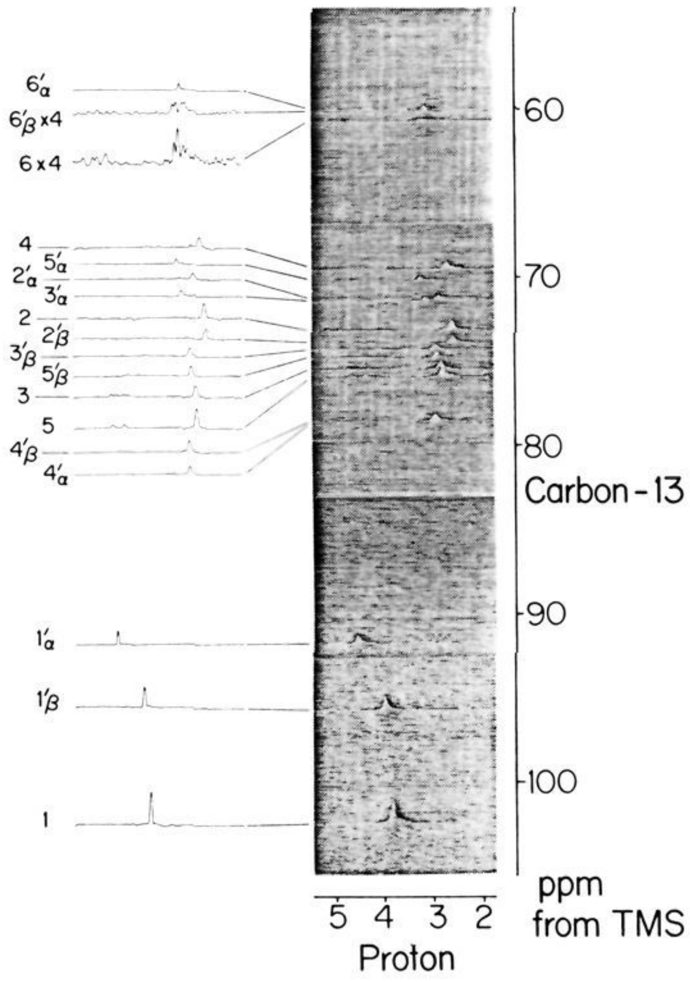

Figure 3. The carbon-13–proton 2D shift correlation spectrum of **1**, again 0.3 M in D_2O, showing carbon-13 chemical shifts in the vertical (f_2) and proton shifts in the horizontal (f_1) frequency axes. Individual zero-filled traces are shown for each of the carbon-13 chemical shifts, allowing the chemical shifts of the directly bound protons to be measured with a precision better than 0.05 ppm, assigned via the carbon shifts of ref 10. The vertical scale was increased fourfold for the 6′β and 6 traces.

2B would still provide a considerable analysis problem even if it were measured at a proton frequency of 1 GHz, well beyond the limits of present NMR technology. It is important to note that the signals in the shift correlation experiment are governed by proton spin population differences and relaxation times (except the unmodulated carbon signals) which enhances the sensitivity of the technique. We emphasize that the total amounts of machine time required are by no means prohibitive, and the experiments can be performed on a "routine" basis.

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References and Notes

(1) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
(2) Freeman, R.; Morris, G. A. *Bull. Magn. Reson.* **1979**, *1*, 5.
(3) Aue, W. P.; Karhan, J.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 4226.
(4) Bodenhausen, G.; Freeman, R.; Morris, G. A.; Turner, D. L. *J. Magn. Reson.* **1978**, *31*, 75.
(5) Hall, L. D.; Sukumar, S.; Sullivan, G. R. *J. Chem. Soc., Chem. Commun.* **1979**, 292.
(6) Freeman, R.; Morris, G. A. *J. Chem. Soc., Chem. Commun.* **1978**, 684.
(7) Hall, L. D.; Morris, G. A.; Sukumar, S. *Carbohydr. Res.*, **1979**, *76*, C7.
(8) Nagayama, K.; Wüthrich, K.; Bachmann, P.; Ernst, R. R. *Naturwissenschaften* **1977**, *64*, 581.
(9) Nagayama, K.; Bachmann, P.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1978**, *31*, 133.
(10) Pfeffer, P. E.; Valentine, K. M.; Parrish, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 1265.
(11) DeBruyn, A.; Anteunis, M.; Verhegge, G. *Bull. Soc. Chim. Belg.* **1974**, *84*, 721.

