a silicon MASS NMR experiment (insert in Figure 2B) compared to *three* sets of ^{17}O resonances. This permits, in principle, a far more detailed structural analysis using ^{17}O NMR, since isotropic chemical shifts, chemical shift tensors,[14] electric quadrupole coupling constants, and electric-field gradient tensor asymmetry parameters for *each* nonequivalent oxygen appear to be measurable.

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Registry No. MgO, 1309-48-4; α-Al_2O_3, 1344-28-1; cristobalite, 14464-46-1; diopside, 14483-19-3; ^{17}O, 13968-48-4.

Metal Formyl Complex via Hydride Transfer from $HRu(CO)_4^-$: Model for Catalytic Hydrogenation of Carbon Monoxide

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Catalytic systems for homogeneous hydrogenation of the carbon monoxide molecule have been postulated to proceed through initial formation of a metal formyl complex,[1,2] although the intramolecular migration of a hydride ligand to coordinated CO has been shown in several complexes to be a difficult process.[3-5] *Inter*molecular hydride donation from boron hydride reagents has been used as a general synthetic route to metal formyl complexes.[4] Reactions of early transition-metal hydrides (groups 4A and 5A) with CO or metal carbonyls have also been reported; many of these processes are known or postulated to involve intermolecular hydride transfer to a carbonyl ligand.[7,8] These reactions, however, require the stoichiometric use of powerful hydride donors that are not readily regenerable in a catalytic process. Here we report the generation of a metal formyl complex by hydride transfer from a group 8 metal complex, $HRu(CO)_4^-$, which is plausibly regenerable from H_2 and CO in a catalytic system. We also suggest that this intermolecular hydride-transfer process is a model for the initial activation of carbon monoxide in a catalytic system for CO reduction.

Scheme I

$$HRu_3(CO)_{11}^- + CpRe(CO)_2(NO)^+ \rightleftharpoons HRu_3(CO)_{11}^\bullet + CpRe(CO)_2(NO)^\bullet \quad (1)$$

$$CpRe(CO)_2(NO)^\bullet \rightleftharpoons CpRe(CO)(NO)^\bullet + CO \quad (2)$$

$$CpRe(CO)(NO)^\bullet + HRu_3(CO)_{11}^\bullet \longrightarrow CpRe(CO)(NO)H + Ru_3(CO)_{11} \quad (3)$$

$$Ru_3(CO)_{11} + CO \longrightarrow Ru_3(CO)_{12} \quad (4)$$

In our study of a soluble iodide-promoted ruthenium catalytic system for CO hydrogenation,[9] it was noted that catalyst concentration effects and the involvement of two essential catalyst components, $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$, indicated the operation of intermolecular processes. Since $HRu_3(CO)_{11}^-$ is an apparent hydride donor in the presence of CO,[10] a possible catalytic step could comprise transfer of the hydride ion to a carbonyl ligand in $Ru(CO)_3I_3^-$ or, more probably, $Ru(CO)_4I_2$ derived from the former complex by reaction with CO. This neutral Ru(II) complex contains highly electrophilic carbonyl ligands, as indicated by relatively high ν(CO) frequencies.[11,12] Reduction of a carbonyl ligand in this complex could be initiated by hydride transfer from $HRu_3(CO)_{11}^-$ or from $HRu(CO)_4^-$,[13] a complex expected from fragmentation of the trinuclear hydride cluster under H_2/CO pressure. Reactions of $Ru(CO)_4I_2$ with PPN[$DRu_3(CO)_{11}$] and PPN[$DRu(CO)_4$] (PPN = bis(triphenylphosphine)iminium) were therefore investigated by ^2H NMR. (This technique was employed because of the possible greater stability of deuteroformyl complexes[14] and the ease in identifying reduction products.) The complexes reacted at an observable rate at −60 °C, but there was no evidence of metal formyl production. Only in a more rapid reaction of $Ru(CO)_4I_2$ with $LiDB(CH_2CH_3)_3$ was evidence for a highly unstable formyl complex (a short-lived signal at β 13.65) observed. We therefore directed our attention toward reactions of the ruthenium hydride complexes with metal carbonyls such as $Fe(CO)_5$[15] and $[CpRe(CO)_2(NO)]PF_6$[16,17] (Cp = η^5-C_5H_5), which are known to form relatively stable formyl complexes upon reaction with boron hydrides. Neither $HRu(CO)_4^-$ nor $HRu_3(CO)_{11}^-$ react with $Fe(CO)_5$ at 25 °C over many hours. The rhenium cation, however, is expected to be a better model for $Ru(CO)_4I_2$, on the basis of its ν(CO) frequencies.[18]

