(18) Subak, E. J. Jr.; Loyola, V. M.; Margerum, D. W., unpublished results.
(19) Natarajan, P.; Endicott, J. F. *J. Phys. Chem.* **1973**, *77*, 2049.
(20) Trott, T.; Henwood, R. W.; Langford, C. H. *Environ. Sci. Technol.* **1972**, *6*, 367.
(21) Balzani, V.; Carassiti, V.; Moggi, V.; Sabbatini, N. *Inorg. Chem.* **1965**, *4*, 1247.
(22) Hamburg, A.; Margerum, D. W., unpublished results.
(23) Margerum, D. W.; Dukes, G. R. In "Metal Ions in Biological Systems", Sigel, H., Ed.; Marcel Dekker: New York, 1974; Vol. 1, Chapter 5.
(24) Paniago, E. B.; Margerum, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 6704.
(25) Pagenkopf, G. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1968**, *90*, 501.

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Alane Reduction of Coordinated Carbon Monoxide: Selective Ethene Production

Sir:

With the objective of designing catalyst systems for the selective conversion of synthesis gas, a mixture of carbon monoxide and hydrogen, into added value chemicals, we have examined the stoichiometric reduction of coordinated carbon monoxide using soluble metal complexes. Other workers have demonstrated the reduction of carbon monoxide to give methane,[1,2] mixtures of alkanes,[3,4] methanol,[5] and mixtures of linear alcohols[6] using homogeneous systems. The results presented here, which we believe complement those of Muetteries et al.[3] show that under mild conditions coordinated carbon monoxide can be converted into ethene with >95% selectivity.

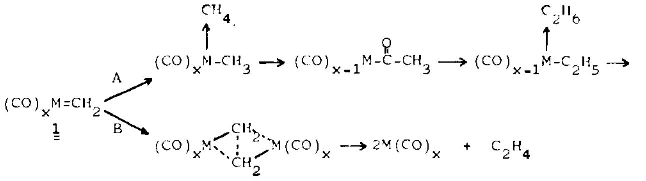
We have previously shown[7] that diborane—a Lewis acid reducing agent—smoothly reduces a coordinated acyl ligand to ethyl probably via initial BH_3 coordination to the acyl oxygen. Since BH_3 proved ineffectual in reducing coordinated carbon monoxide and since, in agreement with other workers,[1,8,9] we believe that dual coordination of CO, i.e., through both the carbon and the oxygen, may well be important in activating it toward reduction, we turned out attention to alane (AlH_3). Compared with BH_3, AlH_3 is both a stronger Lewis acid and a more powerful hydridic reducing agent.

Treatment of $Ru_3(CO)_{12}$ with a 15-fold excess of alane in tetrahydrofuran[10] at 25 °C results in the rapid evolution of methane, ethene, ethane, propene, and propane in the approximate molar ratio 1:1.7:0.5:0.2:0.1.[11] Only ~10% of the CO present in the $Ru_3(CO)_{12}$ is converted into hydrocarbons and further addition of AlH_3/THF has no visible effect. During the reduction no ruthenium metal is formed and the solution remains homogeneous. Attempts to isolate a characterizable ruthenium complex from this solution have been unsuccessful. Addition of 1 M H_2SO_4 to the mixture results in a further gas evolution. This gas contains, in addition to hydrogen resulting from decomposition of excess AlH_x, methane, ethane, and propane in the molar ratio 19:5:1. At this stage conversion of coordinated carbonyl to hydrocarbon products corresponds to ~30%.[12] On addition of the acid the solution turns black and ceases to be homogeneous. With AlD_3, in place of AlH_3, the principal products, before addition of acid are completely deuterated hydrocarbons indicating that the alane is the only source of hydrogen.[13] After addition of the acid 40% of the liberated ethane is $C_2D_4H_2$.

