Amphoteric ligands. 4. Reactions of HMn(CO)5 with (aluminoamino)phosphine ligands. Structure of (OC)3Mn[CHOAlMe2N(CMe3)PPh2][PPh2N(CMe3)Al(HCH2)Me]

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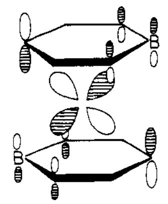
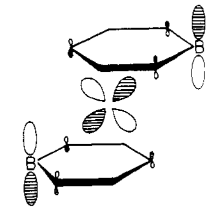
that α-C is the most negative carbon atom, more negative than β-C and γ-C atoms, in accord with the classical view of resonance structure for borabenzene anion. This might explain why α-C is much more reactive than β-C or γ-C atoms toward electrophiles. The electrophilic substitutions seem to be charge controlled. Others[39,40] and we[16,21] have suggested that electrophilic attacks at some other organometallic compounds as well are essentially charge controlled.

Others[40–43] and we[19–21] have also suggested that nucleophilic attacks at various organometallic complexes are frontier controlled. This notion has recently been extended by a proposal that coordinated olefin is activated toward nucleophilic attack by slippage of the metal fragment attached to it.[44] Our calculations on $(BBz)_2Fe$ indicate that nucleophilic attack at boron may well be assisted by slippage of the borabenzene ring. Drawings **10** and **11** shown schematically the composition of the vacant molecular



s = 1.4 Å

10



s = 2.0 Å

11

orbital designated xz^* in *trans*-$(BBz)_2Fe$ when the Fe atom is nearly above the center of each ring (S = 1.4 Å) and when it is much nearer to the p-C than to the B atom (S = 2.0 Å). As the BBz^- rings slip and the B atoms get farther from the Fe atom, the lobes of this frontier orbital decline at the p-C atoms and grow at the B atoms. According to our calculations (see Figure 4c), the high-lying, filled molecular orbitals of $(BBz)_2Fe$ would be raised in energy by a total of about 10 kcal mol^{-1} as the rings slip from **10** to **11**. Since this gain in energy is rather small, the substrate molecule is likely to "afford" it in the course of its reaction with an incoming nucleophile.

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Registry No. $(BBz)Fe^+$, 86563-66-8; BB_Z^-, 55926-39-1; $(BB_Z)_2Fe$, 68344-23-0; $(BB_Z)_2Co$, 68378-62-1.

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Amphoteric Ligands. 4. Reactions of $HMn(CO)_5$ with (Aluminoamino)phosphine Ligands. Structure of $(CO)_3Mn[CHOAl(CH_3)_2N(C(CH_3)_3)P(C_6H_5)_2]$-$[P(C_6H_5)_2N(C(CH_3)_3)Al(HCH_2)(CH_3)]$

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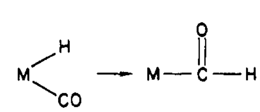
The amphoteric ligands Ph_2PN-t-$BuAlR_2$ (**1a**, R = Et; **1b**, R = Me) react with $HMn(CO)_5$ to give $(CO)_4Mn(CHOAlR_2N$-t-$BuPPh_2)$ (**2**), a product resulting from net migration of hydrogen from Mn to CO. However, NMR studies indicate that direct migration is not occurring. Instead, proton transfer from Mn to P is the initial process observed. From the reaction of $CpMo(CO)_3H$ with **1b** it is possible to isolate an analogue to the proposed proton-transfer intermediate $[CpMo(CO)_3][AlMe_2N$-t-$BuPPh_2H]$. Complexes **2** react with a second equivalent of **1**; for R = Me the product was characterized by X-ray crystallography as

$(CO)_3Mn(CHOAlMe_2N$-t-$BuPPh_2)(PPh_2N$-t-$BuAl(HCH_2)(CH_3))$

in which a C–H bond from an Al–Me group is acting as one of the ligands to Mn. Crystal data: orthorhombic; space group *Pbca*; a = 18.063 (7) Å, b = 18.446 (8) Å, c = 25.003 (7) Å; Z = 8; final R = 0.053 for 1808 reflections used.

Introduction

Migration step 1 has been widely considered a key element in homogeneous hydrogenation of carbon monoxide.[1]



(1)

However, unequivocal evidence for this transformation in model studies has proven elusive. The intermediacy of a

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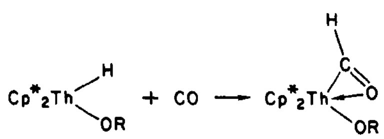
Table I. NMR Shifts (δ) and Coupling Constants (Hz) for $L_nM(C(R)OAl(CH_2CH_3)_2N(C(CH_3)_3)PPh_2)$

a b c d e f

parameter		2a (L_nM = $(CO)_4Mn$, R = H)	3 (L_nM = Cp(CO)Fe, R = CH_3)
^1H	H_b	4.4 (d, J_{PH} = 33)	1.5 (d, J_{PH} = 16)
	H_c	0.4 (m)	0.8 (m)
	H_d	1.52 (t), 1.47 (t, J_{HH} = 8)	1.84 (t), 1.65 (t, J_{HH} = 8)
	H_f	1.14 (s)	1.3 (s)
^{13}C	C_a	65.3 (d, J_{PC} = 76.6)	58.4 (d, J_{PC} = 68.6)
	C_b		28.9 (d, J_{PC} = 21.2)
	C_c	5.0 (br)	6.5 (s), 5.7 (s)
	C_d	10.2 (s), 10.0 (s)	11.1 (s), 11.0 (s)
	C_e	54.3 (d, J_{PC} = 6.2)	54.5 (d, J_{PC} = 7.1)
	C_f	34.1 (d, J_{PC} = 5.9)	34.0 (d, J_{PC} = 6.3)
^{31}P		36.8	33.0

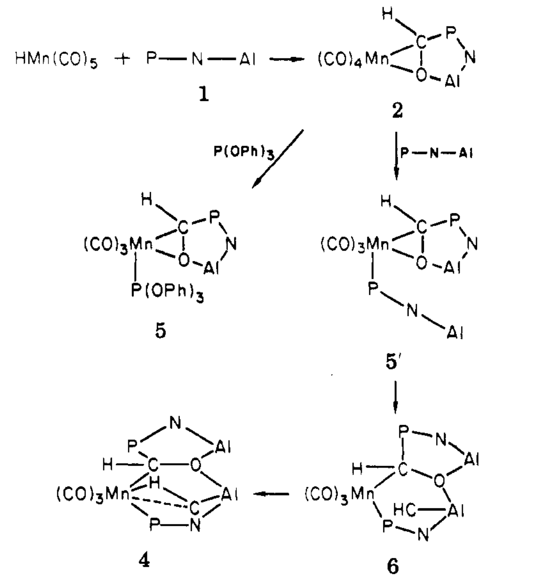
formyl complex has been proposed to account for facile CO substitution in certain hydridometal carbonyls,[2] but the ready availability of a radical chain mechanism for such species[3] leaves this interpretation open to question. A sizable number of hydridometal carbonyl complexes have been shown to give rise to intermediates or products containing C–H bonds,[4] but many of these may well involve alternate mechanisms such as intermolecular nucleophilic attack.[5] Only for a thorium system (eq 2) is there definite evidence for an intramolecular migration step generating a C–H bond.[4d]



(2)

