pattern[17] is quite characteristic of a $CH_2{=}CHO$ grouping, suggesting rearrangement of an acetyl group, via a hydrogen shift, to an ethenolate ligand. Such a rearrangement has precedence for an *early* transition-metal complex,[18] where the strong metal–oxygen bond must provide the driving force; here it is presumably the Al–O bond that favors this rearrangement.

Scheme II shows a proposed mechanism for the overall course of the reaction of **1a** with **2**. We suggest (i) coordination of the Lewis acid center to O induces rapid insertion,[6] (ii) the vacant site thus generated is rapidly trapped by O,[19] (iii) the carbon of the resulting intermediate has substantial carbene-like character and is susceptible to nucleophilic attack (as are carbene complexes of type $L_nM{=}C(OR)R'$), yielding **3**, (iv) although this compound is kinetically favored, it is thermodynamically unstable with respect to **4** and **5**. It is clear that ligands which provide a site for O coordination[20] can lead to pronounced facilitation of CO insertion, as well as to novel types of product structure.

**Acknowledgment.** We are indebted to C. Schramm and V. Parziale for NMR studies and to D. Grimmett and E. Shearin for assistance with ligand synthesis.

**Registry No. 1a**, 5573-37-5; **1b**, 83585-38-0; **1c**, 83585-39-1; **1d**, 5573-84-2; **1e**, 83585-40-4; **1f**, 83585-41-5; **2**, 12080-06-7; **3**, 83585-42-6; **4**, 83585-43-7; **5**, 83585-44-8; **7**, 83585-45-9; **8**, 83585-46-0; $Cp(CO)_2\overline{Mo(O(CH{=}CH_2)Al(Et)_2N(Pr\text{-}i)P}(Ph)_2$, 83585-47-1; $CpMo(CO)_3Me$, 12082-25-6.

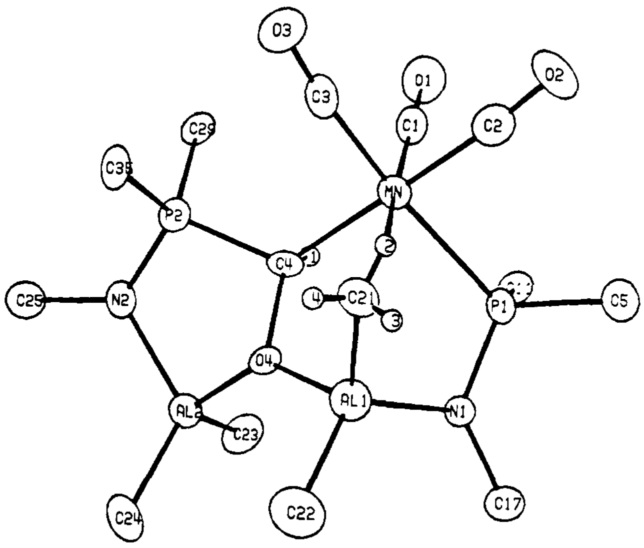


**Figure 1.** Perspective view of the structure of **5b**.

---

[17] Signals at δ 6.4 (dd, $J$ = 6.2, 14.3 Hz), 4.4 (dd, $J$ = 1.6, 14.3 Hz), and 4.1 (dd, $J$ = 1.6, 6.2 Hz) in addition to Ph, Cp, *i*-Pr, and Et signals.

[18] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724. Note though that labeling studies reveal that the rearrangement in this Zr complex does *not* proceed by a 1,2-H shift.

[19] Recent evidence suggests that a $\eta^2$-acyl intermediate is involved in insertion reactions of CpFe(CO)LR (Flood, T. C. *Top. Stereochem.* **1981**, *12*, 89–90. Brunner, H.; Vogt, H. *Angew. Chem., Int. Ed. Engl.*, **1981**, *20*, 405–406) as well as in thermal (not photochemical) decarbonylation of CpFe(CO)L(COR) (Brunner, H.; Vogt, H. *Chem. Ber.* **1981**, *114*, 2186–2207.

[20] A related example, wherein an appended crown ether was used to coordinate $Li^+$ and thus stabilize an acyl (formed by addition of PhLi to a metal carbonyl rather than by insertion), was reported while this work was in progress: Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941–5943.

