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.

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(6) ^{13}CO enrichment was performed on $Fe(CO)_5$, which was used to synthesize $Fe_6C(CO)_{16}^{2-}$ 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 $[Co_3(CO)_9CCO]^+$ by reaction of $Co_3(CO)_9CCl$ with $AlCl_3$.[11] In that case CO migration from cobalt to carbon is thought to be facilitated by the Lewis acid.

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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.

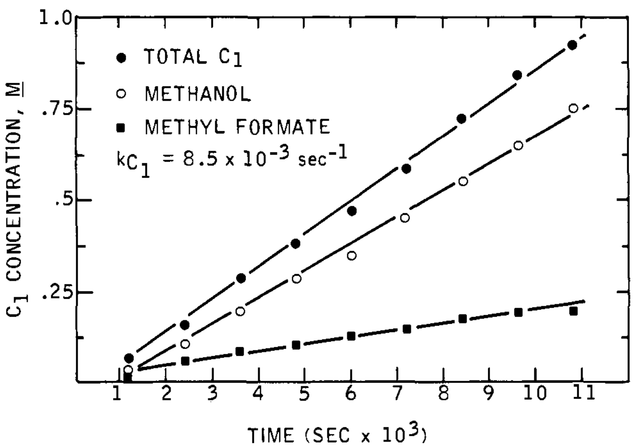

Figure 1. Catalytic hydrogenation of CO: 1300 atm of $CO-H_2$ (60:40), 268 °C, 10 mM $Ru(acac)_3$ in THF.

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. $H_4Ru_4(CO)_{12}$,[2] $H_3Ru_4(CO)_{12}^-$,[3] $Ru_3(CO)_{12}$, and $Ru_6C(CO)_{16}^{2-}$ [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 ($CO \rightarrow CH_3O$-) 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

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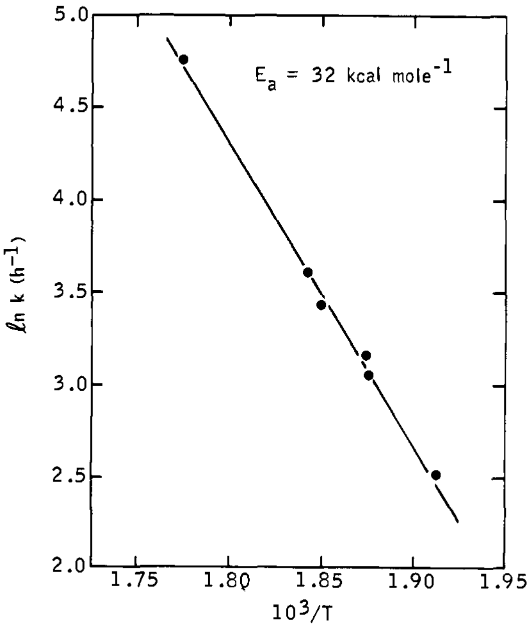

Figure 2. Arrhenius plot of C_1 formation.

concentration was found. Solutions (10 and 20 mM) of $Ru(acac)_3$ in THF under 1300 atm of 40:60 $CO-H_2$ catalyzed CO hydrogenation with rates of 8.5×10^{-3} and 1.05×10^{-2} s^{-1}, at 268 and 270 °C, respectively. These data are consistent with the involvement of a mononuclear ruthenium complex in the rate-determining step, but further characterization of the active species must await a full kinetic study.

Additional investigation of the system was necessitated by the claims contained in a recent patent application[10] which came to our notice after the conclusion of the initial phase of our work, and which seemed to conflict with our observations. THF solutions of $Ru_3(CO)_{12}$, purportedly acting as an intact trinuclear cluster, were reported to catalyze the synthesis of *n*-alkanes up to C_{30} from CO and H_2 at 250-300 °C and 150-200 atm. Ruthenium pentacarbonyl, present under reaction conditions, was apparently inactive for hydrocarbon synthesis. In an effort to determine whether the trinuclear cluster was indeed acting in this unexpected manner, a series of infrared experiments was performed on solutions of $Ru_3(CO)_{12}$ under synthesis gas.[11]

