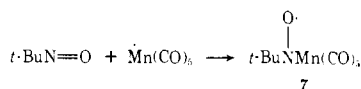


observed in the present investigations do not occur by way of intermediate carbanions such as might be generated by reactions similar to eq 1 and 3. It is important to note, however, that for such a process to be competitive with the rearrangement of the cyclopropylcarbonyl radical would require a minimum increase of $>10^{10}$ in the rate of rearrangement of the cyclopropylcarbonyl anion over that observed for cyclopropylcarbonylmagnesium bromide. While perhaps not impossible, an increase of such magnitude seems physically unreasonable under the present circumstances. We, therefore, feel justified in concluding that the rearrangement leading to 4 and 6 occurs essentially exclusively by a free radical pathway.

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 (19) (a) Indirect ESR evidence for the involvement of the manganese penta-carbonyl radical in the above reaction with tropylium cations was obtained by reacting the manganate anion with a mixture of *tert*-nitrosobutane and the tropylium salt in the ESR cavity. An intense spectrum of 18 lines of equal intensity was obtained under flow conditions which is appropriate for the nitroxide adduct 7 ($a^N = 17.39$ G, $a^{Mn} = 12.56$ G, $g = 2.0056$). Control



experiments with each reagent and *tert*-nitrosobutane did not yield nitroxide radicals under the same conditions.

(b) Cf. also A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 966 (1974).

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Homogeneous Catalysis by Ruthenium Carbonyl in Alkaline Solution: the Water Gas Shift Reaction

Sir:

Methods of activating the reactions of carbon monoxide have long been a major area of catalysis research.¹ Of particular interest, both from the standpoint of its fundamental chemistry and for its obvious commercial value, is the water gas shift reaction (eq 1).



By this process, the reducing equivalents of CO can be converted to the more useable form of molecular hydrogen with relatively little loss in thermochemical potential.² Current methods for effecting this conversion involve heterogeneous catalysis at high temperature,³ and to our knowledge there are no published examples of systems which catalyze this reaction cleanly in homogeneous solution.⁴ In considering possible homogeneous catalysts, metal carbonyl complexes are logical candidates given the recent reports that certain coordinated carbonyls are activated toward nucleophilic attack of water.⁵ In addition, various metal carbonyl clusters have been shown as homogeneous catalysts in the oxidation and/or reduction of carbon monoxide.⁶ In these contexts we are exploring the possible catalysis of the water gas shift reaction by metal carbonyl complexes, and here we describe conditions where a homogeneous solution prepared from triruthenium dodecacarbonyl [$\text{Ru}_3(\text{CO})_{12}$] is an active catalyst under relatively mild conditions. It is additionally noteworthy that the catalyst is very active toward decomposition of formate to H_2 and CO_2 under conditions active for the water gas shift reaction.

For a run under typical conditions, the catalysis solution

contained the following components in 15 ml of purified ethoxyethanol solvent: $\text{Ru}_3(\text{CO})_{12}$ (0.126 g, 2×10^{-4} mol), KOH (~ 0.5 g, ~ 0.01 mol), and H_2O (1.0 g, 0.06 mol). When this solution was heated at 100 °C with stirring under 1 atm of carbon monoxide, the initially yellow color of the solution (attributed to the dissolved $\text{Ru}_3(\text{CO})_{12}$) changed to a deep red-brown. Periodic sampling of the gaseous phase over the solution (total volume ~ 320 ml at 25 °C) and analysis by high resolution VPC (Hewlett Packard 5830A programmable GC) demonstrated conversion of the initially pure CO phase to one containing substantial amounts of H_2 and CO_2 . Analysis of the gas phase after 73 h gave a composition of 5.6% H_2 , 6.5% CO_2 , plus 88% CO, while analysis after 144 h gave 10.4% H_2 , 8.5% CO_2 , plus 77% CO. The latter figures indicate production of $\sim 1.4 \times 10^{-3}$ mol of H_2 representing 7 mol of H_2 per mole of $\text{Ru}_3(\text{CO})_{12}$ initially added. The catalyst maintains an approximately constant activity over this sampling period with no observable changes in appearance. Also, the catalyst activity remains approximately constant or is perhaps slightly enhanced after flushing the system with fresh CO and restarting. (In contrast, carrying out the reaction under a N_2 rather than a CO atmosphere leads to an apparently stoichiometric reaction giving some H_2 and CO_2 but also simultaneous catalyst decomposition to metallic ruthenium.) When the temperature of reaction solutions is raised to 110 °C the rate of H_2 formation is approximately quadrupled over that at 100 °C and a similar increase is noted again for the 10° raise to 120 °C. When the temperature was lowered back to 100 °C the catalyst activity returned approximately to that noted above. Over a period of 30 days the total hydrogen produced by this system equaled $\sim 3 \times 10^{-2}$ mol, which represents a ratio of 150 mol of H_2 per mole of $\text{Ru}_3(\text{CO})_{12}$ initially added or 3 mol of H_2 per mole of KOH added.⁷ Notably, the gas phase analyses also indicated trace quantities of a peak with the same retention time as methanol; however, GC analysis of the solvent at reaction conclusion showed no methanol as a solution phase product. Methane, another possible CO reduction product, was not found in either analysis.