The difficulty of demonstrating hydride migration may be contrasted with the general facility of alkyl migration.[6] Shriver has demonstrated that the addition of Lewis acids such as $AlCl_3$ can strongly favor alkyl migration both thermodynamically[7] and kinetically,[8] but this approach did not work for hydride migration: various systems examined show no reaction,[9] M–H bond cleavage,[9] or Lewis acid–metal hydride adduct formation.[9,10] We have shown that amphoteric ligands $Ph_2PNRAlR'_2$ (1) can facilitate alkyl migrations in contrast to simple Lewis acids AlR_3.[11] We

Scheme I



anticipated that these ligands might similarly be effective in inducing hydride migration. As we show here, reactions leading to C–H bonds are observed, but direct migration does not appear to be involved. A preliminary account of this work has been presented.[12]

Results and Discussion

Reactions of $HMn(CO)_5$. A benzene solution of equimolar $HMn(CO)_5$ and Ph_2PN-*t*-$BuAlEt_2$ (**1a**) darkens to orange over several minutes, and evaporation of solvent affords an orange oil (**2a**). This compound, like most of the related ones prepared in this work, proved resistant to attempted crystallization; and chromatography invariably led to decomposition. Nonetheless, unequivocal characterization was achieved by NMR spectroscopy. In particular, most of the parameters (Table I) show close similarity to those found for $Cp(CO)Fe(C(CH_3)OAlEt_2N$-*t*-$BuPPh_2)$ (**3**), the crystallographically characterized product of the reaction between **1a** and $CpFe(CO)_2CH_3$.[11] Both **2a** and **3** exhibit ^{31}P NMR signals around 30 ppm and ^{13}C NMR signals around 60 ppm (J_{PC} = ca. 75 Hz), characteristic of the direct P–C bonding arrangement established for **3**. Furthermore, in the coupled ^{13}C NMR spectrum of **2a**, an additional doublet splitting of 168 Hz is observed for this signal, demonstrating that the carbon is bonded to a single hydrogen. The ^1H NMR spectrum of **2a** shows a doublet at δ 4.46 (J_{PH} = 33.2 Hz) instead of the CH_3 signal found for **3**. ^2H NMR spectroscopy on the product obtained from $DMn(CO)_5$ and **1a** shows a single broad signal at δ 4.5, establishing that this hydrogen atom is the one originally bonded to Mn. Thus **2a** contains a heterocyclic η^2 ligand similar to that in **3**. The carbonyl region of the ^{13}C NMR spectrum shows four equal signals (the IR also reveals four CO stretching peaks), completing the characterization of **2a** as $(CO)_4Mn(CHOAlEt_2N$-*t*-$BuPPh_2)$.[13]

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Table II. Atomic Positions for Complex 4b[a]

atom	x	y	z
Mn	0.85455 (9)	0.33224 (9)	0.13307 (6)
P(1)	0.8178 (2)	0.3114 (2)	0.2230 (1)
P(2)	0.7755 (2)	0.2134 (2)	0.0393 (1)
Al(1)	0.6919 (2)	0.3423 (2)	0.1599 (1)
Al(2)	0.5412 (2)	0.1836 (2)	0.1004 (1)
O(1)	0.9710 (4)	0.2219 (5)	0.1383 (3)
O(2)	0.9726 (4)	0.4321 (5)	0.1694 (4)
O(3)	0.9156 (4)	0.3757 (4)	0.0286 (3)
O(4)	0.6988 (3)	0.2625 (3)	0.1187 (2)
N(1)	0.7272 (4)	0.3150 (4)	0.2263 (3)
N(2)	0.7000 (4)	0.1674 (5)	0.0384 (3)
C(1)	0.9233 (6)	0.2638 (6)	0.1369 (4)
C(2)	0.9244 (6)	0.3955 (6)	0.1570 (4)
C(3)	0.8888 (6)	0.3570 (6)	0.0678 (4)
C(4)	0.7769 (5)	0.2496 (6)	0.1066 (4)
C(5)	0.8541 (6)	0.3779 (6)	0.2712 (4)
C(6)	0.8453 (6)	0.4493 (6)	0.2587 (4)
C(7)	0.8654 (7)	0.5028 (7)	0.2933 (5)
C(8)	0.8936 (8)	0.4886 (7)	0.3435 (6)
C(9)	0.9012 (7)	0.4166 (8)	0.3567 (5)
C(10)	0.8831 (6)	0.3614 (6)	0.3218 (4)
C(11)	0.8523 (6)	0.2232 (6)	0.2446 (4)
C(12)	0.8084 (6)	0.1606 (6)	0.2385 (4)
C(13)	0.8363 (7)	0.0919 (6)	0.2482 (5)
C(14)	0.9068 (7)	0.0838 (6)	0.2663 (5)
C(15)	0.9514 (6)	0.1427 (6)	0.2715 (5)
C(16)	0.9231 (6)	0.2115 (6)	0.2606 (5)
C(17)	0.6788 (6)	0.3111 (6)	0.2746 (4)
C(18)	0.6590 (7)	0.3867 (8)	0.2928 (5)
C(19)	0.7137 (7)	0.2724 (8)	0.3214 (5)
C(20)	0.6118 (7)	0.2656 (8)	0.2620 (5)
C(21)	0.7536 (6)	0.4207 (6)	0.1252 (4)
C(22)	0.5935 (7)	0.3803 (8)	0.1530 (5)
C(23)	0.6530 (7)	0.1031 (6)	0.1510 (4)
C(24)	0.5396 (6)	0.2155 (7)	0.0911 (4)
C(25)	0.6682 (6)	0.1274 (6)	−0.0094 (4)
C(26)	0.7291 (7)	0.1025 (6)	−0.0480 (4)
C(27)	0.6169 (6)	0.1769 (7)	−0.0401 (4)
C(28)	0.6280 (8)	0.0611 (7)	0.0107 (5)
C(29)	0.8577 (6)	0.1582 (5)	0.0356 (4)
C(30)	0.9266 (6)	0.1831 (6)	0.0177 (4)
C(31)	0.9875 (7)	0.1401 (6)	0.0203 (4)
C(32)	0.9817 (7)	0.0719 (7)	0.0428 (5)
C(33)	0.9139 (8)	0.0492 (7)	0.0610 (6)
C(34)	0.8539 (6)	0.0915 (6)	0.0573 (4)
C(35)	0.7767 (6)	0.2841 (5)	−0.0116 (4)
C(36)	0.7275 (6)	0.3406 (6)	−0.0042 (4)
C(37)	0.7228 (7)	0.3946 (6)	−0.0414 (4)
C(38)	0.7649 (7)	0.3952 (7)	−0.0863 (4)
C(39)	0.8149 (7)	0.3406 (5)	−0.0933 (4)
C(40)	0.8196 (7)	0.2837 (6)	−0.0578 (4)
H(1)	0.798 (5)	0.208 (4)	0.125 (3)
H(2)	0.798 (5)	0.419 (5)	0.126 (3)
H(3)	0.745 (5)	0.454 (5)	0.141 (3)
H(4)	0.735 (5)	0.435 (5)	0.100 (3)

[a] Positional parameters for atoms H(1), H(2), H(3), and H(4) were refined. The remaining hydrogen atoms were included in calculated positions and were not refined. Their positions were calculated assuming idealized geometries and C–H = 0.95 Å. The temperature factors of all hydrogen atoms were fixed.