---

# Amphoteric Ligands. 2. Formation and Structure of a Novel C–H Bond Containing Product from $HMn(CO)_5$ and an Amphoteric Ligand

David L. Grimmett, Jay A. Labinger,* John N. Bonfiglio,
Steven T. Masuo, Eileen Shearin, and Joel S. Miller*

*Occidental Research Corporation*
*Irvine, California 92713*

*Received July 6, 1982*

Homogeneous reduction of CO with hydrogen is generally assumed to go through a hydride migration step, yielding a formyl intermediate; however, there are very few unequivocal examples in the literature.[1] Addition of Lewis acids such as $BX_3$ and $AlX_3$ has been shown to facilitate *alkyl* migration, but this approach has not been successful for formyl formation.[2,3] Transition-metal complexes containing amphoteric ligands have the ability to simultaneously bond both C and O and thereby favor migration, as we have demonstrated for alkylmetal carbonyls.[4] Herein we report the reaction of $HMn(CO)_5$ with $Ph_2PN\text{-}t\text{-}BuAlR_2$ (**1a**, R = Et; **1b**, R = Me) to form products containing C–H bonds. However, these products are *not* formyl complexes, and they do not appear to form via direct hydride migration.

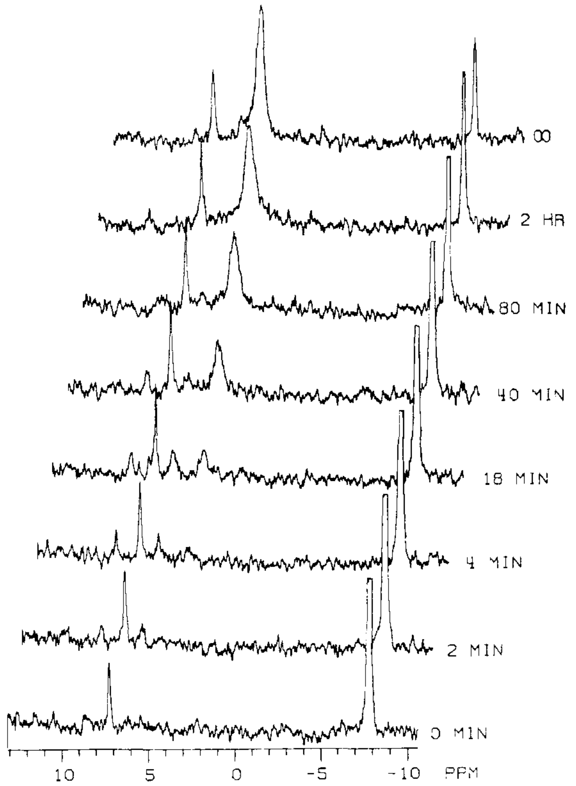


**Figure 2.** $^2H$ NMR vs. time of the reaction of $DMn(CO)_5$ with **1a**, 0 °C in toluene ($C_6D_6$ added as reference).

A benzene solution of **1a** and $HMn(CO)_5$ darkens to orange over a period of ca. 30 min; $^1H$ NMR shows, in addition to shifts

---

[1] A number of systems form C–H bonds from hydridometal carbonyls but many may well involve alternate mechanisms (e.g., intermolecular nucleophilic attack). Solid evidence for a true, intramolecular migration has been obtained only for a thorium system: Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959–6962.

[2] Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100.

[3] $AlX_3$ and $BX_3$ *can* facilitate transition-metal-mediated CO hydrogenation: Wang, H. K.; Choi, H. W.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 2661–2663. Choi, H. W.; Muetterties, E. L. *Ibid.* **1981**, *20*, 2664–2667. These are not catalytic reactions in the widest sense, as the Lewis acid is consumed by the water produced on reduction of CO.

[4] Labinger, J. A.; Miller, J. S., preceding paper in this issue.

0002-7863/82/1504-6858$01.25/0

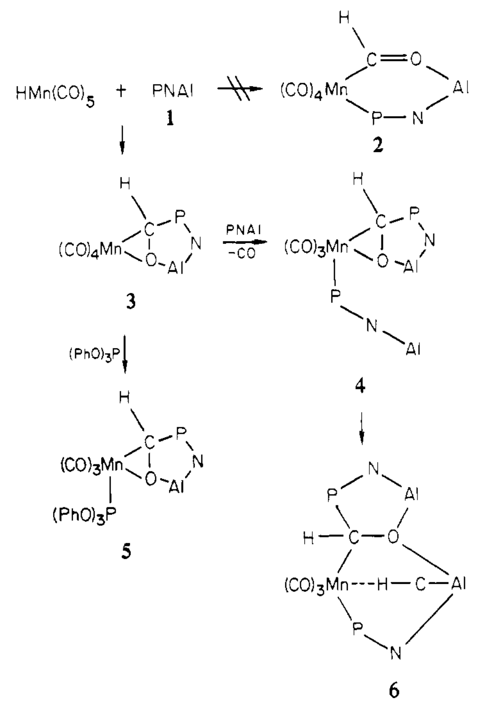
in ligand peaks, disappearance of the Mn–H peak at δ –7.8 and growth of a new signal at δ 4.46 (d, $J$ = 33.2 Hz). A $^2$H NMR study on the reaction of **1a** with $DMn(CO)_5$ confirms that this signal derives from the hydrogen originally on Mn. NMR data for the product[5] are not compatible with formyl structure **2a** but indicate that the product, **3a**, is derived from P–C bond formation, as observed in the reaction of **1a** with $(\eta\text{-}C_5H_5)Fe(CO)_2Me$.[4]