Under relatively mild conditions (80 °C and 135 atm of 1:1 $CO-H_2$), an equilibrium was observable in a solution initially 3.5 mM in $Ru_3(CO)_{12}$ in THF comprising approximately equal concentrations of $Ru_3(CO)_{12}$ and $Ru(CO)_5$. However, under more forcing conditions (180 °C, 265 atm) only $Ru(CO)_5$ could be detected in solution. The rapidity of cluster breakdown was demonstrated by the observation that the infrared spectrum of a sample taken within 15 s of adding $Ru_3(CO)_{12}$ in THF to preheated THF at 180 °C and 265 atm showed no detectable amount of $Ru_3(CO)_{12}$ at a total ruthenium concentration of 10.5 mM. In a similar experiment at 175 °C, $Ru(CO)_5$ in THF (10.5 mM) was stirred under 265 atm of $CO-H_2$ for 6 h. During this time the concentration of the pentacarbonyl remained constant, and no CO hydrogenation products were formed in the system. However, at 271 °C and 265 atm, conditions comparable with those under which hydrocarbon formation had been reported, the concentration of $Ru(CO)_5$ decreased over a 6-h period from 10.5 to 7.5 mM. Analysis of liquid samples taken during the run showed that CO hydrogenation had occurred to methanol and *n*-alkanes (up to $\sim C_{25}$).[12]

At reduced pressures of 200 and 140 atm and 271 °C, $Ru(CO)_5$ decomposition was enhanced as might be expected. No other carbonyl-containing species were detectable in solution by infrared spectroscopy, and inspection of the autoclave revealed the presence of deposited metal.

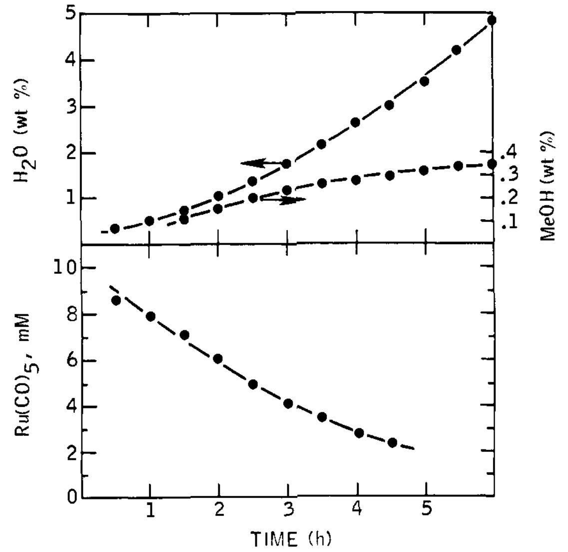

Figure 3. CO hydrogenation at 200 atm, 271 °C.

The catalysts involved in the methanol and alkane syntheses were identified by correlating the rates of methanol and water formation with the concentration of ruthenium in solution, measured as $Ru(CO)_5$ by infrared. A plot of the time dependence of the concentrations of $Ru(CO)_5$, methanol, and water obtained at 200 atm of $CO-H_2$ (40:60) and 271 °C, (Figure 3) shows that methanol formation declines with decreasing $Ru(CO)_5$ concentration, clearly implying that methanol synthesis is homogeneously catalyzed by a soluble ruthenium complex. In contrast to the homogeneous reaction, the rate of formation of hydrocarbon (measured indirectly as water) increases with decreasing $Ru(CO)_5$ concentration, consistent with a heterogeneously catalyzed CO hydrogenation occurring on the surface of increasing amounts of deposited ruthenium metal. Analysis of the product mixtures obtained at both higher (265 atm) and lower (140 atm) pressures of synthesis gas reveals the same correlation of methanol synthesis with soluble ruthenium and hydrocarbon synthesis with a degree of metal deposition.[13]

On the basis of these results it seems that claims of homogeneous catalysis of hydrocarbon formation by $Ru_3(CO)_{12}$ in solution are probably erroneous. It is instructive to recall the *homogeneous* rhodium carbonyl catalyzed ethylene glycol synthesis proceeds with lack of hydrocarbon formation.[14] However, in the case of a heterogeneous rhodium-based catalyst ($Rh/Fe/SiO_2$) operating under conditions conducive to oxygenate synthesis,[15] methane is a major product of CO hydrogenation. Methanation activity is a property common to many transition metals, [16]and, in the absence of evidence for an active species in the liquid phase, hydrocarbon formation in an ostensibly homogeneous CO hydrogenation system may reasonably be seen as diagnostic of metal deposition resulting from catalyst decomposition.[19]