With group 6b metal carbonyl complexes the selectivity to ethene is significantly increased. Thus treatment of $M(CO)_6$, where M = Cr, Mo, or W (0.5 mmol), with AlH_3 (4 mmol) in THF solution at 22 °C results in the selective[14] (95%) formation of ethene. With $Cr(CO)_6$, conversion of carbonyl ligands into ethene increases with increasing AlH_3 concentration reaching a maximum of 17 ± 3% when the $Cr(CO)_6$:AlH_3 molar ratio is 1:6. Further addition of AlH_3 has no effect on the ethene production. Similar results are obtained with $Mo(CO)_6$ and $W(CO)_6$, in that maximum conversion is obtained with a 6 M excess of AlH_3; however the maximum conversion is lower (4% for Mo and 6% for W). With a sixfold excess of AlH_3, ethene evolution is essentially complete within 15 min at 22 °. With AlD_3 in place of AlH_3, C_2D_4 is formed. As was found with $Ru_3(CO)_{12}$, vide supra, acidification of the reaction mixture results in a further gas evolution. Approximately 95% of this gas is hydrogen, derived from the aluminum-hydrido species present in solution; the remaining ~5% consists of methane and ethane in the molar ratio 2:1 for chromium, 10:1 for molybdenum, and 1:5 for tungsten.[15] The *total* conversion of carbonyl ligands into identified[16] organic products, after treatment with AlH_3 followed by acidification, is 33% for $Cr(CO)_6$, 24% for $Mo(CO)_6$, and 25% for $W(CO)_6$[17] indicating that no more than two of the original six carbonyl ligands are converted into identified organic products. We have been unable, as yet, to characterize any inorganic products from these reactions.

Using $LiAlH_4$/THF in place of AlH_3/THF as reducing agent with $Cr(CO)_6$ results in both a reduced conversion (8%) of carbonyl ligands to hydrocarbons and a reduced selectivity (81%) for ethene (the other products being ethane (16%) and propene (3%)).

Although our present data does not permit us to propose detailed mechanisms for these reactions, we feel that the high selectivity to ethene observed strongly suggests the intermediacy of carbenoid metal species. Once formed, such a species, schematically represented as **1**, can be envisaged as either undergoing a reduction–carbonyl insertion–reduction sequence (path A) to give C_1, C_2, and C_3 products or undergoing dimerization (path B) to give ethene. The high selectivity to ethene resulting when path B predominates. Hydrogenation of a carbene fragment and reduction of coordinated acetyl to ethyl, as implicit in path A, have previously been demonstrated[7,18] as has the carbene dimerization[19] implicit in path B.[20] We do not consider that the alternative route to ethene, via β-H elimination from a metal ethyl species, plays a significant role, at least in the $M(CO)_6/AlH_3$ systems, since previous work[7] has shown that decomposition of metal-ethyl species does not generally proceed with such high selectivity to ethene but rather gives a mixture of ethane and ethene.



Primary carbene species have previously been suggested as intermediates in heterogeneous Fischer-Tropsch reactions[21] and dual coordination of carbon monoxide has been suggested to play an important role in activating it toward reduction.[8,9] The present findings add further weight to both of these proposals.

References and Notes

(1) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).
(2) J. C. Huffman, J. G. Stone, W. C. Krusell, and K. G. Caulton, *J. Am. Chem. Soc.*, **99**, 5829 (1977).
(3) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(4) J. A. Labinger, K. S. Wang, and W. R. Scheidt, *J. Am. Chem. Soc.*, **100**, 3254 (1978).
(5) J. M. Manriguez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 6733 (1976).
(6) L. I. Shoer and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 5831 (1977).
(7) J. A. van Doorn, C. Masters, and H. C. Volger, *J. Organomet. Chem.*, **105**, 245 (1976).
(8) (a) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); (b) *ibid.*, **85**, 451 (1976).

0002-7863/79/1501-1633$01.00/0

(9) H. Pichler and H. Schulz, *Chem. Ing. Techn.*, **42,** 1162 (1970).

