Studies of Molybdenum Compounds. 1. Synthesis and Structure of Dioxo(dimethyl)(2,2′-bipyridyl)molybdenum(VI), Prototype of a New Class of Organomolybdenum(VI) Compounds

Gerhard N. Schrauzer,* Laura A. Hughes, Norman Strampach, Paul R. Robinson,[1] and Elmer O. Schlemper*[2]

Department of Chemistry, University of California at San Diego, Revelle College, La Jolla, California 92093

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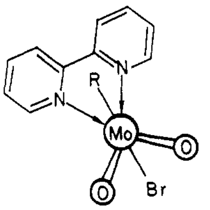
A synthesis of dioxo(dimethyl)(2,2′-bipyridyl)molybdenum(VI), $Mo(O)_2(CH_3)_2(bpy)$, by the reaction of dioxodibromo(2,2′-bipyridyl)molybdenum(VI) with methylmagnesium chloride, is described. The new organomolybdenum complex crystallizes from methanol in pale yellow needles, mp 230 °C dec. Prolonged heating in 1 M KOH/CH_3OH is required to cause quantitative decomposition in terms of the equation $Mo(O)_2(CH_3)_2(bpy) + 2OH^- = 2CH_4 + MoO_4^{2-} + bpy$. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.543$ (1) Å, $b = 9.872$ (1) Å, $c = 8.512$ (1) Å, $\alpha = 101.51$ (9)°, $\beta = 116.93$ (4)°, $\gamma = 80.14$ (8)°, $V = 624.5$ (3) Å^3, $Z = 2$. The three-dimensional X-ray data were measured with the θ–2θ scan technique with a scintillation detector. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to give $R(F_o) = 0.020$ and $R_w(F_o) = 0.034$ for 2152 observations above 2σ. The structure closely resembles that of $Mo(O)_2Br_2(bpy)$: the oxo groups approach a cis configuration (O–Mo–O angle = 110.20 (9)°), while the methyl groups are nearly trans (C–Mo–C angle = 149.03 (10)°). The Mo–O bond distances are 1.707 (2) and 1.708 (2) Å, and the Mo–C distances 2.194 (2) and 2.189 (3) Å. The Mo–N distances are 2.314 (2) and 2.346 (2) Å. The oxo groups are essentially coplanar with the bpy ligand; the dihedral angle between the bpy plane and the plane defined by O, O, Mo, N, N is 2.0°.

Recently,[3] we reported the synthesis of the first members of a class of organomolybdenum(VI) complexes of the type $R–Mo(O)_2–Br(bpy)$ (1), with R, e.g., CH_3 or C_2H_5, obtained



1, R = CH_3 or C_2H_5
2, R = Br

by reacting $(bpy)Mo(O)_2Br_2$ (2) with the respective organomagnesium halides. Through a modification of our initial synthesis technique we have since succeeded in preparing a number of dialkylated complexes of composition $Mo(O)_2R_2(bpy)$ (3), of which some exhibit exceptionally high stabilities.

The dimethyl derivative 4, for example, prepared by the reaction of 2[4] with CH_3MgCl in THF, forms pale yellow crystals which are stable in air up to a temperature of 230 °C, above which decomposition occurs with the formation of hydrocarbons, bipyridyl, and lower molybdenum oxides. The complex is insoluble in, and unaffected by, water and can be recrystallized from hot CH_3OH. However, decomposition in terms of eq 1 occurs on prolonged heating in 1 N $NaOH/CH_3OH$.

$$Mo(O)_2(CH_3)_2(bpy) + 2OH^- = 2CH_4 + MoO_4^{2-} + bpy \tag{1}$$

Complex 4 is also unstable in acidic solutions, or under reducing conditions. However, details of these and other reactions of 4 will be reported elsewhere. In this paper we describe the structure of 4 as determined by X-ray analysis.

