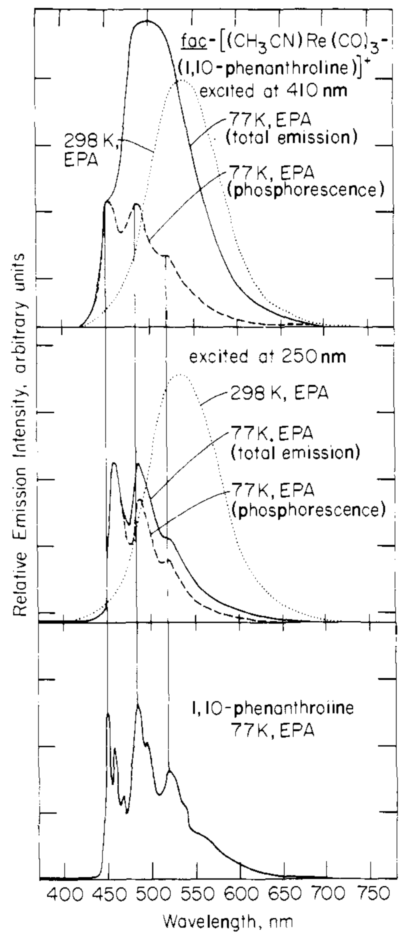


Figure 1. Emission spectra excited at 410 nm (top) and 250 nm (middle) for ~10^{-4} M EPA solutions. The total emission of 1,10-phenanthroline (bottom) is shown for comparison. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except the two marked "phosphorescence" which were recorded with the phosphoroscope attachment in place. The phosphoroscope only allows the detection of emissions longer than ~50 μs.

excitations. The conclusion from this absorption edge excitation is that, while the ReLCT state may be close in energy to the $^3(\pi$-$\pi^*)$, the ReLCT is lower for the systems examined thus far.[10]

Acknowledgments. We thank the National Science Foundation for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975-1980. We thank Professor Robert J. Silbey for valuable discussions concerning the phenomena influencing multiple emission.

References and Notes

(1) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978,** *100*, 2257.
(2) (a) Halpern, W.; DeArmond, M. K. *J. Lumin.* **1972,** *5*, 225. (b) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978,** *58*, 389. (c) Buckner, M. T.; Matthews, T. G.; Lytle, F. E; McMillin, D. R. *J. Am. Chem. Soc.* **1979,** *101*, 5846.
(3) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975,** *75*, 6029.
(4) Watts, R. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1976,** *98*, 674.
(5) Merrill, J. T.; DeArmond, M. K. *J. Am. Chem. Soc.* **1979,** *101*, 2045.
(6) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974,** *96*, 998.
(7) (a) Klassen, D. M. *Inorg. Chem.* **1976,** *15*, 3166. (b) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976,** *98*, 3931. (c) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *Ibid.* **1979,** *101*, 1597.
(8) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979,** *101*, 2888.
(9) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, Calif., 1978.
(10) We are well aware that emissive impurities may well give rise to multiple emissions. However, we have successfully repeated the experimental data found in Table I for several solvents and for different synthetic material prepared independently by two different workers. Free ligand 1,10-phenanthroline impurity emission is ruled out by the data in Figure 1; adding $AgCF_3SO_3$ in small amounts does not alter the emission properties; the complexes are "pure" by elemental analysis and ^{1}H NMR and by IR immediately prior to and after emission spectroscopy measurements. None of the solvents or reagents used in synthesis, workup, or purification exhibits emission like that (lifetime, energy) found for the four cations for L = 1,10-phenanthroline. All sources of "impurity" emission are thus ruled out; the essential results detailed in Table I and Figure 1 are also independent of concentration in the range 10^{-4}–10^{-5} M.

Susan M. Fredericks, John C. Luong, Mark S. Wrighton*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 2, 1979

Homogeneous Carbon Monoxide Hydrogenation on Multiple Sites: A Dissociative Pathway to Oxygenates

Sir:

Transition metal cluster complexes offer the prospect of a new class of selective homogeneous Fischer–Tropsch catalysts by virtue of the proximity of multiple reaction sites on the faces or edges of the cluster, a factor which may have special significance in carbon monoxide hydrogenation catalysis.[1] However, in contrast to the large and increasing number of organo cluster molecules containing hydrocarbon ligands derived from olefins, acetylenes, etc.,[2] there are no examples of organometallic clusters in which the organic moiety was derived solely from CO and H_2, and, in those cases where CO hydrogenation has been reported to be catalyzed by polynuclear complexes,[3] no cluster-bound intermediates have been detected.

