is shortened as the olefin concentration is increased. Analysis of these data provides the bimolecular rate constants (k_q) for these reactions. Figure 1 shows the temperature dependence of these rate constants for a representative group of olefins plotted according to the Eyring formalism. The activation parameters obtained from this treatment are presented in Table I.

It is immediately apparent from inspection of Table I that the variation of k_q for all olefins examined appears primarily to be a response to change in $\Delta S^{\ddagger}$ rather than $\Delta H^{\ddagger}$. A similar result has been reported previously for the reaction of $^1O_2$ in toluene with furans and indoles.[13] In the present case nonzero $\Delta H^{\ddagger}$ are obtained, but in most instances they do not differ significantly from zero or from each other. The apparent lack of correlation between change in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for different olefins is reasonably a manifestation of multiple interaction mechanisms.[14]

Interpretation of the effect of olefin structure on $\Delta S^{\ddagger}$ requires normalization for the destruction of external rotational symmetry, when it exists, in the starting olefin.[15] For example, tetramethylethylene has three 2-fold rotation axes, which are not likely to be preserved at the transition state. In comparison, trimethylethylene does not lose any such symmetry when it reacts. Similarly $\Delta S^{\ddagger}$ must be adjusted statistically for the number of apparently equivalent reactive sites;[16] four for tetramethylethylene, two for cis-2-butene, etc. These normalized activation entropies ($\Delta S^{\ddagger}_{norm}$) are listed in Table I.

The results presented in Table I reveal considerable information about the mechanism of the ene reaction. The most reactive olefin has k_q ca. 3 orders of magnitude below the diffusion limit. Thus there are many nonproductive collisions for every one that leads to consumption of $^1O_2$. These collisions may lead to a weakly bound exciplex or may simply be nonbinding encounters. Comparison of k_q with previously reported values for the consumption of oxygen by these olefins in methanol[17] (k_r) and the observation that quantum yields for reaction approach unity at high olefin concentration indicate that k_q is primarily a measure of the reaction rate and not of physical quenching of $^1O_2$.

The $\Delta S^{\ddagger}_{norm}$ values appear to fall clearly into two groups, the cis olefins and the non-cis olefins, indicating a change in transition-state structure between these classes. The magnitude of $\Delta S^{\ddagger}$ does not depend on the solvent, and, therefore, probably reveals intrinsic properties of the transition state. Gas-phase dimerization of cyclopentadiene, a prototypical bimolecular reaction with an ordered transition state, has $\Delta S^{\ddagger}$ = −34 eu.[18] Comparison with our $\Delta S^{\ddagger}_{norm}$ shows that the transition state for the cis olefins is somewhat less constrained than that of the prototype and that for their non-cis counterparts is more constrained.[19]

These findings support the path for the ene reaction described by Stephenson[8a] and by Bartlett.[7] Thus, the initial reversibly formed encounter complex, or exciplex, of $^1O_2$ and olefin is not in the required reaction geometry. Movement to this geometry is the irreversible entropy-controlled process that brings the reactants to the transition state. The systematic grouping of $\Delta S^{\ddagger}_{norm}$ indicates that this transition state already reflects the preference for reaction on the more crowded side and the interaction of the allylic hydrogen with an oxygen atom that is required of the postulated reaction "intermediate". Structure 4 for non-cis olefins and structure 5 for cis olefins with the oxygen loosely directed toward the allylic hydrogens[19] are representations of the

transition state consistent with all available data.

Consistent with the theoretical analysis of Kearns,[21] Paquette and co-workers[11] noted that the relative reactivity of various sites on polyenes toward $^1O_2$ can be predicted by consideration of "isolated" ionization potentials. It is apparent from our data that the ionization potential is not the sole determinant of reaction rate. For example, cis- and trans-2-butene have identical ionization potentials, but they differ considerably in reactivity. However, within a class, the cis olefins for example, there is some correlation of ionization potential with reactivity, and this is reflected in the measured $\Delta H^{\ddagger}$. Thus, it appears that "donor–acceptor" interactions play some role in the transition state for the ene reaction. The simple observation that non-cis olefins react slower than cis olefins permits accurate prediction of the site of reactivity of alkenes[20] and polyenes. Consideration of the ionization potentials may permit further discrimination among olefins within a class.

