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

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 $(\eta^5\text{-}C_5(CH_3)_5)_2Sm(C_6H_5)(THF)$.[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, $(\eta^5\text{-}C_5H_5)_2Y[o\text{-}C_6H_4CH_2N(CH_3)_2]$,[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 $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 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 $(\eta^5\text{-}C_5H_5)_2Y[o\text{-}C_6H_4CH_2N(CH_3)_2]$, 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 $(\eta^5\text{-}C_5H_5)_2Y[o\text{-}C_6H_4CH_2N(CH_3)_2]$ 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 $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$ 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 $(\eta^8\text{-}C_8H_8)Ln[o\text{-}C_6H_4CH_2N(CH_3)_2](THF)$. 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. $Er[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 90024-42-3; $Yb[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 89936-32-3; $Lu[o\text{-}C_6H_4CH_2N(CH_3)_2]_3$, 89936-33-4; $Li[o\text{-}C_6H_4CH_2N(CH_3)_2]$, 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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Molecular Orbital Studies of Organometallic Hydride Complexes. 3. Structural and Electronic Effects on the Reactivity in $(\eta^5\text{-}C_5H_5)ML_2H$ and $(\eta^5\text{-}C_5H_5)ML_3H$ Systems[1]

Bruce E. Bursten* and Michael G. Gatter

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received January 24, 1984

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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Table I. Classification of $(\eta^n\text{-}C_nH_n)ML_mH$ Complexes as Hydride and Proton Donors

Hydride Donors

d^6 three-legged piano stool hydrides	hydride abstractor	d^6 three-legged piano stool product	ref
$CpW(NO)_2H$	$p\text{-}CH_3C_6H_4SO_3H$	$CpW(NO)_2SO_3C_6H_4CH_3$	4
$CpRe(NO)(CO)H$	$C_7H_7^+$	$CpRe(NO)(CO)(\eta^2\text{-}C_7H_8)^+$	7
$CpRe(CO)_2H^-$	$C_7H_7^+$	$CpRe(CO)_2(\eta^2\text{-}C_7H_8)$	8
$CpOs(CO)_2H$	$C_7H_7^+$	$CpOs(CO)_2(\eta^2\text{-}C_7H_8)^+$	11

Proton Donors

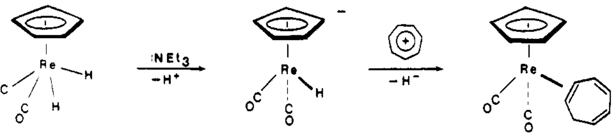
d^4 four-legged piano stool hydrides	proton abstractor	d^6 three-legged piano stool product	ref
$(\eta^6\text{-}C_6H_6)V(CO)_3H$	OH^-	$(\eta^6\text{-}C_6H_6)V(CO)_3^-$	12
$CpM(CO)_3H$ (M = Cr, Mo, W)	H_2O	$CpM(CO)_3^-$	3
$CpMn(CO)_2(SiR_3)H$ (R = Ph, Cl)	NEt_3	$CpMn(CO)_2SiR_3^-$	13
$CpRe(CO)_2H_2$	NEt_3	$CpRe(CO)_2H^-$	8
$CpFe(CO)(SiCl_3)_2H$	$NCCH_3$	$CpFe(CO)(SiCl_3)_2^-$	14

plexes appears to depend on the structures and orbital energetics of the resulting organometallic ions formed upon proton or hydride dissociation.[2] We used this concept to explain the acidic nature of $CpW(CO)_3H$[3] vis-à-vis the hydridic character of $CpW(NO)_2H$[4] (Cp = $\eta^5\text{-}C_5H_5$) (eq 1 and 2). Despite the contrasting modes of hydrogen re-

$$CpW(CO)_3H \rightarrow CpW(CO)_3^- + H^+ \tag{1}$$

$$CpW(NO)_2H \xrightarrow{CH_3CN} CpW(NO)_2(NCCH_3)^+ + H^- \tag{2}$$

activity, we observed that both tungsten hydrides form isostructural and isoelectronically equivalent organometallic ions: $CpW(CO)_3^-$ and $CpW(NO)_2(NCCH_3)^+$ have three-legged piano stool structures and were both found, by Fenske–Hall[5] calculations on the Cr analogues, to have stabilized d^6 electronic configurations. In addition, proton dissociation from $CpW(NO)_2H$ appears unfavorable due to the unstable orbital energetics we found for the yet unknown d^8 two-legged piano stool anion $CpW(NO)_2^-$. This preferential formation of a d^6 three-legged stool cation rather than the alternate d^8 two-legged anion can also account for the hydridic nature of $CpRe(NO)(CO)H$.[6] Attempts to prepare $CpRe(NO)(CO)^-$ have been unsuccessful,[7] but $CpRe(NO)(CO)H$ readily donates H^- to the tropylium cation $C_7H_7^+$ to form cycloheptatriene that subsequently coordinates in an η^2 fashion to the formally 16-electron cation $CpRe(NO)(CO)^+$, yielding the 18-electron d^6 three-legged product $CpRe(NO)(CO)(\eta^2\text{-}1,2\text{-}C_7H_8)^+$, shown in eq 3.[6] We now report that we can extend these