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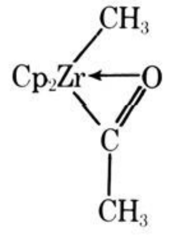
Heterobimetallic Hydrogen Transfer in the Reduction of Metal Acyl Complexes

Sir:

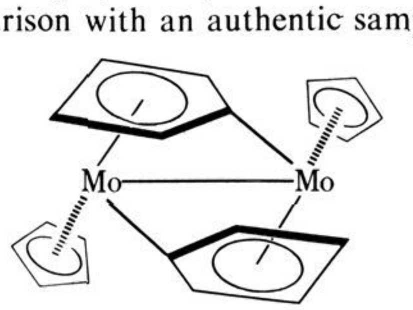
Several groups have demonstrated the ability of certain early transition metal complexes to activate carbon monoxide towards reduction by hydrogen.[1] Stoichiometric reactions produce methane or coordinated methoxide or enediols. A major obstacle to the anticipated catalytic utilization of such reactions is the formation of metal–oxygen bonds which are resistant to reduction by H_2. One solution to this problem might be found among the less oxophilic metals further to the right in any transition series.[2] Labinger[3] has pointed out, however, that the hydride complexes of such metals lack the "hydridic" reactivity which is claimed[1a] to be important in effecting CO reduction. We report here that several such "impotent" hydrides are in fact quite capable of hydrogenating *a particular class of metal acyl complexes, a reaction which* is a probable component in CO hydrogenation reactions.

Acyl complex I forms readily (1 atm, 25 °C) from CO and $Cp_2Zr(CH_3)_2$.[4] It is unreactive toward H_2 (1 atm, overnight); however, I reacts with Cp_2MoH_2 in the time of mixing (C_6D_6, 25 °C) to produce $Cp_2Zr(CH_3)OCH_2CH_3$.[5] This reaction



I

sequence, which represents reduction of CO to the alkoxide oxidation level, is completely selective, there being no evidence for any hydrogen transfer to the $Zr–CH_3$ group.[6] The isotopomer $Cp_2Zr(CH_3)OCD_2CH_3$ is formed when Cp_2MoD_2 is employed; no hydrogen scrambling between the methyl and methylene protons occurs under these mild conditions. The high rate of this reaction is remarkable in view of the instability of the possible product fragment "Cp_2Mo", and the fate of this unit is of some interest. If the reaction is performed under 1 atm of CO, the molybdenum is transformed predominantly to Cp_2MoCO. In CD_3CN, the observed spectra are consistent with the product being $Cp_2Mo(NCCD_3)$.[7] Under molecular nitrogen in C_6D_6, Cp_2MoCO remains a major product, being formed by facile decarbonylation[4] of I to $Cp_2Zr(CH_3)_2$; this dimethyl compound is unreactive toward Cp_2MoH_2 at 25 °C. Quantitative measurements of the reaction stoichiometry establish that, under dinitrogen, 1 mol of Cp_2MoH_2 produces in excess of 1 mol of $Cp_2Zr(CH_3)OCH_2CH_3$. This observation may be accommodated by assuming ring to molybdenum hydrogen migration at some stage of the mechanism, followed by transfer of this new hydrogen to I. In accord with this contention, a second molybdenum-containing product is formed which exhibits a complex ^1H NMR pattern characteristic of both η^5-C_5H_5 and C_5H_4X units; we have identified this product as II by comparison with an authentic sample.[8] Hydrogen



II

transfer from Cp_2MoH_2 to $Cp_2ZrCl[\eta^2\text{-}C(O)CH_3]$[9] is again specific to the acyl group, no metathesis of Cl for H on zirconium being observed. This acyl is more resistant to decarbonylation than I in the hydrogen-transfer reaction, and con-

