)-C(10)	1.482 (9)	C(22)-C(23)	1.38 (1)
C(10)-C(11)	1.50 (1)	N(2)-C(18)	1.506 (8)	C(24)-C(25)	1.41 (1)
		Bond Angles			
N(1)-Lu-N(2)	114.0 (2)	N(2)-C(10)-C(11)	112.4 (5)	C(10)-N(2)-C(17)	109.3 (6)
N(2)-Lu-N(3)	149.8 (2)	C(10)-C(11)-C(16)	118.7 (6)	C(10)-N(2)-C(18)	108.2 (5)
N(2)-Lu-C(7)	96.4 (2)	C(11)-C(12)-C(13)	119.9 (8)	Lu-N(3)-C(19)	104.2 (4)
N(1)-Lu-C(16)	82.6 (2)	C(13)-C(14)-C(15)	120.7 (8)	C(19)-N(3)-C(26)	109.2 (6)
N(3)-Lu-C(16)	98.5 (2)	Lu-C(16)-C(11)	113.2 (5)	C(19)-N(3)-C(27)	107.1 (6)
N(1)-Lu-C(25)	152.6 (2)	C(11)-C(16)-C(15)	114.2 (7)	N(1)-C(1)-C(2)	112.4 (6)
N(3)-Lu-C(25)	71.3 (2)	C(19)-C(20)-C(21)	118.6 (7)	C(1)-C(2)-C(7)	119.6 (6)
C(16)-Lu-C(25)	119.9 (2)	C(21)-C(20)-C(25)	124.4 (8)	C(2)-C(3)-C(4)	121.1 (7)
Lu-N(1)-C(8)	99.6 (4)	C(21)-C(22)-C(23)	119.1 (8)	C(4)-C(5)-C(6)	119.2 (7)
Lu-N(1)-C(9)	122.4 (4)	C(23)-C(24)-C(25)	122.7 (8)	Lu-C(7)-C(2)	117.0 (5)
C(8)-N(1)-C(9)	107.3 (6)	Lu-C(25)-C(24)	132.5 (5)	C(2)-C(7)-C(6)	114.6 (6)
Lu-N(2)-C(17)	116.5 (4)	N(1)-Lu-N(3)	91.2 (2)	C(10)-C(11)-C(12)	118.4 (7)
Lu-N(2)-C(18)	108.0 (4)	N(1)-Lu-C(7)	68.6 (2)	C(12)-C(11)-C(16)	122.9 (7)
C(17)-N(2)-C(18)	107.1 (6)	N(3)-Lu-C(7)	108.7 (2)	C(12)-C(13)-C(14)	119.6 (8)
Lu-N(3)-C(26)	106.1 (5)	N(2)-Lu-C(16)	70.1 (2)	C(14)-C(15)-C(16)	122.7 (8)
Lu-N(3)-C(27)	121.7 (5)	C(7)-Lu-C(16)	140.1 (2)	Lu-C(16)-C(15)	132.6 (6)
C(26)-N(3)-C(27)	108.0 (7)	N(2)-Lu-C(25)	89.8 (2)	N(3)-C(19)-C(20)	113.0 (6)
C(1)-C(2)-C(3)	119.1 (7)	C(7)-Lu-C(25)	96.6 (2)	C(19)-C(20)-C(25)	117.1 (6)
C(3)-C(2)-C(7)	121.3 (7)	Lu-N(1)-C(1)	109.1 (4)	C(20)-C(21)-C(22)	119.1 (8)
C(3)-C(4)-C(5)	119.8 (7)	C(1)-N(1)-C(8)	108.9 (6)	C(22)-C(23)-C(24)	120.8 (8)
C(5)-C(6)-C(7)	124.0 (7)	C(1)-N(1)-C(9)	108.7 (6)	Lu-C(25)-C(20)	113.5 (5)
Lu-C(7)-C(6)	127.9 (5)	Lu-N(2)-C(10)	107.4 (4)	C(20)-C(25)-C(24)	113.9 (6)

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$

mol wt	577.6
space group	*C*2/*c*
cell constants	
a, Å	24.237 (6)
b, Å	9.388 (3)
c, Å	26.423 (6)
β, deg	123.95 (6)
cell vol, Å^3	4987.3
molecules/unit cell	8
ρ(calcd), g cm^{-3}	1.54
μ(calcd), cm^{-1}	41.8
radiatn	Mo Kα
max cryst dimens, mm	0.20 × 0.30 × 0.35
scan width, deg	$0.80 + 0.20 \tan \theta$
std reflctns	(800), (020), (006)
decay of stds	<3%
reflctns measd	3375
2*θ* range	1-46
reflctns considered obsd	2607
no. of parameters varied	280
GOF	0.92
R	0.023
R_w	0.029

spectroscopy (Ln = Lu),[9] complexometric (Ln = Er, Yb) and complete elemental analysis[10] (Ln = Lu), and an X-ray crystal structure determination.

Crystals for the structure determination were grown by admixing pentane into a toluene solution of $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ and cooling the mixture at -40 °C until colorless plates of the complex separated.