We report here the synthesis and characterization of the first member of a new class of organometallic clusters which owe their formation to the reactivity of the encapsulated carbon atom found in the carbidocarbonyl cluster $Fe_6C(CO)_{16}^{2-}$.[4] When suitably exposed (in this case by oxidation of the cluster), the isolated carbon atom, which has no counterpart in mononuclear systems, exhibits a chemistry conducive to carbon–carbon bond formation by reaction with carbon monoxide. A cluster-bound organic fragment is thus built up from CO in a manner unique to cluster chemistry.

A deep red solution of $(Et_4N)_2[Fe_6C(CO)_{16}]$ (I, 3.0 g), in methanol (200 mL) was treated dropwise with a solution of tropylium bromide[5] (3.0 g) in methanol (30 mL), under nitrogen, until the color had changed to green-black, and the infrared absorptions of I at 2028, 1964, 1931, and 1772 cm^{-1} in methylene chloride solutions of evaporated aliquots of the reaction mixture were replaced by new bands at 2024 (s), 1998 (s), 1980 (sh), 1970 (sh), 1925 (m), and 1650 cm^{-1} (w). The product, II, was isolated by evaporation of the methanol, washing with pentane (to remove bitropyl), extraction into methylene chloride, and crystallization as black prisms (1.8 g) from methylene chloride–butanol. ^{1}H NMR (100 MHz, CD_2Cl_2) showed only a sharp singlet at δ 3.35 (3 H) in addition to cation resonances at 3.05 (8 H) and 1.20 (12 H). ^{13}C NMR (20 MHz, CD_2Cl_2, ~30% ^{13}C enriched)[6]: 237, 214, 175 ppm (Me_4Si) in approximate intensity ratio 1:12:1. These data, together with elemental analysis, supported the formulation of II as $(Et_4N)[Fe_4C(CO)_{12}\cdot CO_2CH_3]$. In view of the novelty of a tetranuclear cluster containing a lone carbon atom, an X-ray crystallographic study was performed.[7]

Crystals of II were grown from methylene chloride–butanol. The molecule crystallizes in the orthorhombic space group P_{bca} (D_{2h}^{15}, No. 61) with a = 12.099 (3), b = 17.889 (6), c =

0002-7863/79/1501-7417$01.00/0

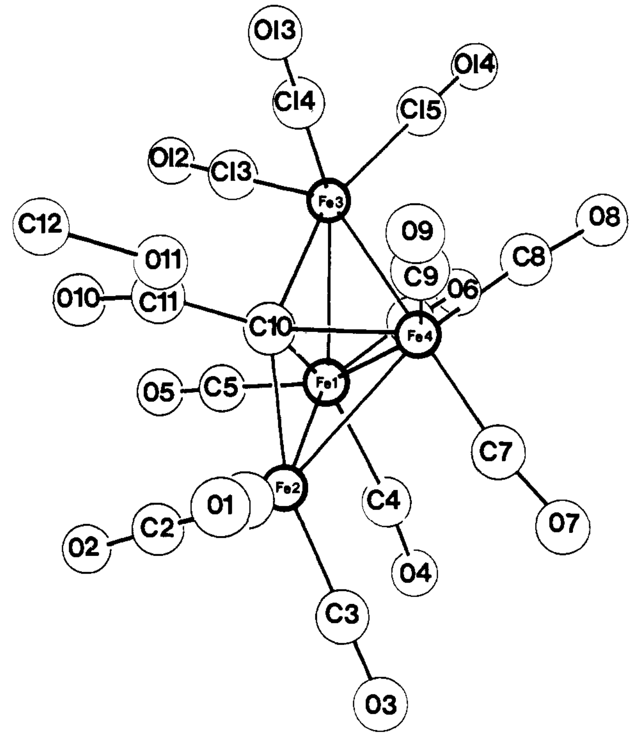


Figure 1. The $Fe_4(CO)_{12}C{\cdot}CO_2CH_3$ anion.

