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.

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[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 η^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

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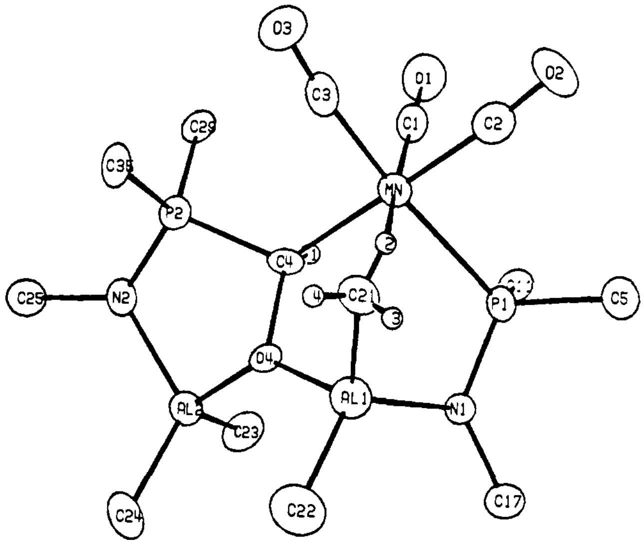

Figure 1. Perspective view of the structure of **5b**.

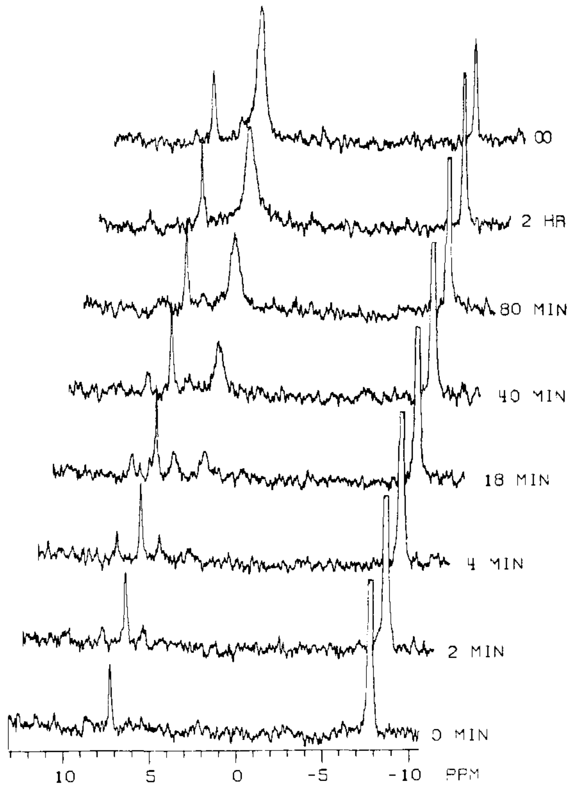

Figure 2. ^2H NMR vs. time of the reaction of $DMn(CO)_5$ with **1a**, 0 °C in toluene (C_6D_6 added as reference).

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.

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

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[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.

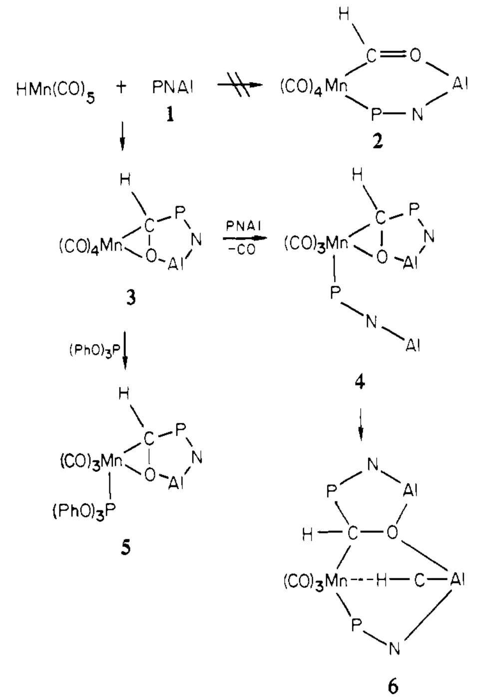
in ligand peaks, disappearance of the Mn–H peak at δ −7.8 and growth of a new signal at δ 4.46 (d, J = 33.2 Hz). A ^{2}H NMR study on the reaction of **1a** with $DMn(CO)_5$ confirms that this signal derives from the hydrogen originally on Mn. NMR data for the product[5] are not compatible with formyl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

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(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.