Reaction of $HRu_3(CO)_{11}^-$ with $CpRe(CO)_2(NO)^+$ was complete within minutes under an N_2 atmosphere at 25 °C, but a metal formyl complex could not be detected by IR or NMR spectroscopy. The major products were $Ru_3(CO)_{12}$ and CpRe(CO)(NO)H.[19] This reaction is *retarded* by an atmosphere of carbon monoxide, requiring several hours for completion; again, a metal formyl species could not be detected. Since hydride donation by $HRu_3(CO)_{11}^-$ has previously been shown to be greatly accelerated by CO,[10] it appears unlikely that a rhenium formyl complex is formed as an intermediate by hydride transfer in this reaction. (The CpRe(CO)(NO)(CHO) complex is reported to have a

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[1] (a) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855. (c) Fahey, D. R. *Ibid.* **1981**, *103*, 136. (d) Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 188.

[2] Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959 and references therein.

[3] (a) Calderazzo, F. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (c) Pettit, R.; Mauldin, C.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 151. It is proposed in this paper than an intermolecular hydrogen atom transfer may be involved in a CO reduction process. (d) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466.

[4] Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

[5] Facile conversions of metal hydrides to formyl complexes have recently been reported to two systems.[2,6] However, these reactions have not yet been shown to be related to catalytic processes.

[6] Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.*, **1982**, *104*, 32.

[7] Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3254.

[8] (a) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 264. (d) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (e) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1979**, *101*, 218. (f) Wong, K. S.; Labinger, J. A. *Ibid.* **1980**, *102*, 3652. (g) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* **1980**, *102*, 2858.

[9] Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508.

[10] Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444.

[11] Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A* **1969**, 792.

[12] Reported[11] in cyclohexane solvent: 2161 m, 2107 vs, 2096 s, 2066 s cm^{-1}.

[13] Walker, H. W.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, C43.

[14] Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1981**, *206*, C43.

[15] Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.

[16] Fischer, E. O.; Strametz, H. *Z. Naturforsch. B* **1968**, *23*, 278.

[17] Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.

[18] Reported[16] in acetone: 2105, 2049 cm^{-1}.

[19] (a) Stewart, R. P.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32. (b) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982.

0002-7863/83/1505-2485$01.50/0

half-life of hours in solution at 25 °C.[17]) A more probable pathway involves the electron-transfer process shown in Scheme I, similar to the reported reactions of $CpV(CO)_3H^-$ with neutral metal carbonyl complexes.[20] A radical process is also implicated by the fact that CO substitution in $CpRe(CO)_2(NO)^+$ is not normally a rapid reaction.[21,22]

The $HRu(CO)_4^-$ hydride also reacts rapidly with $CpRe(CO)_2(NO)^+$ at 25 °C. Addition of $[CpRe(CO)_2(NO)]PF_6$ to an acetone solution of $PPN[DRu(CO)_4]$ causes rapid disappearance of the ^2H NMR signal at δ -7.77; hydride resonances for CpRe(CO)(NO)D (δ -8.44) and $DRu_3(CO)_{11}^-$ (δ -12.70) are observed to appear. Also evident is the characteristic formyl resonance of CpRe(CO)(NO)(CDO) at δ 16.18.[17,23] The possible stoichiometry of the formyl-producing reaction is given by eq 5.[24]

$$3\ HRu(CO)_4^- + 2\ CpRe(CO)_2(NO)^+ \longrightarrow HRu_3(CO)_{11}^- + 2CpRe(CO)(NO)(CHO) + CO \quad (5)$$