(20) Adam, W.; Carballeira, N.; Cheng, C.-C.; Sakanishi, K.; Gleiter, R. *J. Org. Chem.* **1979**, *44*, 851.
(21) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554.

Amphoteric Ligands. 1. Facile Acyl Formation and Crystal Structure of a Novel Complex Containing an η^2(C,O)-Acylphosphonium Ligand[†]

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Reduction of carbon monoxide with hydrogen is difficult to achieve. Simultaneous activation at both C and O should substantially weaken the CO bond and facilitate reaction with metal-bound hydrogen.[1] A complex containing an amphoteric ligand—one that has both metal- and oxygen-binding centers—appears particularly attractive, as the chelate effect will contribute to other factors[2] tending to stabilize reduced forms of CO in such a molecule. In this and the following communication[3] we report that such ligands can indeed greatly facilitate formation of CO insertion products, although neither the structure of the product nor the mechanism of its formation need always correspond to straightforward expectations.

In choosing a suitable system, a key consideration will be minimizing self-aggregation of the amphoteric ligand. Ph_2PN-t-$BuAlEt_2$ is reported to be monomeric in solution (according to cryoscopy in benzene[4]) and should be a suitable choice. We have prepared a series of aluminoaminophosphines, $R_2PNR'AlR''_2$, **1**,

(13) Gorman, A. A.; Lovering, G.; Rogers, M. A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3050.
(14) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 342.
(15) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.
(16) Reference 14, p 133. The number of equivalent sites is dependent on the actual mechanism of the reaction. We have chosen the most general case with each methyl group as apparently equivalent. However, the mechanism we suggest below indicates that two cis groups can be counted as one site. The conclusions are independent of the counting scheme.
(17) Reference 3, pp 291–295.
(18) Wasserman, A. *Montatsh. Chem.* **1982**, *83*, 542.
(19) Reference 14, pp 68–69.

†This and the following paper are dedicated to the memory of Martin B. Dines, friend and colleague, 1943–1982.
(1) See, for example: Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447–474. Muetterties, E. L.; Stein, J. *Ibid.*, **1979**, *79*, 479–490. Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 117–130.
(2) Shriver, D. F. *ACS Symp. Ser.* **1981**, *152*, 1–18.
(3) Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S., following paper in this issue.
(4) Clemens, D. F.; Sisler, H. H.; Brey, W. S., Jr. *Inorg. Chem.* **1966**, *5*, 527–533.

Figure 1. Perspective view of complex **3**.

Scheme I

$$R_2PCl + R'NH_2 \rightarrow R_2PNHR' \xrightarrow[\substack{X = Cl, I}]{\substack{BuLi \quad R''_2AlX}} R_2PNR'AlR''_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{1}$$
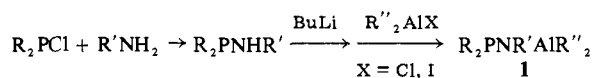
by the general route of Scheme I.[5]

For initial studies we selected $CpFe(CO)_2Me$, **2** ($Cp = \eta\text{-}C_5H_5$), which is inert to ordinary phosphine ligands under ambient conditions but which undergoes facile acetyl formation in the presence of strong Lewis acids such as $AlBr_3$.[6] A benzene solution of equimolar **1a** and **2** darkens within minutes. After prolonged standing and workup a substance is obtained that, though not pure, exhibits major spectral parameters compatible with the expected product **4**[7] and quite similar to those of a model compound, $CpFe(CO)(Ph_2PNH\text{-}t\text{-}Bu)(C(OAlEt_3)Me)$.[8] However, **4** is *not* an initial product, as readily seen by monitoring the ^2H NMR

Scheme II

spectrum of a mixture of **1a** and **2**-d_3[13] over time. Rapid and virtually complete formation of an intermediate, **3**, with a CD_3 signal at δ 1.4 is observed. Over a day or so **3** reacts further to give **4** along with regeneration of some **2** and another product, **5**, giving three approximately equal intensity ^2H signals at δ 4.0, 4.5, and 6.0.