Single crystals of the extremely air-sensitive compound were sealed under nitrogen in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 15 reflections ($\theta > 15°$) accurately centered on the diffractometer are given in Table II. The space group (either *Cc* or *C*2/*c*) was shown to be *C*2/*c* by the successful solution and refinement.[11]

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(8) Infrared spectra are obtained on Nujol mulls of the complexes. The complexes exhibit identical infrared spectra characteristic of the ((dimethylamino)methyl)phenyl ligand. $[Er(o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, cm^{-1}: 1284 (w), 1234 (m), 1171 (w), 1146 (w), 1093 (m), 1038 (w), 1026 (m), 1009 (s), 976 (w), 845 (m), 743 (s), 714 (m).

(9) ^{1}H NMR (THF-d_8): 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) 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 ($C_6H_4CH_2N(CH_3)_2$).

(10) 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, 28.4. 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. Hydrolysis of $Ln[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$ (Ln = Er, Lu) yields solely *N*,*N*-dimethylbenzylamine in 92% yield.

(11) Data were collected on an Enraf-Nonius CAD-4 diffractometer by the ω-2θ scan technique. The method has been previously described.[12] A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (based on psi scans) was applied. Calculations were carried out with the SHELX system of computer programs.[13] Neutral atom scattering factors for Lu, N, and C were taken from Cromer and Waber,[14] and the scattering for lutetium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[15] Scattering factors for H were from ref 16. The structure was solved by the application of standard heavy-atom techniques. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.090$. The hydrogen atoms were located with the aid of a difference Fourier map. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.023$ and $R_w = 0.029 = \{\sum w(F_o - F_c)^2/\sum w(F_o)^2\}^{1/2}$. A final difference Fourier showed no feature greater than 0.4 e/Å^3. 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 III.[17]

(12) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

Table III. Final Fractional Coordinates for the Non-Hydrogen Atoms of Lu[o-$C_6H_4CH_2N(CH_3)_2$]$_3$

atom	x/a	y/b	z/c	U_{eqv}, Å^2
Lu	0.31856 (1)	0.53232 (3)	0.15898 (1)	0.032
N(1)	0.2237 (3)	0.3678 (6)	0.0793 (3)	0.043
N(2)	0.3730 (3)	0.6703 (6)	0.1185 (3)	0.040
N(3)	0.3260 (3)	0.4009 (6)	0.2435 (3)	0.050
C(1)	0.1604 (4)	0.4136 (8)	0.0705 (4)	0.053
C(2)	0.1546 (3)	0.5729 (7)	0.0711 (3)	0.044
C(3)	0.0910 (4)	0.635 (1)	0.0409 (4)	0.057
C(4)	0.0833 (4)	0.779 (1)	0.0419 (4)	0.062
C(5)	0.1386 (4)	0.8659 (9)	0.0721 (3)	0.055
C(6)	0.2016 (4)	0.8045 (8)	0.1016 (3)	0.048
C(7)	0.2130 (3)	0.6574 (7)	0.1022 (3)	0.042
C(8)	0.2228 (4)	0.4073 (8)	0.0247 (3)	0.049
C(9)	0.2281 (4)	0.2105 (7)	0.0842 (4)	0.060
C(10)	0.3771 (4)	0.5766 (8)	0.0756 (3)	0.050
C(11)	0.4019 (3)	0.4307 (7)	0.1010 (3)	0.043
C(12)	0.4391 (4)	0.3577 (9)	0.0839 (4)	0.058
C(13)	0.4624 (4)	0.222 (1)	0.1062 (4)	0.064
C(14)	0.4498 (4)	0.1619 (9)	0.1458 (4)	0.064
C(15)	0.4129 (4)	0.2349 (8)	0.1634 (4)	0.063
C(16)	0.3870 (3)	0.3733 (7)	0.1418 (3)	0.048
C(17)	0.3411 (4)	0.8064 (8)	0.0878 (4)	0.058
C(18)	0.4428 (3)	0.7047 (8)	0.1711 (3)	0.052
C(19)	0.3894 (3)	0.4504 (9)	0.2987 (3)	0.053
C(20)	0.3955 (3)	0.6099 (8)	0.3029 (3)	0.044
C(21)	0.4254 (4)	0.673 (1)	0.3594 (4)	0.059
C(22)	0.4330 (4)	0.819 (1)	0.3640 (4)	0.070
C(23)	0.4091 (4)	0.8980 (9)	0.3117 (4)	0.060
C(24)	0.3786 (4)	0.8332 (8)	0.2558 (4)	0.050
C(25)	0.3709 (3)	0.6844 (7)	0.2484 (3)	0.042
C(26)	0.2704 (4)	0.451 (1)	0.2460 (4)	0.075
C(27)	0.3266 (6)	0.2417 (9)	0.2455 (5)	0.091