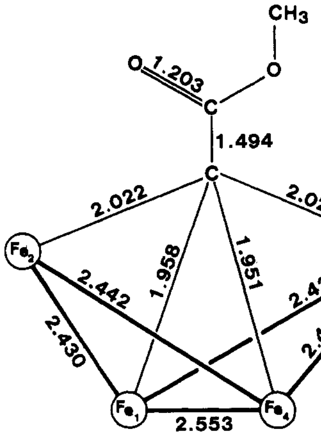


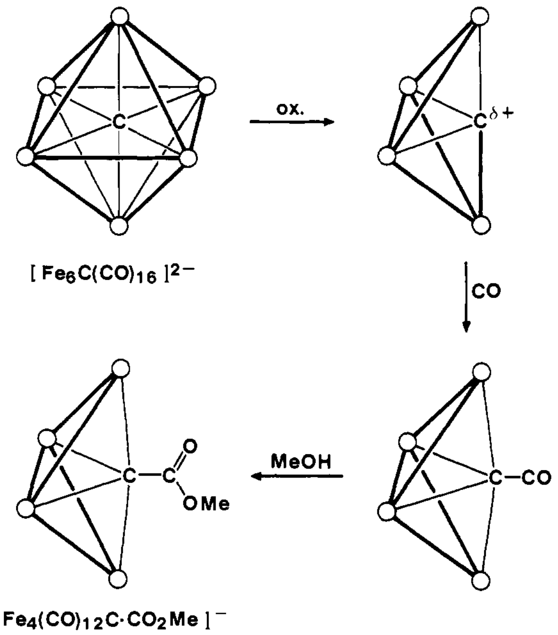
Figure 2. The $Fe_4C{\cdot}CO_2CH_3$ core.

27.704 (14) Å; ρ_{calcd} = 1.64 g cm^{-3} for mol wt 760.8 and Z = 8; ρ_{obsd} = 1.59 g cm^{-3}. Using anisotropic temperature factors for the iron atoms only, 1816 statistically significant reflections ($I > 4\sigma(I)$) have been refined to R = 0.072, R_w = 0.080.

The essential features of the structure are shown in Figure 1. The iron cluster is based on a tetrahedron, distorted by elongation along one edge, Fe(2)-Fe(3), into a butterfly configuration (similar to that found for $Fe_4(CO)_{13}H^-$ [8]), with a dihedral angle of 130°. Each iron atom is bonded to three terminal carbonyls and also to a μ_4-carbomethoxymethylidyne group, C(10)-C(11)-O(10)-O(11)-C(12), a functionality hitherto unreported. The methynyl carbon atom, C(10), is situated 2.022 (3) Å from Fe(2) and Fe(3), and 1.955 (3) Å from Fe(1) and Fe(4) (Figure 2). The carbomethoxy group lies in a plane perpendicular to the Fe(2)-Fe(3) vector.[9]

The formation of II from I may be seen as resulting from the removal of two vertices from the octahedral dianion, exposing the central carbon atom (Scheme I). One molecule of liberated CO then reacts with the apparently electrophillic carbon, to give a metallaketene species, III, which then undergoes reaction with solvent methanol, yielding II.[10] Similar reactions have been observed when I is oxidized in the presence of other nucleophiles in THF. In view of the reactivity of the cluster bound carbon atom it may be more appropriate to regard such encapsulated atoms as carbocationic rather than carbidic,[12] and it is instructive to recall that the ^{13}C NMR resonances of such carbon atoms in those "carbidocarbonyl" clusters which have been studied lie well downfield,[13] more consistent with their assignment as shielded carbonium ions than as carbides.

Scheme I



Although attempts have apparently been made to investigate the chemistry of isolated carbon atoms in carbidocarbonyl clusters,[14,15] this is the first example of a reaction at the carbon site. The observation of carbon-carbon bond formation by reaction with CO raised the prospect of an alternative to alcohol carbonylation for the synthesis of an acetate. This possibility was realized in the hydrogenation of II (120 °C, 220 psi) in THF to yield methyl acetate (~50%). Since the acetyl methyl carbon originated as the methylidyne carbon in II, and since the methylidyne carbon was derived from CO (demonstrated by the labeling at this position when ^{13}CO-enriched $Fe(CO)_5$ was used to prepare II), a new pathway is established for the transition metal mediated synthesis of an organic molecule from CO and H_2. Postulated mechanisms for such reactions, either via homogeneous or heterogeneous catalysis, have often involved the intermediacy of formyl, hydroxycarbene, and hydroxymethyl species in the hydrogenation of adsorbed or coordinated CO, i.e., the C-O bond is preserved for several steps in the process.[16] The original dissociative mechanism proposed by Fischer and Tropsch[17] involved surface carbide hydrogenation, but this fell into disfavor, although a related route has recently been proposed in which surface carbon atoms are regarded as the primary intermediate in methanation and Fischer-Tropsch synthesis.[18] Such a pathway has not received consideration for homogeneous CO hydrogenation, but our current work suggests that this alternative is worthy of attention.