Compound **3** was isolated by cooling a reaction mixture in toluene–hexane after several minutes. Its spectral properties[14] indicate insertion has occurred; however, they do not seem consistent with an acyl structure. An X-ray crystal structure determination[15] established that a P–C rather than a P–Fe bond has formed, giving a novel heterocycle which bonds Fe in η^2 fashion through C and O (Figure 1). η^2-Acyl ligands are well-known, but in **3** the ligand is not an acyl; perhaps it is best described as an acylphosphonium ion, where an oxygen nonbonding electron pair additionally interacts with Al.[16]

Compounds **4** and **5** have not been separated (these compounds, especially the Al–Et links, do not survive any chromatographic methods tried so far), but the identity of the latter is indicated by the ^1H NMR spectrum of a nondeuterated sample: the signals at δ 6.0 and 4.5 appear as double doublets, with splittings 14,6 Hz and 14,2 Hz, respectively. (The signal at δ 4.0 is obscured by Cp resonances.) Helpfully, the reaction of $CpMo(CO)_3Me$ with **1d** gives as virtually sole product an analogue of **5**; the NMR

(5) **1a**, R = Ph, R′ = *t*-Bu, R″ = Et; **1b**, R = Ph, R′ = *t*-Bu, R″ = Me; **1c**, R = Ph, R′ = *t*-Bu, R″ = Ph; **1d**, R = Ph, R′ = *i*-Pr, R″ = Et; **1e**, R = Ph, R′ = Ph, R″ = Et; **1f**, R = Me, R′ = *t*-Bu, R″ = Et. **1a** and **1d** had been previously prepared by direct reaction of R_2PNHR' with AlR_3'',[4] but in our hands the route of Scheme I is more general and gives cleaner products.

(6) 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. Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272–1273. Note that AlR_3 does *not* similarly effect insertion: while addition of $AlMe_3$ to **2** causes a color change, the NMR shows only broadened reactant signals.

(7) ^1H NMR (C_6D_6) δ 7.7 (m), 7.2 (m, C_6H_5), 3.8 (d, J = 0.8 Hz, C_5H_5), 2.7 (s, CH_3CO), 1.73 (t, J = 8 Hz), 1.65 (t, J = 8 Hz, $AlCH_2CH_3$), 1.2 (s, $C(CH_3)_3$), 0.7 (m, $AlCH_2CH_3$); ^{31}P NMR δ 84.1; ^{13}C NMR δ 330.8 (d, J = 27.5 Hz, FeC(OAl)Me); IR (CH_2Cl_2) 1940 cm^{-1} (terminal CO). The region where the acyl CO stretch is expected is partially obscured by ligand peaks, but a shoulder at 1460 cm^{-1} shifts to 1570 cm^{-1} on treatment with THF, consistent with conversion of Al-bound acyl **4** to ordinary acyl **6**. The chelate structure of **4** is also supported by (a) the nonequivalence of the two Et groups, (b) the upfield ^{31}P shift relative to that observed for **6** (δ 100.3) or other models.[8] This upfield shift is typical of a phosphorus ligand that is part of a six-member chelate ring.[9]