The molecular structure and atom numbering scheme are shown in Figure 1. The molecule possesses no crystallographically imposed symmetry. Although very few studies of lanthanoid–aryl complexes have been revealed, some relevant comparisons can be made. In [Li(THF)$_4$][Lu($C_6H_3(CH_3)_2$)$_4$], the Lu–C lengths range from 2.42 (1) to 2.50 (1) Å and average 2.45 Å.[18] A shorter prediction can be obtained from (η^5-$C_5(CH_3)_5$)$_2$Sm(C_6H_5)(THF).[19] Despite the steric requirements of the $C_5(CH_3)_5^-$ groups, the Sm–C(σ) distance is 2.51 (1) Å. Since Sm is ca. 0.11 Å larger than Lu in +3 ionic radius, one would expect the Lu–C(σ) distance to be near 2.40 Å. In the only other structural determination of the title ligand bonded to a group 3A metal, (η^5-C_5H_5)$_2$Y[o-$C_6H_4CH_2N(CH_3)_2$],[20] the Y–C lengths, 2.41 (2) Å, lead to the expectation of Lu–C bond lengths equal to 2.38 Å after the appropriate correction. In Lu[o-$C_6H_4CH_2N(CH_3)_2$]$_3$, the Lu–C distances range from 2.425 (7) to 2.455 (7) Å and average 2.435 (14) Å (Table I).

Interestingly, the Lu–N distances in the title compound fall into a two-short, one-long pattern: 2.468 (6), 2.478 (5), and 2.588 (5) Å. The origin of this pattern may be steric in nature, or it may relate to packing considerations (as these affect the orientation of the –$N(CH_3)_2$ group). In (η^5-C_5H_5)$_2$Y[o-$C_6H_4CH_2N(CH_3)_2$], there are two molecules in the asymmetric unit, one with Y–N = 2.43 (3) Å and one with Y–N = 2.54 (2) Å.[20] The two have different configurations of the –$N(CH_3)_2$ units. Further studies on related complexes will be needed before these effects are understood.

In the five-membered metallocyclic rings, the three carbon atoms and the lutetium atom are planar to 0.02 Å, and the nitrogen atom resides 0.7 Å out of the plane. The torsion angles that involve the nitrogen and three carbon atoms of the rings are −25, 31, and −38°. (The values in (η^5-C_5H_5)$_2$Y[o-$C_6H_4CH_2N(CH_3)_2$] are 32 and 34° for the two independent molecules.)

All attempts to extend the synthesis to include early and middle lanthanoid elements failed. Reaction of $PrCl_3$, $NdCl_3$, $SmCl_3$, and $TbCl_3$ with 3 equiv of Li[o-$C_6H_4CH_2N(CH_3)_2$] produced dark brown reaction solutions from which no characterizable products could be isolated. Similarly, reaction of $NdCl_3$ with 4 equiv of lithium reagent also failed to yield a characterizable ate complex. These results suggest that bulkier, chelating ligands must be employed if neutral homoleptic and middle lanthanoid complexes are to be isolated as stable entities.

Nevertheless, the isolation of stable late lanthanoid hydrocarbyls incorporating the ((dimethylamino)methyl)phenyl ligand provides an excellent opportunity to assess the chemical reactivity of these complexes and to compare that reactivity with the previously described heteroleptic aryl complex (η^8-C_8H_8)Ln[o-$C_6H_4CH_2N(CH_3)_2$](THF). These studies are now under active investigation.

Acknowledgment. We thank S. M. Vincent for X-ray fluorescence analyses. J.L.A. and W.E.H. also acknowledge the National Science Foundation for support of this work.

Registry No. Er[o-$C_6H_4CH_2N(CH_3)_2$]$_3$, 90024-42-3; Yb[o-$C_6H_4CH_2N(CH_3)_2$]$_3$, 89936-32-3; Lu[o-$C_6H_4CH_2N(CH_3)_2$]$_3$, 89936-33-4; Li[o-$C_6H_4CH_2N(CH_3)_2$], 60528-57-6; $ErCl_3$, 10138-41-7; $YbCl_3$, 10361-91-8; $LuCl_3$, 10099-66-8; $PrCl_3$, 10361-79-2; $NdCl_3$, 10024-93-8; $SmCl_3$, 10361-82-7; $TbCl_3$, 10042-88-3.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, and structure factors (18 pages). Ordering information is given on any current masthead page.

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

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Molecular Orbital Studies of Organometallic Hydride Complexes. 3. Structural and Electronic Effects on the Reactivity in (η^5-C_5H_5)ML_2H and (η^5-C_5H_5)ML_3H Systems[1]

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Summary: Organometallic hydride complexes of the three-legged piano stool structural type, i.e., $CpML_2H$, are proposed to preferentially function as hydride donors while four-legged piano stool hydrides $CpML_3H$ are expected to behave as proton donors. This dependence of H reactivity on structure is used to explain the reactivity of $CpRe(CO)_2H_2$.

We recently reported that the preferential acidic or hydridic nature observed in organometallic hydride com-

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(1) Part 2: Bursten, B. E.; Gatter, M. G. *Organometallics*, earlier paper in this issue.

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