The potential of clusters in CO hydrogenation catalysis has attracted some attention,[17] as has the hypothesis that the reduction of CO to methanol or methane would be most readily achieved via cluster intermediates.[18] Our observation of methanol synthesis catalyzed by an apparently mononuclear ruthenium species and the recent report of oxygenate synthesis catalyzed by a mononuclear cobalt complex[8] demonstrate that mononuclear complexes have some utility in this area of catalysis.

Acknowledgments. The author acknowledges with gratitude the excellent technical assistance of E. W. Hill and R. Cook and thanks Drs. G. Doyle and M. G. Romanelli for stimulating and fruitful discussions.

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(4) Synthesized by the reduction of $Ru_3(CO)_{12}$ by $Mn(CO)_5^-$ in refluxing diglyme: J. S. Bradley, G. B. Ansell, and E. W. Hill, submitted for publication.

(5) High pressure experiments, up to 20 000 psig, were performed in a 400-cm^3 Hastalloy-lined stirred autoclave equipped with liquid sampling facilities. In a typical run the catalyst solution was pressured into the preheated autoclave containing solvent, and brought quickly to the desired temperature and pressure. Samples for infrared and GLC analysis were taken periodically, via a double block, into a 70-cm^3 bomb and cooled to −50 °C before venting, to prevent loss of volatiles. Gas was added to the reactor as it was consumed, maintaining a reasonably constant pressure. Infrared analysis was performed on a Beckman 4250 spectrophotometer equipped with absorbance accessory; gas–liquid chromatography was performed on a Perkin-Elmer 910 chromatograph using a Chromosorb 102 column.

(6) Rate constant defined as moles of CO hydrogenated/gram-atom of Ru per second.

(7) This inverse dependence of rate on P_{CO} is consistent with similar effects in both cobalt-catalyzed hydroformylation of olefins and also heterogeneous methanation catalysis reflecting the competition for active sites on the catalyst between CO and other reactant molecules.

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

(9) The higher figure was suggested as evidence for a free-radical rate-determining step for homogeneous CO hydrogenation in which homolytic cleavage of the cobalt–hydrogen bond and transfer of a hydrogen atom to free CO yields a formyl radical, which then undergoes hydrogenation to the observed products. This novel proposition requires the test of further kinetic investigation.

(10) C. Masters and J. A. Van Doorn (to Shell), German Offen. 2 644 185 (1975).

(11) The solutions were allowed to equilibrate before sampling into precooled receivers; samples were stored in the dark at −78 °C until analysis was performed to preclude photochemical or thermal cluster formation from $Ru(CO)_5$, a reaction which occurs at a rate sufficient to frustrate attempts at quantitative determination of the relative concentrations of the monomeric and trimeric carbonyls.

(12) Water, the byproduct of hydrocarbon formation, was also present, and, since this was the only source of water in the system, water concentration was used as a convenient measure of hydrocarbon formation.

(13) The validity of this correlation was confirmed by recharging the autoclave, after thorough THF washing to remove soluble ruthenium carbonyl, with pure THF and heating to 270 °C under 265 atm of $CO–H_2$. Hydrocarbon synthesis was again observed, but in the absence of added ruthenium carbonyl. Indeed this was used as a test for the adequacy of ruthenium metal removal after each run (a tedious mechanical process) and no attempt to catalyze CO hydrogenation homogeneously was made until a successful blank run was achieved.

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(15) P. C. Ellgen and M. M. Bhasin (to Union Carbide), U.S. Patent 4 014 913 (1977).

(16) M. A. Vannice, *J. Catal.*, **37**, 449 (1975).

(17) C. Masters, *Adv. Organomet. Chem.*, **17**, 61 (1979).

(18) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 451 (1976).

(19) NOTE ADDED IN PROOF. Since the submission of this communication a note has appeared from Shell workers reassessing their earlier claims[10] and confirming our conclusion that hydrocarbon synthesis in this system is heterogeneously catalyzed by deposited ruthenium metal: M. J. Doyle, A. P. Kouwenhoven, C. A. Schaap, and B. Van Oort, *J. Organomet. Chem.*, **174**, C55 (1979).