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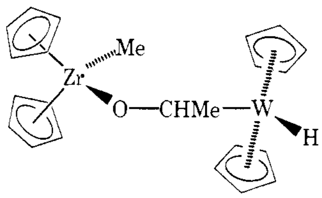
sequently II is a major product; Cp_2MoCO is formed in only 10% yield. Consistent with this observation, if Cp_2MoD_2 is employed with $Cp_2ZrCl[\eta^2\text{-}C(O)CH_3]$, a significant amount of $Cp_2ZrCl(OCHDCH_3)$ accompanies the $Cp_2ZrCl(OCD_2CH_3)$. We have established that a formal hydrogenated analogue of II, $[(\eta^5\text{-}C_5H_5)MoH]_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$,[10] is not a viable intermediate in the hydrogen transfer to the acyl since it is unaffected by I under the reaction conditions.[11]

We have attempted to probe the generality of this reaction, and also to intercept a possible intermediate, by employing Cp_2ReH as a hydride source. This monohydride reacts smoothly with I at 25 °C in C_6D_6, yielding a product which shows no proton resonance in the hydride region.[12] The former acetyl methyl group appears as a doublet due to coupling to a single vicinal proton. The presence, in the recrystallized product, of two equally intense cyclopentadienyl singlets (at 60 MHz), one each in regions characteristic of Cp_2Zr and Cp_2Re units, is consistent with a dimer of formula $Cp_2ZrCH_3(OCHMe)ReCp_2$.[13] The presence of a chiral center in the -OCHMe- bridge leaves both C_5H_5 rings on rhenium equivalent[16] regardless of which metal is bound to the chiral carbon; similarly, both linkage isomers require diastereotopic inequivalence of the ring protons on zirconium. The 220-MHz ^1H NMR spectrum of $Cp_2ZrCH_3(OCHMe)ReCp_2$ (in C_6D_6) shows that the Cp_2Zr signal at δ 5.83 is in fact a doublet with a separation of 0.0016 ppm (0.35 Hz). In view of this small anisochrony, we prefer the Zr-OCHMe-Re structure.

Finally, we have been able to exploit the decreased rates typically found for third transition series metals in order to directly observe the primary product in acyl hydrogenation by Cp_2MH_2 species. Compound I reacts with Cp_2WH_2 in C_6D_6 at 25 °C to produce a bimetallic complex exhibiting a methyl doublet characteristic of the $-OC(H)CH_3-$ unit.[17] This doublet is collapsed when Cp_2WD_2 is employed as the reductant. This complex is a monohydride, and the Cp rings on tungsten exhibit diastereotopic inequivalence. Structure III is consistent with all of these observations. This complex has a limited lifetime (minutes) at 25 °C. The products of this subsequent reaction are currently under study.



III

We[1c] and others[1a,18] have proposed the concept of Lewis acid activation of possible Fischer-Tropsch intermediates. Acyl I was selected for this study because the dihapto binding of the acetyl group provides such activation in a sterically compact manner. The significance of this mode of activation is clearly indicated since the acetyl stretching frequency persists when refluxing heptane solutions of $CpFe(CO)_2[C(O)Me]$ or $Co[C(O)Me](acacen)$ are treated with Cp_2MoH_2.

This work, as well as that reported earlier,[2] demonstrates that this bimolecular approach constitutes a viable alternative to metal clusters as a strategy for ligand activation and hydrogenation. It is also clear that it is exceptionally easy to generalize the bimolecular approach to heterobimetallic[19] systems, while the production of heterometallic clusters MM′M″ . . . constitutes a formidable synthetic challenge.

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References and Notes

(1) (a) Manriquez, J.; McAlister, D.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978,** *100*, 2716. (b) Wolczanski, P.; Threlkel, R.; Bercaw, J. *Ibid.* **1979,** *101*, 218. (c) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *Ibid.* **1977,** *99*, 5829. (d) Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *Ibid.* **1978,** *100*, 3254.

(2) Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1979,** *164*, C29.

(3) Labinger, J. A.; Komadina, K. *J. Organomet. Chem.* **1978,** *155*, C25.

(4) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977,** 1946.

(5) ^1H NMR (C_6D_6): δ 5.78 (s, 10 H), 3.83 (q, 2 H), 1.00 (t, 3 H), 0.32 (s, 3 H). This product has been synthesized independently by the reaction of Cp_2ZrMe_2 with EtOH.

(6) Cf. Renaut, P.; Taunturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978,** *150*, C9.