(8) $CpFe(CO)(Ph_2PNH\text{-}t\text{-}Bu)(C(O)Me)$ (**7**) was prepared and purified as reported for closely related compounds:[10] ^1H NMR δ 7.8 (m), 7.25 (m, C_6H_5), 5.0 (d, J = 9.5 Hz, NH), 4.1 (d, J = 1.2 Hz, C_5H_5), 2.85 (d, J = 0.6 Hz, CH_3CO), 1.0 (s, $C(CH_3)_3$); ^{31}P NMR 99.8; δ ^{13}C NMR δ 277.8 (d, J = 26.7 Hz, FeC(O)Me). Addition of 1 equiv of $AlEt_3$ (toluene solution) to **7** gives a darker but still clear solution of adduct **8** (similar adducts have been reported for the parent compound $CpFe(CO)_2(C(O)Me)$[11]): ^1H NMR δ 7.7 (m), C_6H_5 (remainder of signal for phenyl protons obscured by toluene peak); 4.0 (d, J = 1 Hz, C_5H_5), 3.1 (d, J = 16 Hz, NH), 2.45 (s, CH_3CO), 1.65 (t, J = 8 Hz, $AlCH_2CH_3$), 0.95 (s, $C(CH_3)_3$), 0.45 (q, J = 8 Hz, $AlCH_2CH_3$); ^{31}P NMR δ 96.5; ^{13}C NMR δ 323.8 (d, J = 29.0 Hz, FeC(OAl)Me). Note in particular the large downfield shift of the acyl ^{13}C signal for **8** relative to **7**; more modest shifts in less tightly bonded acyl–Lewis acid adducts have been observed previously.[12]
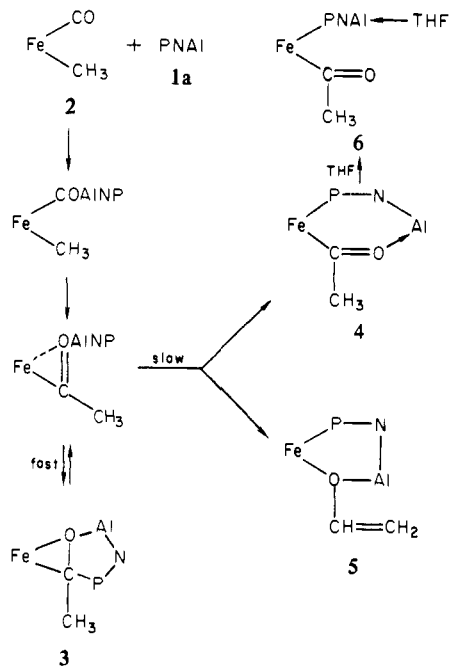
(9) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

(10) Brunner, H.; Vogt, H. *J. Organomet. Chem.* **1980**, *191*, 181–192.

(11) Stimson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980**, *19*, 1141–1145.

(12) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772.

(13) Prepared in the usual manner (King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, pp 151–152) with CD_3I.

(14) ^1H NMR δ 8.8 (m), 7.2 (m, C_6H_5), 4.3 (s, C_5H_5), 1.84 (t, J = 8 Hz), 1.65 (t, J = 8 Hz, $AlCH_2CH_3$), 1.50 (d, J = 16 Hz, CH_3CO), 1.3 (s, C-$(CH_3)_3$), 0.6 (m, $AlCH_2CH_3$); ^{31}P NMR δ 33.0; ^{13}C NMR δ 58.4 (d, J = 68.6 Hz, FeC(Me)OAlNP); IR (Nujol) 1887 cm^{-1} (terminal CO).

(15) The structure was determined by Molecular Structure Corp., College Station, TX. Crystal data: triclinic, space group $P\bar{1}$; a = 10.474 (2) Å, b = 15.687 (3) Å, c = 9.707 (1) Å; α = 97.98 (1)°, β = 115.01 (1)°, γ = 71.81 (1)°. Data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods; all atoms including hydrogens were located and refined; final R = 0.049, R_w = 0.068. Selected bond distances (Å) C_1–Fe, 1.983 (3); O_1–Fe, 1.969 (2); C_1–O_1, 1.401 (3); O_1–Al, 1.842 (2); Al–N, 1.936 (2); N–P, 1.619 (2); P–C_1, 1.827 (2). Atoms Al, O_1, C_1, and P are nearly coplanar; the dihedral angle between this plane and that defined by C_1, O_1, and Fe is 114.5°. Bonding of the Cp and terminal CO ligands is normal. Full details of this structure will be reported subsequently.