The analogous reaction of HMn(CO)$_5$ with PPh$_2$N-*t*-BuAlMe$_2$ (**1b**) proceeds much more slowly, requiring several hours for completion. At early stages the ^{1}H NMR spectrum of the reaction mixture exhibits a doublet at δ 4.5, indicating **2b** is present. However, as the reaction proceeds, this signal disappears while a new doublet of doublets grows in. Again, deuterium labeling establishes that this signal comes from the Mn-bonded hydrogen atom. The additional coupling to ^{31}P, as well as other NMR data (see Experimental Section), indicates a complex of 2:1 ligand–metal stoichiometry. In this case a crystalline sample could be obtained, and X-ray crystallography (see below) established the structure **4b** for this product.

Table III. Bond Distances (Å)

atoms 1	atoms 2	dist	atoms 1	atoms 2	dist
Mn	P(1)	2.376 (3)	C(5)	C(7)	1.362 (15)
Mn	Al(1)	3.019 (4)	C(7)	C(8)	1.38 (2)
Mn	C(1)	1.773 (15)	C(8)	C(9)	1.37 (2)
Mn	C(2)	1.820 (15)	C(9)	C(10)	1.38 (2)
Mn	C(3)	1.803 (13)	C(11)	C(12)	1.409 (15)
Mn	C(4)	2.175 (12)	C(11)	C(16)	1.358 (14)
Mn	C(21)	2.45 (2)	C(12)	C(13)	1.385 (15)
Mn	H(2)	1.91 (12)	C(13)	C(14)	1.36 (2)
P(1)	N(1)	1.641 (8)	C(14)	C(15)	1.36 (2)
P(1)	C(5)	1.839 (12)	C(15)	C(16)	1.395 (15)
P(1)	C(11)	1.825 (11)	C(17)	C(18)	1.51 (2)
P(2)	N(2)	1.606 (8)	C(17)	C(19)	1.51 (2)
P(2)	C(1)	1.810 (12)	C(17)	C(20)	1.51 (2)
P(2)	C(29)	1.802 (11)	C(21)	H(2)	0.80 (10)
P(2)	C(35)	1.823 (10)	C(21)	H(3)	0.75 (11)
Al(1)	O(4)	1.800 (7)	C(21)	H(4)	0.75 (10)
Al(1)	N(1)	1.847 (8)	C(25)	C(26)	1.532 (15)
Al(1)	C(21)	2.02 (2)	C(25)	C(27)	1.512 (15)
Al(1)	C(22)	1.919 (13)	C(25)	C(28)	1.508 (15)
Al(2)	O(4)	1.846 (7)	C(29)	C(30)	1.400 (15)
Al(2)	N(2)	1.903 (9)	C(29)	C(34)	1.346 (15)
Al(2)	C(23)	1.962 (11)	C(30)	C(31)	1.36 (2)
Al(2)	C(24)	1.941 (12)	C(31)	C(32)	1.38 (2)
O(1)	C(1)	1.159 (13)	C(32)	C(33)	1.37 (2)
O(2)	C(2)	1.145 (13)	C(33)	C(34)	1.34 (2)
O(3)	C(3)	1.147 (11)	C(35)	C(36)	1.382 (14)
O(4)	C(4)	1.462 (12)	C(35)	C(40)	1.393 (14)
N(1)	C(17)	1.493 (13)	C(36)	C(37)	1.366 (15)
N(2)	C(25)	1.519 (13)	C(37)	C(38)	1.36 (2)
C(4)	H(1)	0.96 (10)	C(38)	C(39)	1.36 (2)
C(5)	C(6)	1.362 (14)	C(39)	C(40)	1.377 (15)
C(5)	C(10)	1.402 (14)			

Scheme I shows the sequence of transformations observed for these reactions. **2a** can be converted to **4a** by addition of a second equivalent of **1a**, but little if any **4a** is detected in the reaction of equimolar **1a** and HMn(CO)$_5$; it is not at all obvious why **2b** goes on to **4b** so readily. **2a** undergoes ready substitution by simple phosphorus ligands such as P(OPh)$_3$ to give **5**. Hence, it seems reasonable to propose that **5′** is an intermediate for the conversion of **2** to **4**. **5′** contains a free Lewis acidic Al center that should have a stronger affinity for oxygen than does Mn. Detachment of O from Mn generates coordinatively unsaturated **6**; the vacant site is then occupied by a C–H bond acting as ligand. Space-filling models indicate that the polycyclic framework of **4** constrains one of the alkyl groups on Al to be close to the Mn atom, which would favor the latter interaction. A mixed-ligand diadduct **4c** can also be generated from **2a** plus **1b**. The coordinated C–H group in **4c** comes from a methyl group, not an ethyl group. This shows that there is no exchange of amphoteric ligands during reaction: the first-added ligand remains bonded to carbon.

Structure of 4b. Although **4b**, like the other compounds, was difficult to crystallize, small crystals were finally obtained from cold benzene–hexane solution. The molecular structure is shown in Figure 1; atomic positions and bond distances and angles are given in Tables II–IV. From the viewpoint of the Mn coordination sphere, the molecule is a disubstituted alkylmetal carbonyl, RMn(CO)$_3$LL′. In this description R is an aluminoxyphosphinomethyl group derived from migration of H to CO, addition of phosphorus to the carbon center, and coordination of Al to the oxygen. L is a phosphine ligand, while L′ is a coordinated C–H bond from an Al–CH$_3$ group. (The hydrogens of both R and L′ were located and refined in the crystallographic study.) Alternatively, the molecule

Table IV. Bond Angles (deg)