The following observations support our conclusion that the described system is a *homogeneous catalyst*, for the water gas shift reaction. (1) The identity of the H_2 product was confirmed by mass spectrometry. (2) When the reaction was carried out with a solution prepared from deuterium exchanged solvent (CH_3OD or $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OD}$) and D_2O ,⁸ D_2 ($>90\%$), HD (4–8%), and H_2 ($<2\%$) were the hydrogen products as analyzed by mass spectrometry. This confirms that water or water exchangeable hydrogen is the source of the molecular hydrogen produced and that this hydrogen is not the product of solvent decomposition.⁹ (3) Formation of H_2 clearly exceeds the molar quantities of KOH and $\text{Ru}_3(\text{CO})_{12}$ added and thus cannot represent the stoichiometric reaction of base with coordinated carbon monoxide. That this system can be catalytic in base undoubtedly results from the fact that under the reaction conditions potassium bicarbonate in ethoxyethanol is unstable and decomposes to CO_2 plus KOH.¹⁰ (4) Lastly, the homogeneity of the reaction solution is indicated by its clarity (no turbidity) when examined visually with a strong light and by the fact that an active catalyst solution displayed the same rate of H_2 production at 110 °C before and after filtration of the catalyst solution through a Fluoropore filter (FHLP, 0.5 μ pore size) under a purified nitrogen atmosphere.

Formate ion or formic acid are potential products or intermediates in a reaction system involving the oxidation of carbon monoxide by water.^{4,11} Thus it is of interest to note that the present catalyst solution is very active toward the decomposition of formate to H_2 plus CO_2 (eq 2).



On the basis of the VPC analysis of the H₂ produced, quantitative decomposition to H₂ plus CO₂ occurs when formic acid (1 ml) was added to a catalyst solution and heated in a bomb at 110 °C overnight. Since the same solution had been used previously to effect the water gas shift reaction under similar conditions, it is evident that any formate produced during the water gas shift reaction would have decomposed to H₂ plus CO₂. A more quantitative indication of the activity of this system toward formate decomposition is the observation that at 75 °C a catalyst solution prepared from 0.063 g of Ru₃(CO)₁₂ (1 × 10⁻⁴ mole), 0.44 g of KOH plus 1.0 ml of H₂O in 15 ml of ethoxyethanol in an all-glass apparatus decomposed an added 0.25-ml sample of 77.5% aqueous HCO₂H (5 × 10⁻³ mol of HCO₂H) with a half-life of ~300 s.