(3)

simple concepts to explain the hydrogen atom reactivities recently observed for the new dihydrido complex $CpRe(CO)_2H_2$ as well as other related systems.

In 1982, Hoyano and Graham reported that the weakly acidic $CpRe(CO)_2H_2$ could undergo double deprotonation in strongly basic solutions.[8] However, some very recent work by Yang and Bergman has reformulated this hydride as being only monoprotic:[9]

$$CpRe(CO)_2H_2 \rightarrow CpRe(CO)_2H^- + H^+ \tag{4}$$

$$CpRe(CO)_2H^- \not\rightarrow CpRe(CO)_2^{2-} + H^+ \tag{5}$$

Our model would certainly support these latest findings. Single proton dissociation from $CpRe(CO)_2H_2$ seems reasonable since our calculations indicate that the resulting conjugate base $CpRe(CO)_2H^-$ is an electronically stabilized d^6 three-legged piano stool complex.[10] We also agree that a second proton dissociation is unlikely since this would lead to the formation of the d^8 two-legged stool dianion $CpRe(CO)_2^{2-}$, a complex which we find calculationally to be as electronically destabilized as the isoelectronic $CpRe(NO)(CO)^-$ monoanion. Rather, we believe that $CpRe(CO)_2H^-$ can function as a hydride donor since loss of H^-, followed by coordination of a two-electron donor ligand, would yield yet another d^6 three-legged piano stool. We thus formulate the hydrogen reactivities of $CpRe(CO)_2H_2$ as shown in eq 6 and 7. Indeed, this suc-

$$\text{proton donor} \quad CpRe(CO)_2H_2 \rightarrow CpRe(CO)_2H^- + H^+ \tag{6}$$

$$\text{hydride donor} \quad CpRe(CO)_2H^- \xrightarrow{:L} CpRe(CO)_2{:}L + H^- \tag{7}$$

cessive protonic/hydridic nature of $CpRe(CO)_2H_2$ appears to explain some of the seemingly anomalous reactivity of the complex. For example, Hoyano and Graham found that hydride abstraction from $CpRe(CO)_2H_2$ by tropylium cation did not occur unless triethylamine was added to the reaction mixture[8] (eq 8 and 9). The authors were unable

$$CpRe(CO)_2H_2 \xrightarrow{C_7H_7^+} \text{no reaction} \tag{8}$$

$$CpRe(CO)_2H_2 \xrightarrow[NEt_3]{C_7H_7^+} CpRe(CO)_2(\eta^2\text{-}1,2\text{-}C_7H_8) \tag{9}$$

to propose an explanation for this behavior but in light of the protonic/hydride nature of the dihydride proposed in eq 6 and 7, we propose the scheme shown in eq 10. The fact that hydride abstraction occurs only in the presence of triethylamine (eq 9) suggests that deprotonation of $CpRe(CO)_2H_2$ by NEt_3 occurs first to afford the d^6 $CpRe(CO)_2H^-$ which, in a manner analogous to that of

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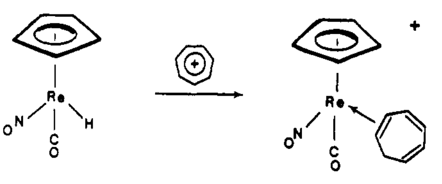

(10)

CpRe(NO)(CO)H, then undergoes hydride abstraction with $C_7H_7^+$ to afford the final d^6 product $CpRe(CO)_2(\eta^2\text{-}1,2\text{-}C_7H_8)$. This proposed mechanism provides another example of how the H reactivities in $CpML_nH$ complexes are influenced to give electronically stabilized d^6 three-legged piano stool products. Another closely related example is the compound $CpRe(CO)_2(CH_3)H$, prepared by methylation of $CpRe(CO)_2H^-$. In a scheme proposed by Yang and Bergman,[9] this hydride also behaves as a proton donor affording the d^6 three-legged piano stool product $CpRe(CO)_2(CH_3)^-$.