atoms				atoms				atoms			
1	2	3	angle	1	2	3	angle	1	2	3	angle
P(1)	Mn	Al(1)	61.8 (1)	Mn	Al(1)	C(22)	154.7 (5)	C(12)	C(13)	C(14)	120 (1)
P(1)	Mn	C(1)	91.7 (4)	O(4)	Al(1)	N(1)	105.5 (4)	C(13)	C(14)	C(15)	120 (1)
P(1)	Mn	C(2)	89.2 (4)	O(4)	Al(1)	C(21)	107.5 (5)	C(14)	C(15)	C(16)	119 (1)
P(1)	Mn	C(3)	173.1 (4)	O(4)	Al(1)	C(22)	108.1 (5)	C(11)	C(16)	C(15)	123 (1)
P(1)	Mn	C(4)	89.7 (3)	N(1)	Al(1)	C(21)	113.0 (5)	N(1)	C(17)	C(18)	110 (1)
P(1)	Mn	C(21)	88.6 (4)	N(1)	Al(1)	C(22)	120.0 (5)	N(1)	C(17)	C(19)	114 (1)
P(1)	Mn	H(2)	94 (4)	C(21)	Al(1)	C(22)	102.1 (7)	N(1)	C(17)	C(20)	109 (1)
Al(1)	Mn	C(1)	135.5 (4)	O(4)	Al(2)	N(2)	90.6 (4)	C(18)	C(17)	C(19)	108 (1)
Al(1)	Mn	C(2)	124.2 (4)	O(4)	Al(2)	C(23)	112.1 (4)	C(18)	C(17)	C(20)	113 (1)
Al(1)	Mn	C(3)	121.3 (4)	O(4)	Al(2)	C(24)	108.9 (5)	C(19)	C(17)	C(20)	103 (1)
Al(1)	Mn	C(4)	58.9 (3)	N(2)	Al(2)	C(23)	110.2 (4)	Mn	C(21)	Al(1)	84.2 (6)
Al(1)	Mn	C(21)	41.8 (4)	N(2)	Al(2)	C(24)	118.5 (5)	Mn	C(21)	H(2)	40 (9)
Al(1)	Mn	H(2)	57 (3)	C(23)	Al(2)	C(24)	114.1 (5)	Mn	C(21)	H(3)	131 (11)
C(1)	Mn	C(2)	87.4 (5)	Al(1)	O(4)	Al(2)	138.3 (4)	Mn	C(21)	H(4)	129 (10)
C(1)	Mn	C(3)	89.4 (6)	Al(1)	O(4)	C(4)	108.6 (6)	Al(1)	C(21)	H(2)	121 (10)
C(1)	Mn	C(4)	88.2 (5)	Al(2)	O(4)	C(4)	111.3 (6)	Al(1)	C(21)	H(3)	104 (10)
C(1)	Mn	C(21)	176.1 (5)	P(1)	N(1)	Al(1)	108.1 (5)	Al(1)	C(21)	H(4)	111 (11)
C(1)	Mn	H(2)	168 (3)	P(1)	N(1)	C(17)	128.4 (7)	H(2)	C(21)	H(3)	102 (14)
C(2)	Mn	C(3)	84.1 (6)	Al(1)	N(1)	C(17)	122.6 (7)	H(2)	C(21)	H(4)	118 (15)
C(2)	Mn	C(4)	175.4 (5)	P(2)	N(2)	Al(2)	112.3 (5)	H(3)	C(21)	H(4)	93 (14)
C(2)	Mn	C(21)	96.6 (5)	P(2)	N(2)	C(25)	126.1 (7)	N(2)	C(25)	C(26)	111.7 (9)
C(2)	Mn	H(2)	82 (3)	Al(2)	N(2)	C(25)	120.5 (7)	N(2)	C(25)	C(27)	110 (1)
C(3)	Mn	C(4)	97.1 (5)	Mn	C(1)	O(1)	176 (1)	N(2)	N(25)	C(28)	108 (1)
C(3)	Mn	C(21)	90.8 (5)	Mn	C(2)	O(2)	174 (1)	C(26)	C(25)	C(27)	108 (1)
C(3)	Mn	H(2)	84 (4)	Mn	C(3)	O(3)	174 (1)	C(26)	C(25)	C(28)	108 (1)
C(4)	Mn	C(21)	87.9 (5)	Mn	C(4)	P(2)	123.4 (6)	C(27)	C(25)	C(28)	111 (1)
C(4)	Mn	H(2)	103 (3)	Mn	C(4)	O(4)	116.4 (7)	P(2)	C(29)	C(30)	124 (1)
C(21)	Mn	H(2)	16 (3)	Mn	C(4)	H(1)	99 (7)	P(2)	C(29)	C(34)	117 (1)
Mn	P(1)	N(1)	108.6 (3)	P(2)	C(4)	O(4)	103.8 (7)	C(30)	C(29)	C(34)	118 (1)
Mn	P(1)	C(5)	114.4 (4)	P(2)	C(4)	H(1)	98 (7)	C(29)	C(30)	C(31)	121 (1)
Mn	P(1)	C(11)	109.2 (4)	O(4)	C(4)	H(1)	115 (7)	C(30)	C(31)	C(32)	119 (1)
N(1)	P(1)	C(5)	107.3 (5)	P(1)	C(5)	C(6)	117 (1)	C(31)	C(32)	C(33)	119 (1)
N(1)	P(1)	C(11)	111.2 (6)	P(1)	C(5)	C(10)	125 (1)	C(32)	C(33)	C(34)	121 (1)
C(5)	P(1)	C(11)	106.2 (6)	C(6)	C(5)	C(10)	117 (1)	C(29)	C(34)	C(33)	121 (1)
N(2)	P(2)	C(4)	102.7 (5)	C(5)	C(6)	C(7)	122 (1)	P(2)	C(35)	C(36)	116 (1)
N(2)	P(2)	C(29)	113.6 (5)	C(6)	C(7)	C(8)	122 (1)	P(2)	C(35)	C(40)	126 (1)
N(2)	P(2)	C(35)	112.2 (5)	C(7)	C(8)	C(9)	116 (1)	C(36)	C(35)	C(40)	118 (1)
C(4)	P(2)	C(29)	104.2 (5)	C(8)	C(9)	C(10)	122 (2)	C(35)	C(36)	C(37)	120 (1)
C(4)	P(2)	C(35)	112.6 (5)	C(5)	C(10)	C(9)	120 (1)	C(36)	C(37)	C(38)	122 (1)
C(29)	P(2)	C(35)	111.0 (6)	P(1)	C(11)	C(12)	120 (1)	C(37)	C(38)	C(39)	118 (1)
Mn	Al(1)	O(4)	75.8 (2)	P(1)	C(11)	C(16)	123 (1)	C(38)	C(39)	C(40)	121 (1)
Mn	Al(1)	N(1)	81.2 (3)	C(12)	C(11)	C(16)	116 (1)	C(35)	C(40)	C(39)	120 (1)
Mn	Al(1)	C(21)	54.0 (5)	C(11)	C(12)	C(13)	122 (1)	Mn	H(2)	C(21)	124 (12)

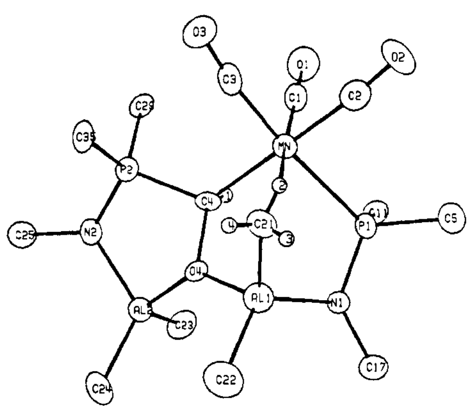
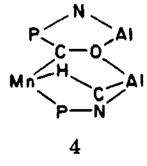


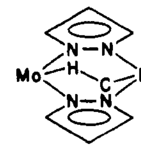
Figure 1. Perspective view of complex **4b**. For clarity, only the first carbon atoms of the phenyl and *tert*-butyl groups are shown.

can be described as a polycyclic heterocycle, incorporating a five-membered ring fused to a bicyclo[2.2.2]octane framework:



4

The possibility of a saturated carbon center acting as a ligand by means of a three-center C–H–M interaction was first considered about 1970; since then a number of examples have been established crystallographically. The structure most closely related to that of **4b** is the Mo complex **7**, which can be viewed as having the same bicyclooctane framework.[14] Parameters of the C–H–M interaction for previously reported examples are compared to those for **4b** in Table V. The H–Mn distance of 1.91 (12) Å is comparable to values found for other first-row transition-metal complexes, with the exception of the



7

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(16) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117–2126.
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Table V. Structural Parameters of Three-Center C-H-M Interactions

complex	M-H, Å	M-C, Å	C-H, Å	C-H-M, deg	(M-C)-(M-H), Å	ref
4b	1.91 (12)	2.45 (2)	0.80 (10)	124 (12)	0.54	this work
$(Et_2BPz_2)Mo(CO)_2(\eta^3\text{-}CH_2CPhCH_2)$ (**7**)	2.27 (8)	3.055 (7)	0.97 (8)	137	0.78	14
a	[2.15]		[1.10]		[0.90]	
$(Et_2BPz_2)Mo(CO)_2(\eta^3\text{-}C_7H_7)$	[1.92]^b	2.92	[1.10]		[1.00]	15
$(C_6H_8Me)Mn(CO)_3$ (**8**)	1.86 (2)	2.301 (2)	1.07 (2)	101 (1)	0.44	16
$[(C_8H_{13})Fe(P(OMe)_3)_3]^+$ (**9**)	1.95 (3)	2.384 (4)	1.07 (3)	100 (2)	0.43	17
c	1.874 (3)	2.362 (2)	1.164 (3)	99.4 (2)	0.49	17
$[(C_7H_{10})Cu(dien)]^+$ (**10**)	2.01 (15)	2.78 (1)	0.81 (15)	158 (17)	0.77	18
$[Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-}dppm)Cp_2]^+$ (**11**)	1.64 (4)	2.108 (3)	1.06 (4)	101 (3)	0.47	19
d	1.78 (3)	2.118 (3)	0.83 (4)	103 (3)	0.34	19
$[Mo_2(C_8Me_8H)Cp_2]^+$ ^{e}	1.88 (8)	2.196 (5)	0.89 (7)	99 (5)	0.32	20
$HFe_4(\eta^2\text{-}CH)(CO)_{12}$ ^{e}	1.80 (4)	1.926 (5)	1.00 (4)	82 (2)	0.13	21