Table I. Crystallographic and Data Collection Parameters

space group	$P\bar{1}$	diffractometer	Enraf-Nonius CAD-4
a, Å	8.543 (1)	cryst size, mm	0.1 × 0.2 × 0.3
b, Å	9.872 (1)	λ, Å (Mo Kα)	0.710 73
c, Å	8.512 (1)	μ, cm^{-1}	10.257, transmission range 92.2-99%
α, deg	101.51 (9)	scan speed	variable to maintain 3% counting statistics to a max time of 90 s/scan
β, deg	116.93 (4)		
γ, deg	80.14 (8)		
V, Å^3	624.5 (3)		
ρ_{obsd}, g/cm^3	1.69 (6)	θ-2θ scan, 96 steps/scan	
ρ_{calcd}, g/cm^3	1.6814 (7)	background	16 steps on each side of peak
Z	2		
fw	316.12	peak	64 steps
$R(F_o)$	0.020	takeoff angle	2.8°
$R_w(F_o)$	0.034	scan width in θ	$(0.55 + 0.35 \tan \theta)$°
total no. of observns	4135	observns above 2σ	2152

Experimental Section

Synthesis of $Mo(O)_2(CH_3)_2(bpy)$. A suspension of 3 g of 2[4] in 30 cm^3 of absolute tetrahydrofuran was placed into a bottle of 160 cm^3 capacity. The bottle was closed with a rubber serum cap and placed into an ice bath. After 20 min of cooling, 5 cm^3 of a 2.8 M solution of CH_3MgCl in THF was rapidly injected into the bottle by means of syringe, while the bottle was being shaken. After 1 h of reaction at 0 °C, the crystals of product were collected by vacuum filtration and washed with anhydrous ether. The crude product was dissolved in a 2:1 mixture of CH_2Cl_2 and CH_3OH. From the filtrate, pale yellow crystals of 4 precipitated upon evaporation of the CH_2Cl_2. The crystals were collected by filtration and dried: mp 230 °C dec; yield, 1.4 g (66%, based on 2). Anal. Calcd for $C_{12}H_{14}MoN_2O_2$: C, 45.86; H, 4.46; Mo, 30.56; N, 8.92; O, 10.20; mol wt, 314.02. Found: C, 45.97; H, 4.71; Mo, 30.68; N, 8.90; O, 9.74; mol wt (melting point depression in CH_2Cl_2), 346.

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(1) Union Science and Technology Division, Brea, CA.

(2) University of Missouri, Columbia, MO.

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Table II.[a] Positional and Thermal Parameters for $[Mo(O)_2(CH_3)_2(C_{10}H_{10}N_2)]$

atom	x	y	z	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Mo	0.19823 (2)	0.25681 (2)	0.20280 (2)	0.01429 (2)	0.00960 (2)	0.00927 (2)	−0.00217 (4)	0.01410 (3)	0.00430 (3)
O(1)	0.0528 (2)	0.2128 (2)	−0.0134 (2)	0.0202 (3)	0.0181 (2)	0.0111 (2)	−0.0053 (4)	0.0151 (3)	0.0069 (4)
O(2)	0.3796 (2)	0.3155 (2)	0.2123 (2)	0.0204 (2)	0.0141 (2)	0.0167 (2)	−0.0082 (3)	0.0225 (3)	0.0059 (3)
N(1)	0.0197 (2)	0.1946 (2)	0.3105 (2)	0.0125 (2)	0.0096 (2)	0.0105 (2)	−0.0003 (3)	0.0128 (3)	0.0044 (3)
N(2)	0.3256 (2)	0.2923 (2)	0.5149 (2)	0.0144 (2)	0.0082 (2)	0.0102 (2)	−0.0031 (3)	0.0131 (3)	0.0019 (3)
C(1)	0.3077 (3)	0.0458 (3)	0.2646 (3)	0.0177 (3)	0.0100 (2)	0.0148 (3)	−0.0018 (5)	0.0170 (5)	0.0006 (5)
C(2)	0.0595 (4)	0.4547 (3)	0.2586 (3)	0.0271 (4)	0.0108 (3)	0.0222 (4)	0.0075 (6)	0.0289 (6)	0.0129 (5)
C(3)	−0.1362 (3)	0.1458 (3)	0.1973 (3)	0.0133 (3)	0.0142 (3)	0.0121 (3)	−0.0048 (5)	0.0091 (5)	0.0047 (5)
C(4)	−0.2525 (3)	0.1162 (3)	0.2531 (3)	0.0132 (3)	0.0140 (3)	0.0184 (4)	−0.0043 (5)	0.0133 (5)	0.0057 (5)
C(5)	−0.2073 (3)	0.1360 (2)	0.4333 (3)	0.0155 (3)	0.0112 (3)	0.0206 (3)	−0.0017 (4)	0.0235 (4)	0.0065 (5)
C(6)	−0.0483 (3)	0.1837 (2)	0.5505 (3)	0.0184 (3)	0.0094 (2)	0.0149 (2)	0.0003 (4)	0.0228 (4)	0.0052 (4)
C(7)	0.0642 (2)	0.2116 (2)	0.4858 (2)	0.0141 (3)	0.0074 (2)	0.0109 (2)	0.0003 (4)	0.0151 (3)	0.0031 (3)
C(8)	0.2394 (3)	0.2628 (2)	0.6014 (2)	0.0148 (3)	0.0071 (2)	0.0106 (2)	0.0004 (4)	0.0143 (4)	0.0030 (4)
C(9)	0.3111 (3)	0.2806 (3)	0.07855 (3)	0.0184 (3)	0.0098 (2)	0.0102 (2)	−0.0003 (4)	0.0156 (4)	0.0039 (4)
C(10)	0.4744 (3)	0.3288 (3)	0.8831 (3)	0.0204 (4)	0.0109 (2)	0.0106 (3)	−0.0029 (5)	0.0117 (5)	0.0017 (5)
C(11)	0.5631 (3)	0.3596 (3)	0.7951 (3)	0.0171 (4)	0.0121 (3)	0.0149 (4)	−0.0088 (5)	0.0074 (6)	−0.0005 (6)
C(12)	0.4841 (3)	0.3411 (2)	0.6118 (3)	0.0164 (3)	0.0102 (2)	0.0141 (3)	−0.0064 (4)	0.0148 (4)	0.0026 (4)