(7) Thomas, J. L. *J. Am. Chem. Soc.* **1975,** *97*, 5943. ^1H NMR (CD_3CN): δ 4.43 (s). IR: ν (CN) 1780 cm^{-1} (in CD_3CN). We have synthesized this compound independently by photolysis of Cp_2MoCO in CD_3CN.

(8) Berry, M.; David, S. G.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1978,** 99. Green, M. L. H.; Simpson, S. J. *J. Organomet. Chem.* **1978,** *148*, C27, and private communication. Meunier, B.; Prout, K. *Acta Crystallogr., Sect. B* **1979,** *35*, 2558.

(9) (a) By carbonylation of $Cp_2Zr(CH_3)Cl$.[9b] ^1H NMR (C_6D_6): δ 5.48 (s, 10 H), 2.25 (s, 3 H). IR: $\nu(C{=}O)$ 1556 cm^{-1} (Nujol). $Cp_2Zr(OEt)Cl$[9c] ^1H NMR (C_6D_6): δ 5.97 (s, 10 H), 3.85 (q, 2 H), 0.98 (t, 3 H). (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972,** *34*, 155. (c) Gray, D.; Brubaker, C. H. *Inorg. Chem.* **1971,** *10*, 2143.

(10) (a) The fulvalenide dimer $(CpMoH)_2(C_{10}H_8)$,[10b] which forms from $[(\eta^5\text{-}C_5H_5)MoH)]_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ in a thermal reaction, is neither formed in the reactions described here, nor is it capable of hydrogen transfer to I. (b) Cooper, N. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977,** 145.

(11) These reactions represent the mildest conditions yet reported for dehydrogenation of Cp_2MoH_2. In view of the relatively low ionization potential of Cp_2MoH_2, an electron transfer to the ZrC(O)Me moiety may initiate this rapid reaction of an 18-electron molybdenum complex.

(12) ^1H NMR (C_6D_6): δ 5.83 (s, 10 H), 3.95 (s, 10 H), 1.83 (d, 3 H), 0.30 (s, 3 H). The weak signal due to the proton on the tertiary carbon has been located (by spin decoupling) at δ 5.7. IR ν(C–O): 1030 cm^{-1}.

(13) While compounds of this type have been reported,[1b,14,15] in every case they have been formed from zirconium hydrides; an important aspect of the work reported here is the demonstration that later transition metal hydrides can also effect this hydrogen transfer.

(14) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978,** 269.

(15) Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1978,** *162*, C11.

(16) Rapid rotation about the Re–CH(Me)O bond is assumed.

(17) ^1H NMR (C_6D_6): δ 5.83 (s, 10 H), 4.27 (s, 5 H), 4.20 (s, 5 H), 1.65 (d, 3 H), 0.20 (s, 3 H), −10.8 (br s, 1 H), 5.40 (q, 1 H).

(18) Masters, C. *Adv. Organomet. Chem.* **1979,** *17*, 61. Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977,** *99*, 2796.

(19) We define a reaction system which begins by mixing soluble complexes of two different metals M and M′ as being heterobimetallic and bimolecular.

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Conformations and Rotation Barriers in 1,8-Bis(trimethylelement)naphthalenes

Sir:

The availability[1-3] of naphthalenes substituted in the peri positions by different $(CH_3)_3Z$ groups (Z = group 4a element) presents an exceptional opportunity to investigate the effects of severe internal strain on static and dynamic stereochemistry as a function of Z. Comparison[4] of the X-ray structures of 1,3,6,8-tetra-*tert*-butylnaphthalene (**1**), 1,8-bis(trimethylgermyl)naphthalene (**2**), and 1,8-bis(trimethylstannyl)naphthalene (**3**) has revealed that nonbonded repulsion between the bulky $(CH_3)_3Z$ groups in the 1,8 positions warps the naphthalene framework and imparts C_2 symmetry to all three molecules, with skeletal distortions decreasing in the order **1** ≫ **2** > **3**.[5] Surprisingly, however, this familial resemblance does not extend to the conformations of the $(CH_3)_3Z$ groups, which exhibit the same pattern for **2** and **3** but a distinctly different one for **1** (Figure 1).[4] If, as suggested by empirical force-field (EFF) calculations,[4] the ground-state conforma-

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