^{a} Value "corrected" for the known foreshortening of C-H distances in X-ray determinations. Note that this procedure assumes the *direction* of the C-H bond is known with accuracy, which may not be valid; see footnote *c*. ^{b} Hydrogen atom not located; distances based on calculated positions. ^{c} Neutron diffraction study. Application of the procedure described above^a to the X-ray positions gives a corrected Fe-H distance of 1.94 Å, only marginally closer to the neutron result than the uncorrected value. ^{d} Two crystallographically independent molecules. ^{e} These entries are not strictly comparable to the rest, in that the coordinated C-H group involves an unsaturated carbon atom, so that the M-C interaction should be considerably stronger.

methyl-bridged iron dimer **11** that exhibits a much shorter Fe–H bond length. However, it is not clear that the latter is a strictly analogous bonding situation; it has been described as a protonated bridging methylene.[19]

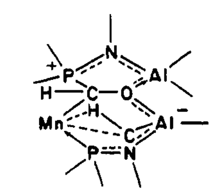
It has been suggested that three-center C–H–M interactions of this type may be classified according to whether or not there is a significant C–M overlap.[16]

12 **13**

For the hypothetical case where M–H and M–C bonding were equally important, the difference between the M–H and M–C distances would be expected to be comparable to the difference in covalent radii, about 0.4 Å. A relatively acute M–H–C angle would also be expected for bonding type **12**. According to these criteria, it appears that the entries in Table V may be classified as follows: **8**, **9**, and **11** are basically of type **12**; **7** and **10**, of type **13**. The present structure **4b** is intermediate. This classification must be qualified, however, by the recognition that geometric constraints are likely to be important. It may be noted that in **8** and **9**, the coordinating C–H group is immediately adjacent to the ligating atoms of the ligand of which it is a part. In **4b**, **7**, and **10** the C–H group is considerably more remote, which ought to afford more flexibility in these molecules.

Aside from the C–H–Mn interaction, the Mn coordination sphere appears unexceptional. Bond lengths Mn–C(4) and Mn–P(1) are similar to those reported for related complexes.[22] The three carbonyls exhibited some variation: the carbonyl trans to the C–H ligand (C(1)–O(1)) has a substantially shorter Mn–C and slightly longer C–O bond distance than the other two, as found for complex **8** as well.[16] This situation has been observed previously in $(CO)_4Mn(C(OAlBrBr_2)CH_3)$[7] and in $(CO)_4Mn(C_6H_4COCH_3)$,[23] where the Mn–C bonds trans to Br and to O, respectively, are shortened. The π-donor ability of the latter ligands was suggested to strengthen back-donation to the trans CO relative to the others. In **4b** there is no π-donor ligand; the C–H ligand should have no π-acceptor ability at all, which might account for Mn–C(1) being shorter than Mn–C(3) (the carbonyl trans to the phosphine ligand). However, this does not explain why Mn–C(1) is shorter than Mn–C(2), since the sp^3-alkyl ligand should not be a π-acceptor either. The geometry about Mn is essentially octahedral; bond angles between cis ligands, excluding the C–H ligand, range from 84.1 (6) to 97.1 (5)°. (Angles between ligands involving the C–H ligand are of questionable significance, since in addition to the large uncertainty in the position of the hydrogen atom, it is not clear whether such angles should be measured to the hydrogen atom or to some point along the C–H bond.)

Any reasonable valence bond picture of **4b** requires P(2) to be a phosphonium center, e.g.



The P(2)–N(2) and P(2)–C(phenyl) distances are all shorter than the corresponding values for P(1), consistent with the higher effective oxidation state (and consequent stronger P–N π bonding) of P(2). Conversely, N(2)–Al(2) is significantly longer than N(1)–Al(1), presumably because the lone pair on N(2) is more involved with P–N π bonding and hence less available for N–Al π bonding. Both N atoms exhibit nearly planar geometry, in agreement with the substantial delocalization proposed. O(4)–Al(1) is substantially shorter than O(4)–Al(2); this may reflect a difference in bonding mode as suggested by the above valence bond picture. Alternatively, it may be due to the effect of the coordination of the C–H group on the electronic nature of Al(1). It may be noted that the Al–C(21) bond is elongated considerably compared to the remaining three Al–C bonds. Geometry about O(4) is also essentially planar.

Examining the polycyclic framework of the molecule, we find that the three groups of atoms—(i) Mn, H(2), C(21),

(19) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41–43.
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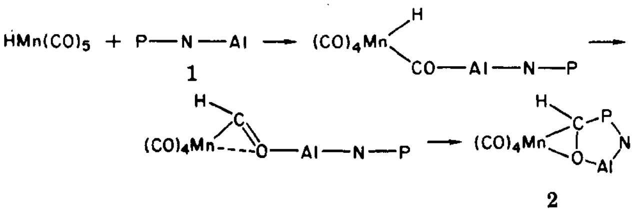
(21) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485–1492.
(22) See, for example: Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1970**, *24*, 3431–3433. Mawby, A.; Pringle, G. *J. Inorg. Nucl. Chem.* **1972**, *34*, 877–883. Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *49*, C27–C29. Doedens, R. J.; Veal, J. T.; Little, R. G. *Inorg. Chem.* **1975**, *14*, 1138–1142. Lindner, E.; Funk, G.; Hoehne, S. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 535.
(23) Knobler, C. B.; Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2062–2066.

Scheme II



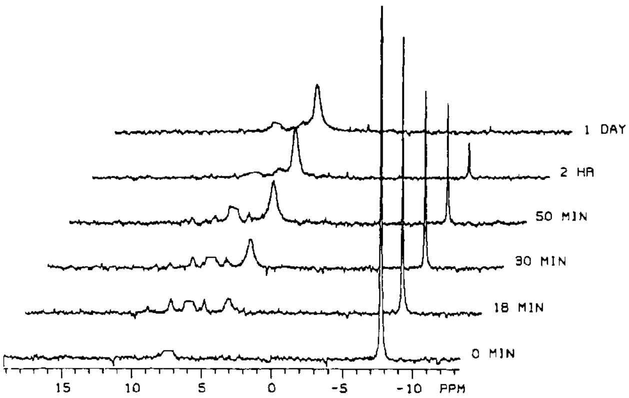


Figure 2. ^{2}H NMR spectra for the reaction of $DMn(CO)_5$ with **1a** (toluene solution, 0 °C) as a function of time. (The truncated strong signal at δ 7.2 is due to C_6D_6 added as reference.)