[a] Numbers in parentheses in this and subsequent tables are the standard deviations from the least-squares refinement.

Table III. Positional Parameters for Hydrogen Atoms

atom	x	y	z	$\beta(11)$
H1(C1)	0.2127	−0.0104	0.2269	5.0000
H2(C1)	0.3778	0.0453	0.3892	5.0000
H3(C1)	0.3783	0.0047	0.2037	5.0000
H1(C2)	0.1413	0.5144	0.3480	5.0000
H2(C2)	−0.0250	0.4401	0.2950	5.0000
H3(C2)	−0.0007	0.4987	0.1522	5.0000
H(C3)	−0.1690	0.1313	0.0714	5.0000
H(C4)	−0.3603	0.0805	0.1680	5.0000
H(C5)	−0.2877	0.1164	0.4763	5.0000
H(C6)	−0.0140	0.1998	0.6767	5.0000
H(C9)	0.2460	0.2607	0.8427	5.0000
H(C10)	0.5266	0.3420	1.0106	5.0000
H(C11)	0.6744	0.3930	0.8619	5.0000
H(C12)	0.5447	0.3654	0.5517	5.0000

Physical Properties. Infrared spectrum: in addition to absorption characteristic of the coordinated 2,2′-bpy, the two IR $\nu_{Mo=O}$ appear at 934 and 905 cm^{-1} (in KBr).

UV–vis absorptions [nm (ϵ), in CH_2Cl_2]: 303 (24 900), 293 (17 000), and 245 (19 600).

^{1}H NMR spectrum in CD_3OD: δ_{bpy} protons, 7.5–9.5 (8); CH_3 protons, 0.58 (6) ppm relative to $Si(CH_3)_4$ (intensities in parentheses, measured on a Varian HR-220/Nicolet TT-100 spectrometer).

Structure Analysis. An outline of crystallographic and data collection parameters is given in Table I. A crystal of approximate dimensions 0.1 × 0.2 × 0.3 mm was mounted in a random configuration on an Enraf-Nonius CAD-4 automated diffractometer for data collection. The crystal was triclinic ($P\bar{1}$) with the unit cell dimensions shown in the table. These were based upon a Delaunay reduction of a cell obtained from the centering of 25 reflections on the diffractometer. There are two symmetry-related molecules in the unit cell. The flotation density of 1.69 (6) g/cm^3, measured in CCl_4–CBr_4 mixtures, agrees with the calculated density of 1.6814 (7) g/cm^3.

Intensity data (294 K) were measured by the θ–2θ step scan technique with Mo Kα radiation (λ = 0.7107 Å) from a graphite monochromator. A total of 4135 Bragg reflections were measured. Equality of Friedel's pairs is in agreement with the successful refinement in the centric space group ($P\bar{1}$). The intensities of three standard reflections measured after each 8000-s exposure to X-rays showed no significant change with time. Empirical absorption corrections were made with the ψ scan technique (μ = 10.3). Averaging of equivalent reflections gave 2316 data points of which 2152 had $F_o > 2\sigma(F_o)$; these were used to refine the structure ($\sigma^2(F_o^2) = \sigma^2_{counting} + (0.05F_o^2)^2$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$).