Recent observations in homogeneous CO hydrogenation catalysis have demonstrated that simple oxygenates may apparently be synthesized without the benefit of multiple site catalysis.[19,20] However, our synthesis of an organic oxygenate from CO and H_2 on a site uniquely available in cluster chemistry lends weight to the argument that the advantages of clusters as catalysts will be found in the provision of totally novel molecular transformations by virtue of the unique environment provided by adjacent metal atoms.

The organometallic chemistry of the iron butterfly is proving wide and varied, and details of other cluster mediated organic syntheses will be reported in due course.

References and Notes

(1) See, for example, E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).

(2) A. J. Deeming and M. Underhill, *J. Chem. Soc., Chem. Commun.*, 277 (1973); R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977); J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1975); C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. Raithby, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 423 (1978).

(3) R. L. Pruett, *Ann. N.Y. Acad. Sci.*, **295**, 239 (1977); M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

(4) M. R. Churchill, J. Wormold, J. Knight, and M. J. Mays, *J. Am. Chem. Soc.*, **93**, 3073 (1971).

(5) Tropylium bromide is a mild one-electron oxidizing agent of particular convenience in organometallic synthesis since its reduction product is easily removed from product mixtures by pentane extraction or sublimation. See, for example, R. B. King and F. G. A. Stone, *Inorg. Synth.*, **7**, 99 (1963).

(6) ^{13}CO enrichment was performed on Fe(CO)$_5$, which was used to synthesize Fe$_6$C(CO)$_{16}^{2-}$ for subsequent oxidation.

(7) Data was collected by Dr. J. M. Troup, Molecular Structure Corporation, College Station, Texas.

(8) M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).

(9) In solution an equilibrium apparently exists between two conformations of the ester group, evidenced by a splitting of the ν(CO) absorption at 1650 cm^{-1}, which remains a sharp single peak in the Nujol mull spectrum. Interconversion of the two isomers is observed by ^{13}C NMR, an averaged spectrum being observed at 60 °C.

(10) An analogous sequence of reactions in a cationic system was reported for the formation of the acylium ion [Co$_3$(CO)$_9$CCO]$^+$ by reaction of Co$_3$(CO)$_9$CCl with AlCl$_3$.[11] In that case CO migration from cobalt to carbon is thought to be facilitated by the Lewis acid.

(11) D. Seyferth, G. H. Williams, and C. L. Nivert, *Inorg. Chem.*, **16**, 758 (1977).

(12) This is consistent with the original suggestion of Mason, based on structural considerations. R. Mason and W. R. Robinson, *J. Chem. Soc., Chem. Commun.*, 468 (1968).

(13) See, for example, V. G. Albano, P. Chini, S. Martinengo, D. G. A. McCaffrey, D. Strumolo, and B. T. Heaton, *J. Am. Chem. Soc.*, **98**, 8106 (1974).

(14) C. R. Eady, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Organomet. Chem.*, **57**, C82 (1973).

(15) C. G. Cooke and M. J. Mays, *J. Organomet. Chem.*, **88**, 231 (1975).

(16) M. A. Vannice, *Catal. Rev.-Sci. Eng.*, **14**, 152 (1976); C. Masters. *Adv. Organomet. Chem.*, **17**, 61 (1979), and references therein.

(17) F. Fischer and H. Tropsch, *Brennst.-Chem.*, **7**, 97 (1926).

(18) V. Ponec, *Catal. Rev.-Sci. Eng.*, **18**, 151 (1978); P. Biloen, J. N. Helle, and W. M. H. Sachtler, *J. Catal.* **58**, 95 (1979).

(19) J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, **100**, 3623 (1978).

(20) J. S. Bradley, *Int. Symp. Homogeneous Catal., 1st., 1978*, Paper 54 (1978), and *J. Am. Chem. Soc.*, following paper in this issue.

John S. Bradley,* G. B. Ansell, E. W. Hill
Exxon Research and Engineering Company
P.O. Box 45, Linden, New Jersey 07036

Received June 11, 1979

Homogeneous Carbon Monoxide Hydrogenation to Methanol Catalyzed by Soluble Ruthenium Complexes

Sir:

The field of homogeneous catalysis by transition metal complexes has received considerable impetus from the recognition of a need for a selective, efficient process for the conversion of synthesis gas, via carbon monoxide hydrogenation, to chemicals, supplementing the traditional petroleum based feedstock on which the chemical industry is based. Since high and often manipulable selectivity is the hallmark of a successful homogeneous catalyst, the search for soluble liquid phase counterparts to classical Fischer-Tropsch catalysts (heterogeneous nonselective systems) has been joined by industrial and academic researchers throughout the world.