(10) AlH_3 in tetrahydrofuran (~1 M) was prepared following the procedure detailed by H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **88,** 1464 (1966).

(11) Gas samples were analyzed using a Hewlett-Packard 5830A gas chromatograph containing dual 6-ft, ⅛-in.-diameter, Poropax Q (50–80 mesh) columns.

(12) In addition to the gaseous hydrocarbon products, small quantities, corresponding to 4% conversion of the $Ru_3(CO)_{12}$ carbonyl ligands, of methanol and ethanol (in the molar ratio 2.5:1) were detected in the solution obtained on acidification.

(13) When d^8 tetrahydrofuran was used with AlH_3, no deuterium incorporation was found in the resulting alkane products, confirming that these are not formed from decomposition of the solvent.

(14) Ethane is the other gaseous product formed; no (<0.001 mmol) methane, propane, or propene were detected.

(15) Small quantities of methanol and ethanol, corresponding to 4, 6, and 2% conversion of the carbonyl ligands for Cr, Mo, and W, respectively, were detected in the solution obtained on acidification.

(16) GLC-mass spectrometric analysis of the reaction mixture indicated the absence of products additional to those reported.

(17) Owing to the large volume of hydrogen evolved on acidification, the accuracy in determining the absolute quantities of methane and ethane by the GLC technique employed at this stage of our work is such that an error of ±5% is introduced into the overall conversion figures.

(18) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **99,** 1651 (1977).

(19) E. O. Fischer and D. Plabst, *Chem. Ber.*, **107,** 3326 (1974); C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 895 (1975); R. R. Schrock and P. R. Sharp, *J. Am. Chem. Soc.*, **100,** 2389 (1978).

(20) Initial kinetic measurements on the $Cr(CO)_6/AlH_3$ system indicate that two metals are involved in the dimerization in a process analogous to that proposed by Schrock and Sharp.[15] With the $Ru_3(CO)_{12}/AlH_3$ system no significant correlation between the percentage of ethene formed and the carbonyl concentration was found. This latter finding is not inconsistent with the proposed scheme since both A and B could occur within a single trimetallic cluster.

(21) H. Pichler and B. Firnhaber, *Brennst.-Chem.*, **44,** 13 (1963).

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Ligand Substitution Kinetics on Ethylenediaminetetraacetato Complexes of Ruthenium(II) and Ruthenium(III) Covalently Attached to Graphite Surfaces

Sir:

The recent successful attachment of a variety of transition metal complexes to electrode surfaces[1–21] is an important first step in their exploitation as electrocatalysts. Since catalytic reactions exhibited by transition metal complexes in homogeneous solution frequently commence with coordination of substrates to the metal center,[22] it is of interest to examine ligand substitution kinetics at metal complexes bound to electrode surfaces. A few preliminary reports have addressed this topic,[2,5,14,20,21] but data that would allow a direct quantitative comparison of the substitution kinetics at a complex in both attached and unattached states have not previously been available. In recent studies[20] we have given procedures for attaching the ethylenediaminetetraacetato complexes of ruthenium(II) and -(III) to graphite electrodes and in this report substitution kinetics with the attached complexes are described. Matsubara and Creutz[23] have very recently reported homogeneous substitution kinetics for the same complexes so that the effects of covalent attachment on the coordination kinetics can be discerned. The attachment produces a substantial decrease in the rate of ligand substitution on the Ru(III) complex and a possible source of this effect is suggested.