Al(1), (ii) Mn, P(1), N(1), Al(1), and (iii) Mn, C(4), O(4), Al(1)—are each approximately planar, with dihedral angles between these planes ranging from 54.3 to 69.7°. (In the idealized bicyclo[2.2.2]octane structure, these dihedral angles would all be 60°.) The fused five-membered ring, on the other hand, is far from planar. Atoms C(4) and O(4) lie 0.20 and 0.47 Å, respectively, out of the best least-squares plane. This may be compared to compound **3**, which contains the same five-membered ring bonded in a quite different fashion to the metal atom; there the ring is considerably less distorted from planarity.[11] Models suggest the distortion in **4b** is largely imposed by the ring fusion.

Mechanistic Considerations. The formation of **2** appears consistent with direct, Lewis acid induced migration (Scheme II), analogous to the alkyl migration leading to complex **3**.[11] However, one can readily conceive of alternate routes to the same product.[24] We attempted to detect an intermediate by following reactions by NMR at low temperature. The ^{1}H NMR spectrum for the reaction of $HMn(CO)_5$ with **1a** (0 °C, toluene-d_8) showed only smooth transformation to **2a**, with no detectable intermediate. In contrast, a similar study using ^{2}H NMR and $DMn(CO)_5$ revealed the formation of an intermediate, **14**, which exhibits a doublet at δ 7.7 (J_{PD} = 75 Hz) (Figure 2). The concentrations of the various species as a function of time (determined by NMR integration) can be fit reasonably well to a two-step mechanism, eq 3 and 4, where $k_1 = 1.7 \times 10^{-3}$ M^{-1} s^{-1} and $k_2 = 1.2 \times 10^{-3}$ s^{-1} (Figure 3).[25]

$$DMn(CO)_5 + \mathbf{1a} \xrightarrow{k_1} \mathbf{14} \qquad (3)$$

$$\mathbf{14} \xrightarrow{k_2} \mathbf{2a} \qquad (4)$$

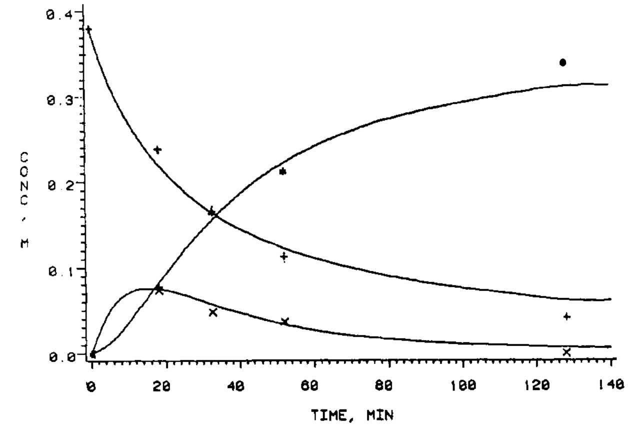


Figure 3. Kinetic plot for the reaction of $DMn(CO)_5$ with **1a**. Experimental points are the concentrations of $DMn(CO)_5$ (+), **14** (×), and **2a** (*) determined by integration of ^{2}H NMR signals (see Figure 2). Solid lines are concentrations calculated for the two-step mechanism with rate constants given in text (calculation by numerical integration).

Although we were not able to isolate **14** and thus cannot completely characterize it, the large P–D coupling constant (the corresponding P–H coupling constant would be about 490 Hz) appears consistent only with D bonded directly to pentavalent phosphorus.[26] A species with the same spectral feature was obtained from the reaction of **1b** with $CpMo(CO)_3H$. This product is proposed to have structure **15**, based upon the large P–H coupling, the ^{31}P NMR shift,[26] and the IR spectrum, which shows two C–O stretches in the normal region for terminal carbonyls and a third at 1570 cm^{-1}. Such a pattern is typical of Lewis acid adducts of the anion $[CpM(CO)_3]^-$.[27] (The reactions of **1a** and **1b** with all three hydrides $CpM(CO)_3H$, M = Cr, Mo, or W, gave products with similar spectra, but most were less stable than **15**. See Experimental Section for details.) By analogy, **14** is assigned a similar structure

$$L_nM{-}C{\equiv}O{\rightarrow}AlR_2{-}N\text{-}t\text{-}Bu{-}PPh_2H$$
$$\mathbf{14},\ L_nM = Mn(CO)_4,\ R = Et$$
$$\mathbf{15},\ L_nM = CpMo(CO)_2,\ R = Me$$

resulting from net proton transfer from metal to phos-

(24) For example, early formation of the P–C bond to give an alkylidene complex, $(CO)_4HMn{=}C(OAlEt_2N\text{-}t\text{-}BuPPh_2)$, is an attractive possibility. Nucleophile-assisted hydrogenation of CO has been demonstrated (Doxsee, K. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7696–7698); also hydride migration to alkylidenes can be quite facile, in contrast to migration to CO (Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659).

(25) It is crucial to distinguish this proposed mechanism from possible alternatives in which **14** is not on the route to **2**. The simplest such reaction

$$\mathbf{14} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DMn(CO)_5 + \mathbf{1a} \xrightarrow{k_2} \mathbf{2a}$$

does not fit the experimental kinetic data. A reviewer (S. J. McLain, whom we thank for his very helpful contribution) has devised a more complex scheme, involving an additional intermediate, which can be fit reasonably well to the data

$$DMN(CO)_5 + \mathbf{1a} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{14} \qquad \mathbf{1a} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} INT \qquad INT + \mathbf{1a} \xrightarrow{k_3} \mathbf{2a}$$

However, this scheme is not consistent with the observed isotope effect (see below): since formation of **14** and **2** are competitive steps here, the suppression of **14** found with $HMn(CO)_5$ would have to be a result of accelerated formation of **2**, which is not found. In contrast, as discussed in the text, the observed behavior is consistent with formation of **14** and **2** being sequential.

(26) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper & Row: New York, 1976; pp 77–91. The ^{31}P NMR resonance for $[MePPh_2N\text{-}t\text{-}BuAlEt_2]^+$ is observed at 32.5 ppm,[11] and an upfield shift on the order of 20 ppm is typical on replacing alkyl by hydrogen in phosphines or phosphonium salts.

(27) (a) Petersen, R. B.; Stezowski, J. J.; Wan, C.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3532–3533. (b) Ulner, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *Ibid.* **1973**, *95*, 4469–4471. (c) Hamilton, D. M.; Willis, W. S.; Stucky, G. D. *Ibid.* **1981**, *103*, 4255–4256. (d) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360–6368.

phorus. Vlcek has shown that the thermodynamic acidities of $CpMo(CO)_3H$ and $HMn(CO)_5$ are very comparable,[28] so it is not surprising that they should behave similarly. It is more surprising that proton transfer to yield a moderately stable phosphonium salt can take place in the presence of the highly proton-sensitive ligands **1**. Normally one would not expect a phosphine such as **1** to be a strong enough base to deprotonate the relatively weak acids $HMn(CO)_5$ and $CpMo(CO)_3H$. We suggest that the initial interaction involves formation of the O–Al bond, as is the case in alkyl migration induced by **1**.[11] This would tend to make the hydride more acidic by withdrawing electron density from the complex and might also stabilize the resulting "salt" against protonolysis of the sensitive bonds in **1**.