It is interesting to note that all 18-electron three-legged piano stool hydrides are formally d^6 species while all 18-electron four-legged hydrides are d^4 complexes. In order to form d^6 three-legged piano stool products, three-legged piano stool hydrides (in the presence of a 2-electron donor ligand) must function as hydride donors and four-legged hydrides must behave as proton donors. Hence, we expect the reactivity patterns shown in eq 11 and 12. In addition

$$\text{hydridic}\quad (\eta^n\text{-}C_nH_n)ML_2H \xrightarrow{L'} (\eta^n\text{-}C_nH_n)ML_2L'^+ + H^- \qquad (11)$$

$$n = 5$$

$$\text{acidic}\quad (\eta^n\text{-}C_nH_n)ML_3H \rightarrow (\eta^n\text{-}C_nH_n)ML_3^- + H^+ \qquad (12)$$

$$n = 5, 6$$

to the complexes examined here, all other characterized three- and four-legged piano stool complexes, tabulated in Table I, appear to support this generalization. Two other silyl hydride complexes,[15] the d^4 $(\eta^6\text{-}C_6H_6)Cr(CO)_2(SiCl_3)H$ and the d^6 $CpCo(CO)(SiCl_3)H$, have not been included in Table I since their acid–base properties have not yet been determined. Our reasoning, however, would predict acidic character for the former and hydridic behavior for the latter.

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Synthesis, Reactivity, and Two-Electron Electrochemistry of the Dinuclear Molybdenum(0) Complexes $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = *t*-Bu, Ph)†

Botao Zhuang,[1a] John W. McDonald,* Franklin A. Schultz,*[1b] and William E. Newton

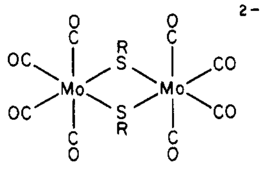
Charles F. Kettering Research Laboratory
Yellow Springs, Ohio 45387

Received February 15, 1984

Summary: New dinuclear Mo(0) complexes $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (R = Ph, *t*-Bu) (**1**), prepared by reaction of $Mo(CO)_6$ with $[Et_4N]SR$ in MeCN, undergo chemically reversible two-electron oxidation in a single step. This behavior is attributed to metal–metal bond formation accompanied by structural rearrangement in the Mo(I) product $Mo_2(CO)_8(SR)_2$ (**2**). **1** and **2** may be interconverted chemically or electrochemically and exhibit markedly different reactivities with solvent (MeCN, DMF) and CO.

Current interest in molybdenum thiolate complexes[2-7] arises from the known presence of Mo–S bonding in a variety of molybdoenzymes, among them nitrogenase. Our efforts to model the Fe–Mo–S cluster[8] at the molybdenum site of this enzyme led us to initiate synthetic studies of low-valent molybdenum complexes via reactions of $Mo(CO)_6$ with monodentate thiolates. Herein we report some initial results that reflect the rich chemistry and electrochemistry of compounds prepared by such reactions.

Reaction of $Mo(CO)_6$ with one equivalent of $[Et_4N][SR]$ (R = *t*-Bu, Ph) in MeCN for 4 h at 45 °C gave a yellow-brown reaction mixture which, after concentration and addition of *i*-PrOH, deposited a bright yellow solid product. Elemental analyses[9] were consistent with the empirical formula $[Et_4N][Mo(CO)_4(SR)]$, and plots of equivalent conductivity vs. the square root of concentration were linear with slopes of ca. −615 units. This value is consistent with that for 2:1 electrolytes[10,11] and suggests a formulation of $[Et_4N]_2[Mo_2(CO)_8(SR)_2]$ (1) for the products. The presence of four strong bands in the CO stretching region (1750–2050 cm^{-1}) of these complexes (Table I) also is consistent with this formulation. In light of these data, the most reasonable structure for the complex anions consists of two $Mo(CO)_4$ fragments bridged by two μ-SR moieties. Remarkably, we have been unable to find any mention of these relatively simple dinuclear species in the literature, although the chemistry of several related monomeric systems has been reported.[5,7,12]



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Our preliminary studies of the chemical reactivity of the dimeric anions are summarized in Scheme I. Oxidation of 1 with 1 equiv of I_2 in CO-saturated toluene yields the

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† Contribution No. 832.

(1) (a) Visiting Scientist from the Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian, The People's Republic of China. (b) Visiting Scientist from the Department of Chemistry, Florida Atlantic University, Boca Raton, FL 33431.
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