Of the $CpRe(CO)_2(NO)^+$ converted to the hydride and formyl products, a 20-30% yield of the formyl (based on integrated ^2H NMR peak intensities) is typically observed. The formation pathway of the coproduced rhenium hydride is uncertain. It seems unlikely that all of this product could be formed by decarbonylation of the relatively stable formyl complex.[25] Instead, it appears probable that an electron-transfer process similar to that outlined in Scheme I produces this hydride directly, via a pathway parallel to eq 5.[26] Studies on the details of these processes are continuing.

The hydride cluster $HRu_3(CO)_{11}^-$ is readily formed from H_2 and a ruthenium source in the iodide-promoted catalytic system noted above.[9] Although this cluster appears to be stable under catalytic conditions, it is not improbable that its fragmentation to $HRu(CO)_4^-$ is involved as an initial step in the catalytic sequence.[28]

Intermolecular transfer of hydride from the reactive mononuclear $HRu(CO)_4^-$ species to an electrophilic carbonyl ligand in another complex has now been demonstrated as a feasible step in the CO reduction process by this catalyst system. The facility of this transfer may be responsible for the relatively high catalytic activity of this system.[9,29]

Registry No. $HRu(CO)_4^-$, 77482-04-3; $CpRe(CO)_2(NO)^+$, 45978-17-4; $HRu_3(CO)_{11}^-$, 77482-10-1; CO, 630-08-0.

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(20) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415.

(21) Tam, W.; Lin, G.; Wong, W.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(22) The exchange of carbonyl ligands in $[CpRe(CO)_2(NO]PF_6$ with ^{13}CO (1 atm) is imperceptibly slow at 25 °C in acetone solvent but is greatly accelerated by *catalytic* amounts of $PPN[HRu_3(CO)_{11}]$, consistent with Scheme I.

(23) Experiments using ^{13}CO-enriched $[CpRe(CO)_2(NO)]PF_6$ also showed a doublet ($^1J_{C-D}$ = 23 Hz) accompanying the ^{12}CDO signal.

(24) The same stoichiometry has been observed in other reductions by $HRu(CO)_4^-$. S. G. Shore, private communication.

(25) An experiment was done that indicates that the formyl complex, once formed, is stable under reaction conditions. $[CpRe(CO)_2(NO)]PF_6$ in THF solution was partially converted to CpRe(CO)(NO)(CDO) by reaction with 0.5 equiv of $LiDB(C_2H_5)_3$. The remaining rhenium cation was then allowed to react with $PPN[HRu(CO)_4]$ at 25 °C. Analysis by ^2H showed no change in the amount of CpRe(CO)(NO)(CDO) present after this reaction.

(26) The possibility has not been excluded that electron transfer followed by hydrogen atom transfer[27] to a carbonyl ligand is involved in formyl formation. Selectivity to the formyl and hydride products would then be determined by the relative amounts and reactivities of the two rhenium complexes of eq 2. We have observed, however, that the formyl/hydride selectivity is unaffected by CO pressure over the range 0-3 atm.

(27) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(28) We do not yet have direct evidence for this cluster fragmentation process, but we have observed that the iron analogue, $PPN[HFe_3(CO)_{11}]$, is completely fragmented in THF solvent under 34 atm of CO at 60 °C. See also: Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1973**, *61*, 365. Although fragmentation of the iron cluster is expected to be much more facile than for the Ru analogue, the pressure employed in the ruthenium-catalyzed reaction (generally above 400 atm[9]) may be sufficient to generate small equilibrium amounts of the mononuclear hydride.

(29) Dombek, B. D. *J. Organomet. Chem.*, in press.