The failure to observe intermediate **14** in the ^1H NMR study may be explained by a kinetic isotope effect. With the assumption that k_1 has a negligible isotope effect (which would be consistent with the proposal that formation of the O–Al bond is rate-determining, as suggested above) while k_2 has $k_H/k_D > 4$, the maximum concentration of **14** calculated from the rate constants determined from the ^2H NMR study is < 5%, so that the signal would not be distinguishable from noise. The overall rate constant obtained from the ^1H NMR study is $(1.3 \pm 0.7) \times 10^{-3}\ M^{-1}\ s^{-1}$, the same as k_1 in the ^2H NMR experiment within experimental uncertainty.[25] The mechanism for the conversion of **14** to **2** remains unclear. This corresponds to a net insertion of a carbon center into a P–H bond, a reaction for which there is no precedent in metal carbonyl chemistry.[29] Also unclear is the reason why **15** shows no tendency to undergo a similar process and form the analogue of **2**. Nonetheless, although the mechanism is not fully characterized, it appears that direct migration of hydrogen to CO is *not* occurring here, in spite of the fact that the product obtained is completely analogous to that formed in an alkyl migration reaction.[11,30] Instead, C–H bond formation is achieved via transfer of H from Mn to P and thence to C.[31]

Experimental Section

General Procedures and Materials. All operations were carried out under argon by using standard Schlenk techniques or a Vacuum Atmospheres Corp. glovebox. Reagents unless specified otherwise were obtained commercially and used without purification; solvents were distilled from sodium benzophenone ketyl. Amphoteric ligands **1a** and **1b** were prepared as described previously.[11] $HMn(CO)_5$ and $CpM(CO)_3H$ were prepared according to literature procedures.[32] $DMn(CO)_5$ and $CpMo(CO)_3D$ were prepared similarly by using D_3PO_4 and CH_3COOD, respectively. NMR spectra were recorded on Varian EM-360 and Nicolet NT-200 instruments; all NMR data are for benzene-d_6 solutions unless noted otherwise.

(28) Miholova, D.; Vlcek, A. A. *Proc. Conf. Coord. Chem., 3rd*, **1971**, 221–226 (*Chem. Abstr.* **1972**, *76*, 64116u). See also: Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263.

(29) *O*-coordinated carbonyls such as that in the proposed structure of **14** have been suggested to have substantial alkylidene and/or alkylidyne character[27d] and thus might reasonably be expected to be more reactive than a simple terminal carbonyl.

(30) Recently it has been shown that *oxidatively* induced migration of H to CO appears to parallel the well-known oxidatively induced alkyl migration, although the possibility of an alternate mechanism for C–H bond formation was not ruled out: Cameron, A.; Smith, V. H.; Baird, M. C. *Organometallics* **1983**, *2*, 465–467.

(31) The generation of a formyl complex from Rh(OEP)H (OEP = octaethylporphyrin) and CO[4c] has been suggested to proceed in similar fashion, via an N-protonated porphyrin intermediate: Woods, B. A.; Wayland, B. B.; Minda, V. M.; Duttahmed, A. 185th National Meeting of the American Chemical Society, Seattle, WA Mar 1983; INOR 144.

(32) King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; pp 156–160.

Table VI. Experimental Details for Structure Determination on Compound 4b

A. Crystal Data

formula	$C_{40}H_{51}Al_2MnN_2O_4P_2$
cryst dimens, mm	$0.15 \times 0.25 \times 0.30$
peak width at half-height, deg	0.20
Mo Kα radiation	λ = 0.710 73 Å
temp, °C	23 ± 1
space group	*Pbca*, orthorhombic
a, Å	18.063 (7) Å
b, Å	18.446 (8)
c, Å	25.003 (7)
V, Å^3	8330.5
Z	8
ρ, g/cm^3	1.27
μ, cm^{-1}	5.0

B. Intensity Measurements

instrument	Enraf-Nonius CAD4 diffractometer
monochromator	graphite crystal, incident beam
scan type	ω-θ
scan rate, deg/min	2–20
scan width, deg	0.7 + 0.350 tan θ
max 2θ, deg	45.0
no. of reflctns	6178 total, 5438 unique
correctns	Lorentz-polarization, linear decay (from 1.00 to 1.05 on *I*)

C. Structure Solution and Refinement

soln	direct methods
hydrogen atoms	H(1)–H(4) refined with B_{iso} = 6.0 Å^2; H(5)–H(51) in calculated positions
refinement	full-matrix least squares
minimizatn function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, $w = (2F_o/\sigma(F_o)^2)^2$
anomalous dispersn	all non-hydrogen atoms
reflctns included	1808 with $F_o^2 > 2.5\sigma(F_o)^2$
parameters refined	472
unweighted agreement factor	0.053
weighted agreement factor	0.057
esd of observn of unit weight	1.22
convergence, largest shift	0.38σ
high peak in final difference map, e/Å^3	0.28 (6)

$(CO)_4$Mn(CHOAlEt$_2$N-*t*-BuPPh$_2$) (2a). A solution of $HMn(CO)_5$ (0.5 g, 2.55 mmol) and **1a** (0.87 g, 2.55 mmol) in 2 mL of benzene was allowed to stand for 1 h, then filtered, and concentrated to dryness, yielding a red-orange tarry material. Repeated attempts at crystallization were unsuccessful, while chromatography on silica or alumina led to immediate decomposition: ^1H NMR δ 7.9 (m), 7.2 (m, C_6H_5), 4.4 (d, J = 33 Hz, Mn(CHOAlNP)), 1.52 (t), 1.47 (t, J = 8 Hz, $AlCH_2CH_3$), 1.14 (s, $C(CH_3)_3$), 0.4 (m, $AlCH_2CH_3$); ^{13}C NMR δ 222.2, 215.7, 211.6, 210.5 (MnCO), 134–132 (m, C_6H_5), 65.3 (J_{PC} = 76.6 Hz, $^1J_{CH}$ = 168.0 Hz, MnCHOAlNP), 54.3 (J_{PC} = 6.2 Hz, $C(CH_3)_3$), 34.1 (J_{PC} = 5.9 Hz, $^1J_{CH}$ = 126.5 Hz, $C(CH_3)_3$), 10.2, 10.0 ($^1J_{CH}$ = 129 Hz, $AlCH_2CH_3$), 5.0 (br, $^1J_{CH} \simeq$ 117 Hz, $AlCH_2CH_3$); ^{31}P NMR δ 36.8; IR (toluene) ν_{CO} 2005 (s), 1980 (s), 1965 (s), 1935 (s) cm^{-1}.

For kinetic studies on formation of **2a**-d_1, approximately 0.3 M solutions of $DMn(CO)_5$ and of **1a** in toluene were prepared in the drybox and taken out in septum-capped vials. Both solutions were cooled below 0 °C and transferred by syringe to a 12-mm NMR tube. The tube was shaken briefly and inserted into the spectrometer, with the probe temperature preset to 0 °C. Accumulation of data could be begun within 90 s of mixing. Adequate spectra were obtained by accumulating 4–8 pulses, requiring 8–15 s for each data point.

4b. A solution of $HMn(CO)_5$ (0.1 g, 0.5 mmol) and **1b** (0.2 g, 0.5 mmol; not completely dissolved at first) in benzene was allowed to stand; over a period of hours it gradually turned orange and residual solid slowly dissolved. After 3 days the golden orange solution was filtered and evaporated to a yellow solid (**4b**): ^1H

(CO)$_3$Mn(CHOAlMe$_2$N-*t*-BuPPh$_2$)(PPh$_2$N-*t*-BuAl(HCH$_2$)(CH$_3$)

4b

NMR δ 7.9 (m), 7.3 (m), 7.0 (m, C_6H_5), 5.17 (dd, J = 4.7, 11.1 Hz, MnCHOAlNP), 1.22 (s), 1.01 (s, $C(CH_3)_3$), 0.18 (s), 0.04 (s), –0.01 (s), –1.75 (s, $Al(CH_3)_2$); ^{31}P NMR δ 41.6 (d), 72.1 (d, J_{PP} = 24 Hz); IR (Nujol) ν_{CO} 2000 (s), 1910 (vs) cm^{-1}.