As part of a program aimed at determining the utility of soluble transition metal complexes in CO hydrogenation catalysis, we have investigated the carbonyl clusters of ruthenium as potential catalysts. Ruthenium metal itself is a well-established heterogeneous Fischer-Tropsch catalyst,[1] and, although this may seem to be adequate justification for selecting ruthenium clusters for this study, it also presented a potential complication. If metal deposition occurred owing to catalyst decomposition during the course of the catalyzed reaction, Fischer-Tropsch products would be formed, and might be erroneously ascribed to a homogeneously catalyzed process. This is a constant potential source of error in homogeneous catalysis, but one which we have satisfactorily removed in the present work.

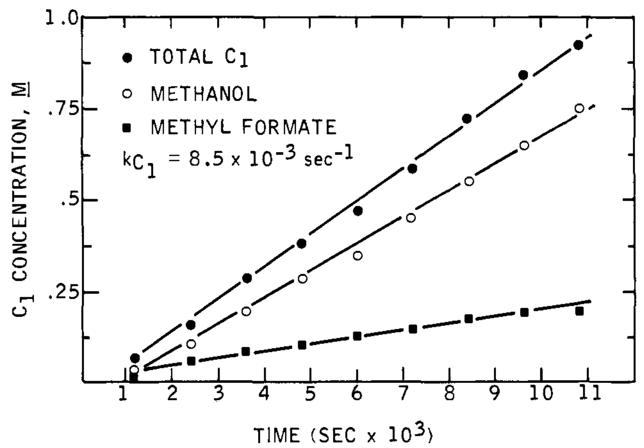


Figure 1. Catalytic hydrogenation of CO: 1300 atm of CO-H$_2$ (60:40), 268 °C, 10 mM Ru(acac)$_3$ in THF.

We have observed the hydrogenation of carbon monoxide at 1300 atm, 225-275 °C, to methanol and methyl formate at convenient rates, in the presence of a number of ruthenium complexes in solution. H$_4$Ru$_4$(CO)$_{12}$,[2] H$_3$Ru$_4$(CO)$_{12}^-$,[3] Ru$_3$(CO)$_{12}$, and Ru$_6$C(CO)$_{16}^{2-}$ [4] all exhibited similar activity, all were converted into a common species under reaction conditions, and Ru(CO)$_5$ was the only ruthenium complex detectable in samples of the reaction mixture. Ru(acac)$_3$ was the most convenient source of ruthenium and was the catalyst precursor of choice in subsequent experiments.[5]

At 268 °C, a THF solution initially 10 mm in Ru(acac)$_3$ catalyzed the formation of methanol and methyl formate from 40:60 CO-H$_2$ at 1300 atm with an overall conversion rate (CO $\rightarrow$ CH$_3$O-) of 8.5×10^{-3} mol of CO/g-atom of Ru per second (Figure 1). The selectivity of the conversion to C$_1$ products (methanol + methyl formate) was >99% with a methanol/formate ratio of 4.1, and the activity of the catalyst remained undiminished over a 3-h run. At no point during the reaction were other CO hydrogenation products detected, and the absence of hydrocarbons in noteworthy (vide infra). The infrared spectra in the 2000-cm^{-1} region of samples taken during the run[5] exhibited only absorptions due to Ru(CO)$_5$ at 2035 and 2001 cm^{-1}, and the stability of the catalyst solution was confirmed by a constant value of the absorbance at 2001 cm^{-1} throughout the run. (A dilution effect due to product formation was within the limits of experimental error in the absorbance measurement.)

Both reaction rate and selectivity to methanol were found to be sensitive to the composition of the feed gas; an increase in P_{CO} results in a suppression of activity and an increase in formate yield. The addition of triphenylphosphine to the catalyst solution had a beneficial effect on methanol selectivity, and, by combining the effect of phosphine addition to that of a hydrogen-rich feed, a selectivity of >95% to methanol was achieved.

Rate constants[6] determined between 250 and 290 °C provided an estimated Arrhenius activation energy of 32 ± 3 kcal/mol^{-1} (Figure 2). This is rather lower than the value of 41 kcal mol^{-1} reported recently for the hydrogenation of CO to alcohols and formates using HCo(CO)$_4$ as catalyst.[8,9]

Within the limits of precision imposed by the experiment, a first-order dependence of hydrogenation rate on ruthenium

0002-7863/79/1501-7419$01.00/0