The analogous reaction of **1b** proceeds more slowly, presumably because of the ligand's greater tendency to aggregate. Initially a very similar NMR signal appears (δ 4.4, d, $J$ = 33 Hz), but this begins to disappear long before the reactants have been consumed and is replaced by a new double doublet signal. A yellow product was crystallized from cold hexane; its NMR[6] is suggestive of a structure related to **3** but containing 2 mol of **1b**. An X-ray structure determination[7] revealed the structure to be **5b** (Figure 1). The product is a roughly octahedral complex of class $RMn(CO)_3LL'$, where the alkyl group R is a novel "aluminoxyphosphinomethyl" derived from reduction of a CO ligand. The geometry about C(4) is approximately tetrahedral, with C(4)–Mn = 2.175 (12), C(4)–P(2) = 1.810 (10), C(4)–O(4) = 1.462 (12), and C(4)–H(1) = 0.96 (10) Å. Of the remaining two non-CO ligands, one is a simple phosphine. The other substituent, unexpectedly, is a C–H bond from one of the Al-bound methyl groups. The Mn–H(2) distance in **5b** is 1.91 (12) Å, quite close to that found in other complexes exhibiting this type of structural feature.[8] Other parameters of the three-center Mn–H–C interaction in **5b** are as follows: Mn–C(21), 2.45 (2) Å; C(21)–H(2), 0.80 (10) Å; Mn–H(2)–C(21), 124 (12)°.

The structure of **5b** contains several other features of interest. Most striking are the multiple rings. The complex includes a five-membered ring fused to a bicyclo[2.2.2]octane-like framework with no two members of any ring being the same—a truly *hetero*cyclic structure! Also, the alkyl group R is formally a derivative of a phosphonium salt. Although this would give a zwitterionic structure, which seems inconsistent with the good solubility in nonpolar solvents, there are several indications of substantial delocalization via $\pi$ bonding. This includes the short Al–N (Al(1)–N(1) = 1.846 (8) Å, Al(2)–N(2) = 1.903 (9) Å) and P–N (P(1)–N(1) = 1.641 (8) Å, P(2)–N(2) = 1.606 (8) Å) distances and the planarity of both N atoms. A complete account of this structure will be presented later.

We envision the transformation of **3** to **5** proceeding as shown in Scheme I, wherein a second molecule of **1b** displaces a CO (possibly the side-bonded group in **3** functions as a cis-labilizing ligand) to give **4**. (Isolated **3a** reacts readily with a simple phosphorus ligand, $P(OPh)_3$, to give **6a**.[9]) The second Al center interacts with and detaches the O from Mn, leaving a vacant site which is occupied by the C–H bond. While **5a** is not formed so readily as **5b**, it can be generated by adding a second equivalent of **1a** to **3a**.[10] It is not clear why the reaction of **1b** with $HMn(CO)_5$ continues all the way to **5b** even with only 1 equiv of **1b**.

Scheme I



A more detailed look at the $^2$H spectrum of the reaction between **1a** and $DMn(CO)_5$ shows that an intermediate is initially formed before **3a** is observed (Figure 2).[11] The doublet signal (δ 7.7, $J$ = 75 Hz; corresponding $J_{PH}$ would be 490 Hz) is only compatible with a species containing a direct P–D bond. Although this intermediate has not been isolated, compounds obtained from reactions of **1** with $CpM(CO)_3H$ (M = Cr, Mo, W, which are of comparable acidity to $HMn(CO)_5$[12]) exhibit the same feature and other spectral properties that indicate they are the ion pairs $(CpM(CO)_3)^-(AlR_2N\text{-}t\text{-}BuPPh_2H)^+$.[13] Thus, we have demonstrated that our amphoteric ligands effect reduction of CO by metal-bound hydrogen under mild conditions. The C–H bond is not formed by direct migration of H to CO but rather by transfer of $H^+$ to the phosphorus of the amphoteric ligand and thence to carbon. It appears that a hydride migration step is not operating even in this system designed to optimize it.