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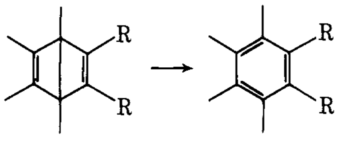
Exciplex Isomerization of Dewar Benzenes. Factors Controlling Diabatic and Adiabatic Reaction Paths

Sir:

There are several photosensitized molecular rearrangements[1-5] which may be referred to as *exciplex isomerizations.* These reactions appear to depend on electron transfer (not energy transfer) properties of sensitizer-quencher pairs and are most readily understood in terms of singlet exciplex formation followed by nonradiative decay to photoisomers.

The most unusual of these isomerizations is the rearrangement of hexamethyl(Dewar benzene) (HMDB) to hexamethylbenzene (HMB). Evans reported[4] that the isomerization which results from quenching the fluorescence of aromatics by HMDB in polar solvents has a quantum efficiency well exceeding unity. A chain reaction involving radical ions was proposed. Taylor found,[5] on the other hand, that the quenching of 1-cyanonaphthalene (CN) emission by HMDB in relatively nonpolar solvents resulted in a new emission identical with the fluorescence of HMB exciplexes. To our knowledge this important observation of sensitized decomposition of HMDB in nonpolar media is the only example of adiabatic exciplex isomerization (an exciplex → exciplex rearrangement).[6] We report herein a study of Dewar benzene excited complexes in which some of the features which control exciplex formation and the efficiency of diabatic and adiabatic isomerization have been identified.



HMDB   HMB
DHD   DTP

R = CH_3
R = CO_2CH_3

Table I. Photochemical and Photophysical Data for HMDB (HMB) Quenching and Isomerization[a]

sensitizer	k_q(HMDB) $\times 10^{-9}$ M^{-1} s^{-1}	k_q(HMB) $\times 10^{-9}$ M^{-1} s^{-1}	$k_q\tau_0$, M^{-1} [b]	i/s, M^{-1} [c]
1,4-dicyanobenzene (DCB)	10.4	13.2		
1-cyanonaphthalene (CN)	3.2	4.4	84.0	85.6
9,10-dicyanoanthracene (DCA)	7.3	8.7	112	119
9-cyanoanthracene (CA)	0.13	2.6		

[a] Cyclohexane solution, room temperature. [b] Stern–Volmer constants for quenching sensitizer fluorescence. [c] Intercept/slope ratios for plots of reciprocal HMDB isomerization quantum yield vs. 1/[HMDB].

Table II. Singlet Sensitizer Properties, HMB Exciplex-Excitation Energies, and Preference for Adiabatic HMDB Rearrangement

sensitizer	τ_f, ns[a]	$E_{1/2}$*(red), V[b]	E_{00}(exc), kcal/mol	*P*
CN	26	2.1	77	20 ± 2
DCB	13	2.7	73	32 ± 2
CA	9	1.4	64	
DCA	15	2.1	57	50 ± 3

[a] Fluorescence lifetimes in hydrocarbon solvents from the literature: M. Yoshida, H. Sakuragi, I. Tanaka, K. Tokumaru, and N. Morikawa, *Bull. Chem. Soc. Jpn.*, **48**, 2399 (1975); M. E. R. Marcondes, V. G. Toscano, and R. G. Weiss, *J. Am. Chem. Soc.*, **97**, 4485 (1975); E. Vander Donckt, M. R. Barthels, N. Antheunis, and M. Swinnen, *Mol. Photochem.*, **8**, 121 (1977); ref 1b. [b] $E_{1/2}$*(red) = $E_{1/2}$(red) + sensitizer singlet energy; sensitizer ground-state reduction potentials (vs. SCE, CH_3CN) are reported: E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967); D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, **98**, 5901 (1976).

Fluorescence quenching efficiencies of HMDB and HMB toward four aromatic nitriles were measured in cyclohexane. Quenching rate constants (Table I) were computed from Stern–Volmer plots using literature data for sensitizer fluorescence lifetimes (Table II). The parallel between quenching rate and redox properties (similar oxidation potentials for HMDB and HMB[4] and varied reduction potentials for the