The structure was resolved by Patterson and Fourier methods. Least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.020$ and $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.034$. Hydrogen atoms were located and held in near "ideal" X-ray positions.[5] Extinction correction was not applied.

The maximum parameter shift on the last cycle was 0.01 times its esd, and the error in an observation of unit weight was 1.12. Atomic scattering factors were taken from ref 6. Final atomic positional parameters are included in Tables II and III. Selected interatomic distances and angles are given in Tables IV and V.

Discussion

Complex 4 could either be a *cis*- or *trans*-dioxomolybdenum derivative with two methyl groups directly attached to molybdenum.

The presence of a *cis*-MoO_2 moiety follows unambiguously from the IR spectrum, which shows two Mo–O IR stretching frequencies at 905 and 934 cm^{-1}. The two respective bands in 1 and 3 appear at very similar frequencies, suggesting a close structural relationship with these compounds. In the ^{1}H NMR spectrum of 4 in CD_3OD, a

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Table IV. Selected Interatomic Distances and Angles

dist	value, Å	angle	value, deg
Mo-O(1)	1.707 (2)	O(1)-Mo-O(2)	110.20 (9)
-O(2)	1.708 (2)	N(1)-Mo-N(2)	68.40 (6)
-C(1)	2.194 (2)	C(1)-Mo-C(2)	149.03 (10)
-C(2)	2.189 (3)		
-N(1)	2.314 (2)	O(1)-Mo-N(1)	92.66 (8)
-N(2)	2.346 (2)	O(2)-Mo-N(2)	88.73 (7)
		O(1)-Mo-N(2)	161.06 (8)
		O(2)-Mo-N(1)	157.13 (8)
N(1)-C(3)	1.344 (3)		
-C(7)	1.345 (3)		
N(2)-C(8)	1.348 (3)	O(1)-Mo-C(1)	97.60 (10)
-C(12)	1.341 (3)	-Mo-C(2)	98.31 (11)
av N-C	1.344 (3)	O(2)-Mo-C(1)	99.31 (9)
		-Mo-C(2)	99.86 (11)
C(7)-C(8)	1.480 (3)	av O-Mo-C	98.8 (1.0)
		N(1)-Mo-C(1)	76.31 (8)
C(3)-C(4)	1.372 (3)	-Mo-C(2)	76.57 (9)
C(11)-C(12)	1.378 (2)	N(2)-Mo-C(1)	78.39 (8)
C(4)-C(5)	1.381 (4)	-Mo-C(2)	77.95 (9)
C(10)-C(11)	1.383 (4)	av N-Mo-C	77.3 (1.0)
C(5)-C(6)	1.366 (4)		
C(9)-C(10)	1.372 (4)	Mo-N(1)-C(3)	120.26 (15)
C(6)-C(7)	1.390 (3)	-N(2)-C(12)	121.75 (15)
C(8)-C(9)	1.386 (3)	-N(1)-C(7)	121.55 (14)
av C-C_{arom}	1.379 (8)	-N(2)-C(8)	119.94 (14)

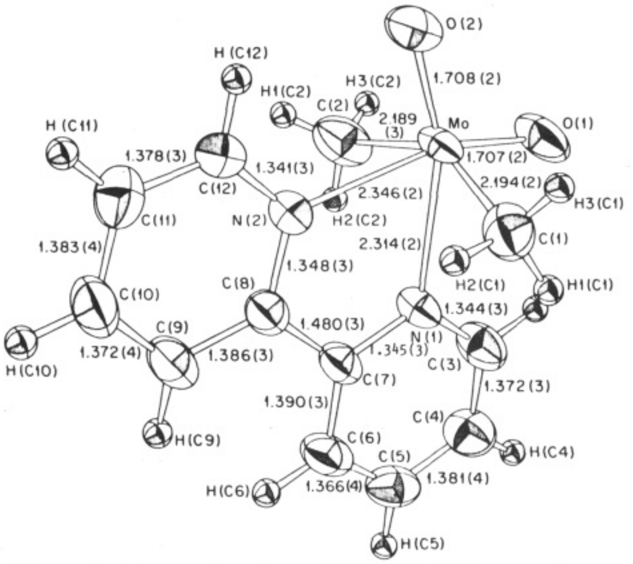

Figure 1. Perspective view of $Mo(O)_2(CH_3)_2$bpy with atom numbering and observed distances in angstroms.