Electrochemical Routes to Paramagnetic Dinuclear and Mononuclear Palladium π Complexes Stabilized by the Pentaphenylcyclopentadienyl Ligand

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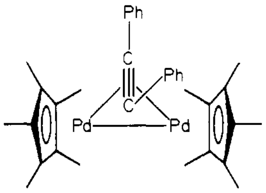
We report an example of the anodic activation of a dinuclear palladium complex to cleavage reactions that give stable mononuclear Pd(II) π complexes. The Pd(II) complexes can in turn be reduced or oxidized in reversible one-electron processes resulting in what appear to be the first persistent paramagnetic Pd(I) or Pd(III) π complexes.

The precursor compound is the diphenylacetylene-bridged dipalladium complex $(\eta^5\text{-}C_5Ph_5)_2Pd_2(\mu\text{-}PhC_2Ph)$,[2] **1**. This compound displays two diffusion-controlled reversible one-electron oxidations ($E°$ = +0.52 and +1.13 V vs. SCE)[3] and a single one-electron reduction ($E°$ = -1.12 V). In CH_2Cl_2 the reduction is fully chemically reversible only at cyclic voltammetry (CV) sweep rates in excess of 200 mV/s, but greater reversibility was observed in THF solutions.[4] Therefore the dimer has a three-step electron-transfer series giving four reasonably stable oxidation states:



1

$$\mathbf{1}^{2+} \rightleftharpoons \mathbf{1}^{+} \rightleftharpoons \mathbf{1} \rightleftharpoons \mathbf{1}^{-}$$

Exhaustive anodic oxidation (+0.7 V) of **1** in CH_2Cl_2 at a platinum basket gave an intense green-black solution (n = 0.96 e^-); voltammetry at the rotating platinumg electrode (rpe) confirmed the quantitative conversion of **1** to the radical cation $[(\eta^5\text{-}C_5Ph_5)_2Pd_2(\mu\text{-}PhC_2Ph)]^+$, $\mathbf{1}^+$ (Figure 1).

The chemical synthesis of $\mathbf{1}^+$ was readily effected by adding a toluene solution of $AgPF_6$ to an equivalent quantity of **1** in the same solvent. After the solution stirred for 5 min, the black precipitate was removed and extracted with CH_2Cl_2; black microcrystals of $\mathbf{1}^+$ were isolable by hexane addition. The identity of $\mathbf{1}^+$ was confirmed by elemental analysis, by its voltammograms ($E°$ values identical with **1**), and by its frozen solution electron spin resonance spectrum in CH_2Cl_2, which showed one line centered at g = 2.044.

Unlike neutral **1**, the radical cation $\mathbf{1}^+$ is a source of diamagnetic Pd(II) complexes, undergoing cleavage reactions with various ligands [L = PPh_3, L_2 = $Ph_2P(CH_2)_2PPh_2$ (dppe) or cyclooctadiene (cod), etc.] to give $[(\eta^5\text{-}C_5Ph_5)PdL_2][PF_6]$, **2**, according to eq 1. The stoichiometry of the reaction, which also can be

$$2(\mathbf{1}^+) + 4L \rightarrow 2[(\eta^5\text{-}C_5Ph_5)PdL_2]^+ + \mathbf{1} + PhC_2Ph \quad (1)$$

accomplished by the electrochemical oxidation of **1** in the presence

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(1) (a) University of Bristol; (b) University of Vermont.

(2) Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.

(3) Data obtained by cyclic voltammetry measurements at a platinum bead electrode in CH_2Cl_2/0.1 M Bu_4NPF_6 electrolyte. Peak separations were typically 70 mV, and i_c/i_a values were unity down to slow sweep rates (ca. 50 mV/s), consistent with a reversible one-electron processes.

(4) In multiple-sweep CV scans or upon bulk cathodic reduction, the solution gives a reversible wave at ca. -0.3 V, which we believe to be due to the pentaphenylcyclopentadienyl anion.

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