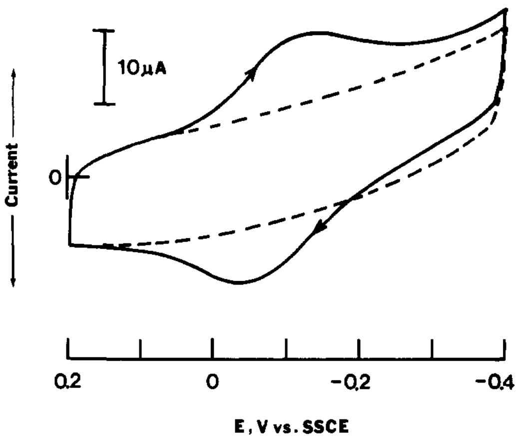

Figure 1. Steady-state cyclic voltammogram for Ru(edta) attached to a graphite electrode with the edge planes of the graphite exposed to the solution. An electrode that had been treated to produce $-CONHCH_2\text{-}4\text{-}C_5H_4N$ groups on its surface was exposed to a 5 mM solution of $Ru^{III}(edta)OH_2$ for 4 h to produce the attachment. Dashed line: before exposure to $Ru^{III}(edta)OH_2$. Solid line: after exposure to $Ru^{III}(edta)OH_2$. Supporting electrolyte: 0.2 M CF_3COONa-0.03 M CF_3COOH (pH 1.5). Scan rate: 200 mV s^{-1}.

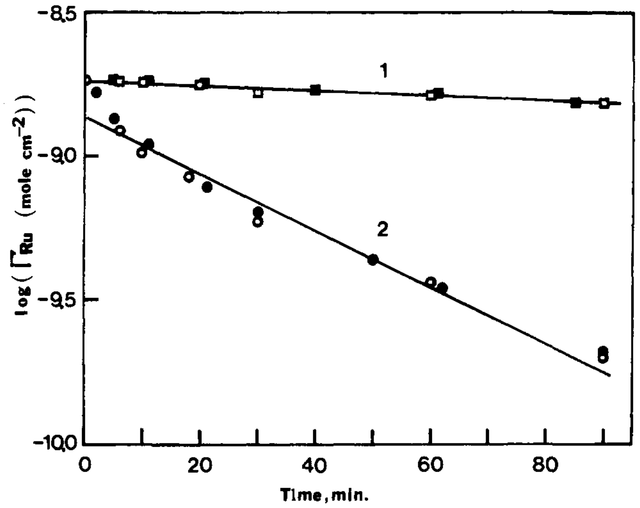

Figure 2. Time dependence of the quantity of Ru(edta) on graphite electrodes. 1: electrode potential maintained at −0.4 V; ruthenium oxidation state, +2; supporting electrolyte pH, 1.5 (■) and 6.4 (□). 2: electrode potential maintained at +0.2 V; ruthenium oxidation state, +3; supporting electrolyte pH, 1.5 (●) and 6.4 (○).

Procedures for pretreating and mounting the pyrolytic graphite electrodes have been given previously[14] as has one method for attaching 4-methylaminopyridine to the graphite surface by means of an amide bond.[14] In the present study, this ligand was attached to electrode surfaces containing carboxyl groups, introduced by plasma etching in oxygen,[19] by treating the electrodes and the ligand with dicyclohexylcarbodiimide in dichloromethane.[19] Following the attachment treatment the electrodes were washed with dichloromethane and methanol and dried under vacuum. The electrochemical cell, graphite electrode holder, and instrumentation for recording cyclic voltammograms have been described.[14] Potentials were measured with respect to a sodium chloride saturated calomel electrode (SSCE).

Aquoethylenediaminetetraacetatoruthenium(III) was prepared according to the procedure of Mukaida et al.[24]

Figure 1 shows a cyclic voltammogram for a pyrolytic graphite electrode to which $Ru^{III}(edta)$ was bound by coordination to previously attached 4-methylaminopyridine ligands. (No response is obtained at electrodes that have not had the ligand attached to their surfaces.) The peak currents and areas of the cyclic voltammograms decreased slowly as the coated electrode was examined periodically in a 0.2 M sodium trifluoroacetate solution at pH 6.4 or 1.5 (trifluoroacetic acid). The rate of loss of the complex from the surface was greater when the electrode was maintained at a potential where the

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