At this stage our comments regarding the possible active ruthenium species in the catalyst system are largely speculative. The active catalyst solution has a color and IR spectrum different from the initial Ru₃(CO)₁₂, thus we conclude that this species is not the principal one present. The complexity of the IR spectrum in the carbonyl stretching region (ν_{CO} 2030 (ms), 2014 (s), 1994 (s), 1972 (s), 1952 (s, sh) cm⁻¹) would suggest the presence of polynuclear carbonyl complexes, perhaps anionic and/or hydridic as well, although the alternative explanation would be several simpler metal carbonyl species. The solid residue isolated after low temperature evaporation of the solvent displays the same carbonyl stretching bands with additionally observed bands at 2070 (w) and 1920 (m) cm⁻¹. The reaction of Ru₃(CO)₁₂ with potassium hydroxide followed by acidification does yield the hydrido carbonyl species H₄Ru₄(CO)₁₂ and H₂Ru₄(CO)₁₃,¹² and anions of such species are produced under similar conditions.¹³ Thus these types of clusters are logical candidates as components of the catalyst solutions. Also, the formation of hydrido anionic carbonyl cluster compounds has been noted for the reactions of hydroxide with the iridium cluster Ir₄(CO)₁₂. In this case, the species produced have been observed to be active in the reduction of CO to formate.¹¹

Continuing work in this laboratory is directed toward a more positive characterization of the active species in the catalyst solution and toward methods of improving the catalyst efficiency and reaction rate by variation of reaction conditions and catalyst composition.

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- (a) Although the homogeneous catalyst described here appears to have only moderate activity, it is instructive to compare this activity to that of a standard commercial heterogeneous catalyst (Girdler G-3A CO conversion catalyst—principally Fe₃O₄) under similar conditions. An estimate of the activity of the commercial catalyst operated in an isothermal plug flow packed bed reactor ($E_a = 28.3$ kcal/mol) indicates that at 110 °C under 1 atm of CO this catalyst would produce several orders of magnitude less H₂ per gram mole of the catalyst per unit time than does the homogeneous catalyst reported here. (b) The ruthenium based homogeneous catalysis has been examined under a variety of conditions. More rapid conversion to H₂ plus CO₂ was observed when the reaction was carried out under higher CO pressure in a stainless steel bomb equipped with a Teflon liner. Activity was noted both in ethoxyethanol and methanol solvents. For example, a run carried out under 48 atm of CO with a catalyst solution of 0.021 g of Ru₃(CO)₁₂, 1.0 g of H₂O, and 0.2 g of KOH in 6 ml of reagent methanol and heated at 110 °C for 96 h led to the formation of 150 mol of H₂ per mole of added Ru₃(CO)₁₂ (corrected for H₂ produced under control conditions).
- The solutions contained about 5–10% exchangeable ¹H owing to the use of KOH (not KOD) as the source of the base.
- In agreement with this conclusion, the IR and NMR spectra of ethoxyethanol solvent (after bulb to bulb low temperature vacuum distillation from the reaction solution) display no features other than those seen in wet ethoxyethanol.
- For example, 0.01 mol of KHCO₃ in solution of 15 ml of ethoxyethanol plus 1 ml of H₂O evolved the theoretical amount of CO₂ after several hours of heating at 120 °C under 1 atm pressure.
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Conjugate Addition of Vinylcopper Complexes Derived from Addition of Alkylcopper Complexes to Acetylenes. A Stereospecific Synthesis of Trisubstituted Olefins

Sir:

The development of general methods for the stereospecific synthesis of trisubstituted olefins¹ has become a major goal of organic chemists mainly because of the occurrence in nature of many compounds of this class having significant biological activity.² Several methods have been reported for the synthesis of simple, nonfunctionalized, trisubstituted olefins,³ but of greater importance are those methods which afford olefins bearing functional groups which may be employed in further structural transformations.⁴ We wish to report a new, convenient, very general, and stereospecific route to functionalized, trisubstituted olefins.

The conjugate addition of vinylcuprates, **1a**, to Michael acceptors such as α,β -unsaturated carbonyl compounds is a commonly used route to disubstituted olefins (e.g., **2a**) bearing various functional groups (eq 1).^{5,6} However, this approach has not been practical for the corresponding trisubstituted olefins, **2b**, in the past because the requisite disubstituted vinylcuprates, **1b**, were not as readily available as the mono-substituted species, **1a**. A prospective solution to this problem was provided in recent reports by Normant of a novel reaction (eq 2) in which alkylcopper complexes derived from alkyl-magnesium halides undergo addition to simple terminal acetylenes to give disubstituted vinylcopper complexes, **3**.⁷ Reactions of **3** with various electrophilic reagents were reported, including reactions with alkyl halides,^{7b-h} to produce