4a. $HMn(CO)_5$ (0.09 g, 0.44 mmol) was added to a solution of **1a** (0.3 g, 0.88 mmol) in 0.5 mL of C_6D_6 and the progress of the reaction followed by ^1H NMR spectroscopy. After 20 min all $HMn(CO)_5$ had been consumed and **2a** was the major species present; after 20 h the latter had completely disappeared and had been replaced by **4a**: ^1H NMR δ 7.9–7.2 (m, C_6H_5), 5.5 (dd, J =

(CO)$_3$Mn(CHOAlEt$_2$N-*t*-BuPPh$_2$)(PPh$_2$N-*t*-BuAl(HCHMe)Et)

4a

5.5, 10.0 Hz, MnCHOAlNP), 1.2 (s), 1.0 (s, $C(CH_3)_3$), –0.6 (m, AlCH_2CH$_3$) (the remaining AlEt signals overlapped and could not be fully resolved); ^{31}P NMR δ 41.1 (d), 70.9 (d, J_{PP} = 22 Hz); IR (Nujol) ν_{CO} 1992 (s), 1968 (w), 1908 (s) cm^{-1}. The same product was obtained on the addition of 1 equiv of **1a** to a solution of **2a**.

4c. A solution of $HMn(CO)_5$ (0.06 g, 0.29 mmol) and **1a** (0.1 g, 0.29 mmol) in C_6D_6 was allowed to react for 4 h and then treated with **1b** (0.09 g, 0.29 mmol). After 15 min the NMR showed nearly complete conversion to **4c**: ^1H NMR δ 7.9–7.2 (m, C_6H_5), 5.2 (dd,

(CO)$_3$Mn(CHOAlEt$_2$N-*t*-BuPPh$_2$)(PPh$_2$N-*t*-BuAl(HCH$_2$)(CH$_3$))

4c

J = 5.3, 11.2 Hz, MnCHOAlNP), 1.2 (s), 1.0 (s, $C(CH_3)_3$), –0.07 (s), –1.9 (s, $AlCH_3$) (AlEt signals were partly obscured by $C(CH_3)_3$ peaks); IR (cyclohexane) ν_{CO} 1997 (s), 1965 (w), 1910 (s) cm^{-1}.

(CO)$_3$(P(OPh)$_3$)Mn(CHOAlEt$_2$N-*t*-BuPPh$_2$) (5). A solution of **2a**, prepared as in the the preceding reaction, was treated with 1 equiv of $P(OPh)_3$. Over 30 min the color faded to light orange, accompanied by gas evolution, and the NMR showed complete conversion of **2a**: ^1H NMR δ 7.9–7.2 (m, C_6H_5), 4.7 (dd, J = 11, 27.5 Hz, MnCHOAlNP), 1.2 (s, $C(CH_3)_3$), 0.5 (m, AlCH_2CH$_3$) (the AlCH$_2$$CH_3$ signal was obscured by the $C(CH_3)_3$ resonance); ^{31}P NMR 36.2 (d), 128.3 (d, J_{PP} = 12 Hz); IR (cyclohexane) ν_{CO} 1990 (s), 1960 (s), 1895 (s) cm^{-1}. The same product was generated by adding **1a** to $HMn(CO)_4(P(OPh)_3)$.

CpMo(CO)$_3$AlMe$_2$N-*t*-BuPPh$_2$H (15). A solution of $CpMo(CO)_3H$ (0.32 mmol) and **1b** (0.32 mmol) in C_6D_6 (0.5 mL) was allowed to react while monitoring the ^1H NMR spectrum. After several hours, the resonances due to starting materials had been completely replaced by those assigned to product. (The latter gradually broadened and decayed on further standing.) Several milliliters of hexane were added, and the mixture was cooled overnight at –40 °C; a brownish, oily material separated out and was dried in vacuo. Attempts at crystallization were unsuccessful: ^1H NMR δ 7.8 (d, J_{PH} = 500 Hz, $HPPh_2$), 7.6 (m), 7.2 (m, C_6H_5), 5.27 (s, Cp), 1.2 (s, $C(CH_3)_3$), –0.4 (s, $AlCH_3$); ^{31}P NMR δ 13.6 (d (with no ^1H decoupling, this signal appeared as a doublet ($J \approx$ 500 Hz) of multiplets; with the decoupler on, it collapsed to a doublet of about 15 Hz splitting; not enough power was available to completely remove the large P–H coupling); IR (C_6H_6) ν_{CO} 1930 (s), 1845 (s), 1570 (m, br) cm^{-1}.

The reaction of $CpW(CO)_3H$ with **1b** proceeded in much the same manner, to give a product with virtually identical spectral parameters. In contrast, the reactions of $CpM(CO)_3H$ (M = Cr, Mo, W) with **1a** were complete within 15 min; although similar NMR peaks developed, the products appeared to form much less cleanly; and decomposition as evidenced by NMR peak degradation was significant after only 1 h.

Structure Determination for 4b. Small prismatic crystals of **4b** were obtained by dissolving a sample in the minimum amount of benzene, adding hexane until clouding was observed, and storing at –40 °C for several weeks. The structure was determined by Molecular Structures Corp., College Station, TX. Experimental details and crystal data are summarized in Table VI. Atom positions and key bond parameters are given in Tables II–IV, other data are available as supplementary material.

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Registry No. **1a**, 5573-37-5; **1b**, 83585-38-0; **2a**, 83632-48-8; **2a**-d_1, 86480-65-1; **3**, 83585-42-6; **4a**, 83632-49-9; **4b**, 83632-50-2; **4c**, 86480-66-2; **5**, 83649-33-6; **1s**, 86497-03-2; $HMn(CO)_5$, 16972-33-1; $CpMo(CO)_3H$, 12176-06-6.

Supplementary Material Available: Listings of calculated hydrogen positions (Table VII), thermal parameters (Table VIII), torsional angles (Table IX), intermolecular contacts (Table X), least-squares planes (Table XI), and observed and calculated structure factors (Table XII) for complex **4b** (35 pages). Ordering information is given on any current masthead page.

Formation, Decay, and Spectral Characterization of Some Alkyl- and Aryl-Substituted Carbon-, Silicon-, Germanium-, and Tin-Centered Radicals[1]

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tert-Butoxyl abstracts hydrogen from M–H bonds (M = Si, Ge, Sn) with rate constants (300 K) of (0.6–2) × 10^7 (M = Si), ~9 × 10^7 (M = Ge), and (2–4) × 10^8 M^{-1} s^{-1} (M = Sn), respectively. The radicals (alkyl)$_3$M· show a strong absorption band at λ < 300 nm and a weaker band/shoulder at longer λ that shifts from 320 (M = C) to 390 nm (M = Sn). The spectra of Ph_3M show little sensitivity to the heteroatom. Arylsilyl radicals add readily to their precursors; for example, Ph_3Si· adds to Ph_3SiH with k_4 = (2.1 × 0.4) × 10^5 M^{-1} s^{-1} at 300 K.

We have recently reported kinetic studies by laser flash photolysis on the reactions of triethylsilyl radicals with a wide variety of substrates,[3–6] on the reactions of *tert*-butoxyl radicals and triplet ketones with silanes,[7] and on