**Acknowledgment.** We thank C. Schramm and V. Parziale for NMR studies.

---

(5) $^1$H NMR δ 7.9, 7.2 (m, $C_6H_5$), 4.4 (d, $J$ = 33 Hz), MnC*H*OAlNP); 1.52 (t), 1.47 (t, $AlCH_2CH_3$), 1.14 (s, *t*-Bu), 0.4 (m, $AlCH_2CH_3$); $^{13}$C NMR 65.3 ($J_{PC}$ = 76.6 Hz, $^1J_{CH}$ = 168 Hz); $^{31}$P NMR 36.8. In structure **2**, the formyl group would be expected to give $^1$H and $^{13}$C shifts of >10 and >300 ppm, respectively.

(6) $^1$H NMR δ 7.9, 7.3, 7.0 (m, $C_6H_5$), 5.17 (dd, $J$ = 4.7 Hz, 11.1 Hz, MnC*H*OAlNP), 1.22, 1.01 (s, $C(CH_3)_3$), 0.18, 0.04, –0.01, –1.75 (s, $AlCH_3$); $^{31}$P NMR δ 41.6, 72.1 (d, $J_{PP}$ = 24 Hz).

(7) The structure was determined by Molecular Structure Corp., College Station, TX. Crystal data: orthorhombic, space group *Pbca*; $a$ = 18.063 (7) Å, $b$ = 18.446 (8) Å, $c$ = 25.003 (7) Å; $Z$ = 8. Data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods. Hydrogen atoms H(1)–H(4) were located and refined, while the remaining H atoms were assigned fixed positions (C–H = 0.95 Å); final $R$ = 0.053, $R_w$ = 0.057.

(8) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117–2126 and references cited therein. The Mn–H distance determined for (6-*endo*-methylcyclohexenyl)manganese tricarbonyl was 1.86 (2) Å; while the Mn–C distance (2.301 (2) Å) and Mn–H–C angle (100 (1)°) suggest a stronger Mn–C interaction than in **5b**; the fact that the coordinated C–H is immediately adjacent to the allylic ligand undoubtedly results in considerably more geometric constraint than is likely to be present in **5b**.

(9) $^1$H NMR δ 4.7 (dd, $J$ = 11, 27.5 Hz, MnCHOAlNP), 1.3 (s, $C(CH_3)_3$), in addition to Ph and AlEt multiplets; $^{31}$P NMR δ 36.2, 128.3 (d, $J_{PP}$ = 12 Hz). **6a** is also formed on adding **1a** to $HMn(CO)_4(P(OPh)_3)$.

(10) $^1$H NMR δ 5.5 (dd, $J$ = 5.5, 10.0 Hz) in addition to Ph, *t*-Bu (two), and AlEt signals; one $AlCH_2CH_3$ triplet appears at high field, δ –0.6, indicating the same interaction as in **5b**; $^{31}$P NMR δ 41.1, 70.9 (d, $J_{PP}$ = 22 Hz). A *mixed* analogue of **5b** can also be prepared by adding an equivalent of **1b** to **3a**; it exhibits a singlet (not a triplet) at high field (δ –1.9) as expected, since the structure of **5b** implies the second ligand to enter is the one that provides the C–H ligand.

(11) NMR peak intensities fit well to a model two-step sequence: $DMn(CO)_5$ + **1a** $\xrightarrow{k_1}$ intermediate; intermediate $\xrightarrow{k_2}$ **3a** with $k_1 \approx 0.1\ M^{-1}\ min^{-1}$ and $k_2 \approx 0.07\ min^{-1}$ at 0 °C.

(12) Miholova, D.; Vleck, A. A. *Proc. Conf. Coord. Chem., 3rd* **1971**, 221–226. Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263.

(13) For example, for $CpMo(CO)_3H$ plus **1b**: IR 1930 (s), 1845 (s), 1570 (s, br) cm$^{-1}$ (cf. a very similar pattern for $(CpW(CO)_3)_3^-,(Al(THF)_3)_3^{3+}$: Petersen, R. B.; Stezowski, J. J.; Wan, C.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3532–3533.); $^1$H NMR δ 7.75 (d, $J$ = 498 Hz, PH$^+$), 7.7, 7.2 (m, Ph), 5.2 (s, Cp), 1.2 (s, *t*-Bu), –0.4 (s, $AlMe_2$). More complete details on these proton-transfer reactions will be reported at a later time.