sharp singlet at 0.584 ppm relative to Me_4Si is assigned to the six methyl protons. The chemical shift of the methyl

Table V. Selected Bond Angles, Bipyridyl Ligand

angle	value, deg	angle	value, deg
N(1)-C(3)-C(4)	122.76 (22)	C(3)-C(4)-C(5)	118.80 (22)
N(2)-C(12)-C(11)	122.69 (22)	C(12)-C(11)-C(10)	118.75 (23)
N(1)-C(7)-C(6)	121.74 (20)	C(4)-C(5)-C(6)	119.27 (21)
N(2)-C(8)-C(9)	121.75 (20)	C(11)-C(10)-C(9)	119.14 (22)
N(1)-C(7)-C(8)	114.71 (18)	C(5)-C(6)-C(7)	119.29 (22)
N(2)-C(8)-C(7)	115.29 (17)	C(10)-C(9)-C(8)	119.34 (22)
C(3)-N(1)-C(7)	118.13 (19)	C(6)-C(7)-C(8)	123.55 (19)
C(8)-N(2)-C(12)	118.31 (19)	C(9)-C(8)-C(7)	122.96 (19)

Table VI. Comparison of $Mo(O)_2(CH_3)_2(bpy)$ with Previous Structures

A. Bond Distances

bond	dist, Å	molecule	ref
Mo-O_t	1.707 (2), 1.708 (2)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	1.643 (17), 1.826 (18)	$Mo(O)_2Br_2(bpy)$	7
	1.705 (7)-1.750 (7)	$Cs_2[Mo(O)_2(Bz)_2]\cdot H_2O$ (Bz = benzohydroximate anion)	8
	1.706 (5), 1.713 (5)	$Mo(O)_2[p\text{-}CH_3C_6H_4C(=S)N(CH_3)O]_2$	9
	1.703 (2)	$Mo(O)_2(S_2CN(C_2H_5)_2)_2$	10
Mo-CH_3	2.189 (3), 2.194 (2)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	2.173 (7), 2.176 (8)	$Mo_2[N(CH_3)_2]_4(CH_3)_2$	11
Mo-CH_2-	2.131	$Mo_2[CH_2Si(CH_3)_3]_6$	12
Mo-$COCH_3$	2.264 (14)	$(C_5H_5)Mo(CO)_3[P(C_6H_5)_3]COCH_3$	13
Mo-N	2.314 (2), 2.346 (2)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	2.449 (19), 2.259 (18)	$Mo(O)_2Br_2(bpy)$	7
N-C	1.341 (3)-1.348 (3)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	1.320 (30)-1.502 (29)	$Mo(O)_2Br_2(bpy)$	7
C-C_{arom}	1.366 (4)-1.390 (3)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	1.316 (38)-1.512 (37)	$Mo(O)_2Br_2(bpy)$	7
C-C_{bridge}	1.480 (3)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	1.455 (25)	$Mo(O)_2Br_2(bpy)$	7

B. Bond Angles

angle	value, deg	molecule	ref
O-Mo-O	110.20 (9)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	103.3 (9)	$Mo(O)_2Br_2(bpy)$	7
	101.5 (4), 103.8 (4)	$Cs_2[Mo(O)_2(Bz)_2]\cdot H_2O$	8
	103.7 (2)	$Mo(O)_2[p\text{-}CH_3C_6H_4C(=S)N(CH_3)O]_2$	9
	105.81 (12)	$Mo(O)_2(S_2CN(C_2H_5)_2)_2$	10
X-Mo-X (X = Br, CH_3)	149.03 (10)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	159.70 (10)	$Mo(O)_2Br_2(bpy)$	7
X-Mo-N	76.31 (8)-78.39 (8)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	66.6 (4)-98.4 (4)	$Mo(O)_2Br_2(bpy)$	7
O-Mo-N	88.73 (7), 92.66 (8) 157.13 (8), 161.06 (8)	$Mo(O)_2(CH_3)_2(bpy)$	this work
	94.7 (7), 95.1 (7) 161.9 (7), 161.5 (7)	$Mo(O)_2Br_2(bpy)$	7

group protons is only 0.04 ppm downfield from that of 1 (with R = CH_3) reported previously.[3] In addition, only the signals of the bipyridyl protons are observed.