(16) From this viewpoint, a related structure is that of $[Cp_2M(Ph_2C=C=O)]_2$ in which each ketene is (η^2-C,O)-bonded to one M and (η^1-O)-bonded to the other: Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995–3002 (M = Ti). Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462–464 (M = Zr).

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.

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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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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 BX₃ and AlX₃ has been shown to facilitate *alkyl* migration, but this approach has not been successful for formyl formation.[2,3] Transition-metal

(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.
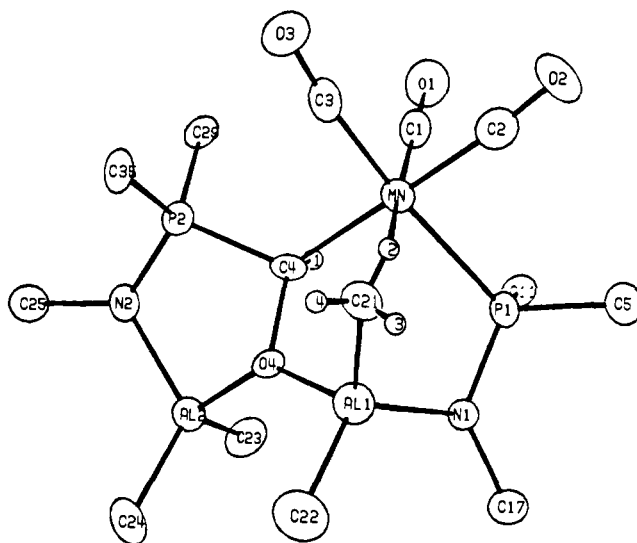

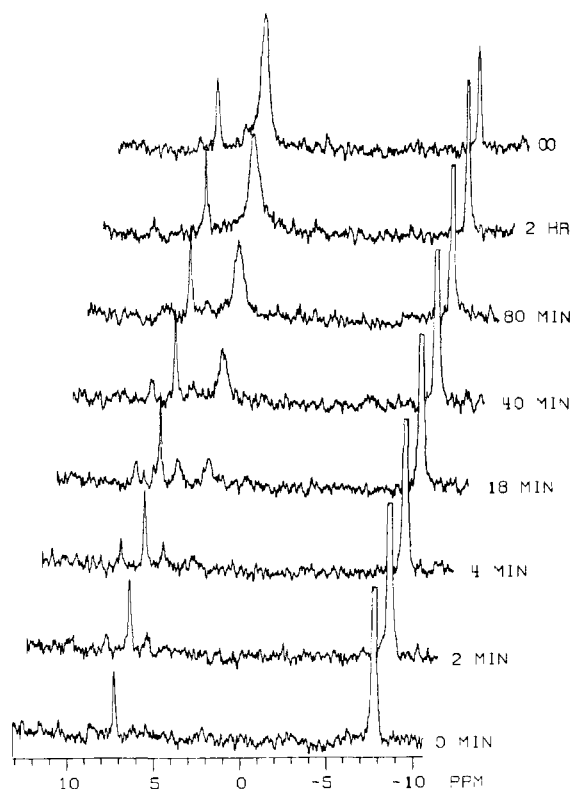**Figure 1.** Perspective view of the structure of **5b**.

Figure 2. ²H NMR vs. time of the reaction of DMn(CO)₅ with **1a**, 0 °C in toluene (C₆D₆ added as reference).

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 Ph₂PN-*t*-BuAlR₂ (**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

(3) AlX₃ and BX₃ *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.