The structure as determined by X-ray analysis (Figure 1) is in accord with the IR and NMR spectroscopic evidence but reveals additional details, most notably an extremely distorted octahedral coordination geometry around the molybdenum atom, which is in part even more pronounced than that in **3**.[7] Although complexes **3** and **4** crystallize in the same space group ($P\bar{1}$), the O–Mo–O angle of 110.20° is 7° wider than in **4**; the C–Mo–C angle of 149.03° is 10° smaller than the Br–Mo–Br angle. These differences in the bond angles are caused by repulsions of the methyl groups by the two *cis*-oxygen atoms. Because of the negative inductive effect of the methyl groups, the charge density on the oxygen atoms in **4** is probably higher than in **3**. However, the average Mo–O bond distances of 1.71 Å in **4** are within experimental error identical with those in **3**. Table VI shows that the average Mo–C bond distances of 2.19 Å are slightly longer than bond lengths reported for methyl carbons bound to dinuclear Mo(II). However, they lie well within the range of 2.131–2.264 Å of previously reported Mo–$C_{\text{aliphatic}}$ bond lengths. Table VI contains additional structural data to facilitate further structural comparisons with other known molybdenum complexes. Bond distances and angles of the Mo(bpy) subunit are identical, within experimental error, for **3** and **4**. The oxo groups are essentially coplanar with the bpy ligand; the dihedral angle between the bpy plane and the plane defined by O, O, Mo, N, N is 2.0°. It is of interest to note the systematic alternation of short and long C–C bonds in the bpy rings of **4**. Presumably due to the lower resolution achieved, this phenomenon has not been observed in the structure of **3**.[7] It was, however, reported previously for other aromatic rings containing heteroatoms.

In forthcoming papers of this series we will describe additional compounds of this type with emphasis on their relevance to catalysis and biocatalysis.

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Registry No. 2, 18057-92-6; **4**, 79084-25-6.

Supplementary Material Available: A listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Thermal and Photochemical Reactions of Dinuclear Metal Carbonyl Compounds with Metal Hydrides[1]

Richard W. Wegman and Theodore L. Brown*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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The thermal or photochemical reaction of bis(tri-*n*-butylphosphine)hexacarbonyldicobalt, $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$, with tri-*n*-butyltin hydride, $HSn(n\text{-}Bu)_3$, leads to H_2 and $(n\text{-}Bu)_3SnCo(CO)_3P(n\text{-}Bu)_3$ as products. The rate law for the photochemical reaction and product distribution are consistent with a pathway involving loss of CO from the $Co(CO)_3P(n\text{-}Bu)_3\cdot$ radical following metal–metal bond rupture, oxidative addition of the H–Sn bond to the cobalt center, a hydrogen atom transfer from a second $HSn(n\text{-}Bu)_3$ to cobalt, and then a reductive elimination of H_2, as the pathway for reaction. A similar reaction pathway is indicated for reaction of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W) with $HSn(n\text{-}Bu)_3$ or $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with $HMo(CO)_3(\eta^5\text{-}C_5H_5)$. On the other hand reaction of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with $HMn(CO)_5$ leads to $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ and $Mn_2(CO)_{10}$ as products, suggesting a simple hydrogen atom transfer reaction between the $Mo(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ radical and $HMn(CO)_5$. The choice between the oxidative addition and hydrogen atom transfer pathways is determined by the donor M–H bond energy; a low M–H bond energy favors hydrogen atom transfer. On the basis of studies to date, the oxidative addition pathway, as described above, is the more common. Reaction of $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ with $HSn(n\text{-}Bu)_3$ leads to $(n\text{-}Bu)_3SnMo(CO)_3(\eta^5\text{-}C_5H_5)$ and H_2. The rate law is of the form $d(\text{product})/dt = \{k_a[HSn(n\text{-}Bu)_3]/(k_b + k_c[HSn(n\text{-}Bu)_3])\}[HMo(CO)_3(\eta^5\text{-}C_5H_5)]$. The rate law suggests the existence of a preequilibrium involving either a formyl intermediate, formed via a hydride migration, or a change in hapticity of the cyclopentadienyl ring to form a η^1-cyclopentadienyl intermediate.

We have recently reported the results of a study of the thermal or photochemical decomposition of cobalt tetracarbonyl hydride, $HCo(CO)_4$, which proceeds in accord with eq 1.[2] The kinetics behavior of the system is strongly

$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2 \qquad (1)$$

suggestive of a radical pathway involving $Co(CO)_4\cdot$ radicals as intermediates. The radical pathway proposed for reaction 1 can be generalized to describe the reaction of any dinuclear metal carbonyl compound with a metal or me-

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(2) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

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