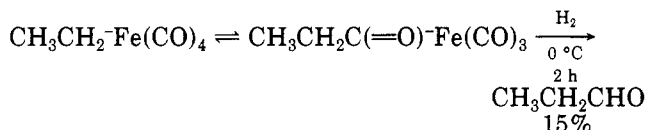


in this case when compared with the analogous reaction of 1 with 5; only a 35% yield of aldehyde was realized after a 2-h period even though a substantially higher concentration of the acyl species was initially present. This experiment attests to the importance of an unsaturated acyl intermediate in the production of aldehyde. Acidification of the mixture from the reaction of 1 with 7 after 2 h with excess acetic acid resulted in a 95% yield of aldehyde, indicating that species 7 was not consumed by other processes and was intact after a 2-h period.

Attempted hydrogenation of 5 in THF with 1 atm of H₂ at 0 °C yielded a small amount (15%) of aldehyde after a 2-h period. Formation of aldehyde by oxidative addition

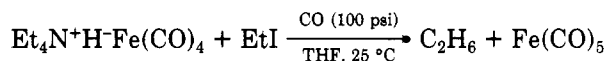


of H₂ to an unsaturated metal acyl species is the product-forming step in the hydroformylation reaction.¹⁰ In this case, the rate of oxidative addition of 1 to 6 must be much faster than to H₂ because the reductive elimination step would be expected to be rapid in either case.

In an attempt to understand how the hydride 1 interacts with 5 (or 6), the reaction of 5 with more traditional hydride sources was performed. Addition of either NaBH₄¹¹ or LiAlH₄ in excess to THF solutions of 5 failed to produce evidence of any reaction having taken place. Infrared analysis showed that 5 remained intact over a 2-h period during which no ethane, propionaldehyde, or propanol formation could be detected by gas chromatographic analysis. Although both of these reducing agents are considerably stronger hydride sources than 1, neither would be expected to coordinate (or oxidatively add) to species 6.

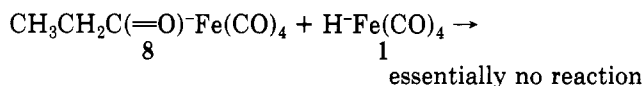
When the rates of reactivity of 1 with both 5 and 7 are contrasted, another potential mechanism by which aldehyde could be produced can be eliminated. The hydride 1 could act as an acid⁵ which transfers a proton to 6 or 7 with subsequent elimination of aldehyde. However, were this to occur, the more basic of the two species, anion 7, would yield aldehyde at a faster rate, and this was not observed.

Protonation of the alkyliron anion 5 would yield the neutral alkyliron hydride 3, an intermediate proposed in the Reppe process. This species has been shown to eliminate alkane in the absence of CO.¹² We found that even under 100 psi of CO pressure this unstable intermediate, prepared in situ from 1 and ethyl iodide at ambient temperature generates ethane and not aldehyde. Therefore, at least under the conditions employed in these studies



aldehyde production is not due to a mononuclear elimination process. Whether the mechanism of aldehyde formation from the binuclear species shown in Scheme II is an elimination process from only one of the two iron atoms or the result of reductive elimination from adjacent metal centers cannot be distinguished on the basis of the present work.

Finally, the reactivity of the acyl species 8 was contrasted with that of the alkyl intermediates 5. The mixture of



8 with H-Fe(CO)₄ (1) produced only traces of aldehyde after 2 h. Quenching of the reaction mixture with HOAc produced 57% propionaldehyde, indicating that a substantial amount of 8 was present at the end of this period.

The principal catalytic cycle of the Reppe-modified hydroformylation reaction is very similar to the oxo process, differing only in the manner in which the initial metal hydride is formed. Further parallels can be developed in reactions of intermediate species in both systems, which demonstrates that binuclear mechanisms are alternate potential pathways in a number of catalytic systems.

Registry No. 1, 18716-80-8; 5, 44966-61-2; 7, 83476-35-1; 8, 45048-27-9; CH₃CH₂CHO, 123-38-6.

Role of Homogeneous Formate Complexes in the Water Gas Shift Reaction Catalyzed by the Group 6 Metal Carbonyls[†]

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Summary: The mechanism of the homogeneous water gas shift reaction catalyzed by the group 6 metal carbonyls involves the intermediacy of a formate complex. Catalytic pressure reactions as well as stoichiometric photolysis and pyrolysis experiments provide support for this mechanism.

Metal formates have not been generally regarded as key intermediates in catalytic reactions of carbon oxides. However, their intermediacy has been observed in a number of catalysis-related reactions. Metal formates have been isolated in many carbon dioxide reductions.¹ Zinc formate may be pyrolyzed to methanol and formaldehyde.² Formates have been suggested in connection with the function of promoters with iron and cobalt catalysts for the Fischer-Tropsch synthesis.³ Formate intermediates have also been observed on magnesia, alumina, and iron-chromia catalysts for the water gas shift reaction (WGSR).⁴ The role of formates in zinc oxide catalyzed WGSR, carbon dioxide reduction, and methanol decomposition has been studied at varying surface coverages and temperatures by means of infrared spectroscopy.⁵

Our interest in formate intermediates is related to the oxide theory⁶ which emphasizes the importance of oxygen-bound species in catalytic reactions. Within this

[†] Dedicated to the memory of the late Professor Rolly Pettit, a friend and a teacher.

(1) Haynes, P.; Slaugh, L. H.; Kohnle, J. F. *Tetrahedron Lett.* 1970, 365.

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(10) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1961, 83, 4023.

(11) Treatment of a neutral alkylmanganese carbonyl species with NaBH₄ has been shown to yield the homologous alcohol, see: Fischer, E. O.; Aumann, R. *J. Organomet. Chem.* 1967, 8, 1.

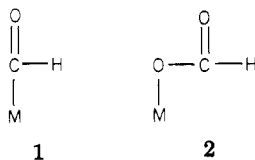
(12) Alper, H. *Tetrahedron Lett.* 1975, 2257.

Table I. $W(CO)_6$ as WGSR Catalyst in MeOH/H₂O^a

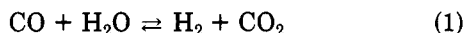
entry	base (mmol)	P_{CO} , psi	mmol of H ₂	mmol of CO ₂	t_{H_2}
1	none	130	0	0	0
2	K ₂ CO ₃ (24)	130	44	16	250
3	K ₂ CO ₃ (24)	200	31	27	170
4	K ₂ CO ₃ (24)	800	18	17	95
5	KOH (24)	200	30	14	165
6	NaO ₂ CH (48)	200	40	13	220
7	NaO ₂ CH (48)	0	43	3	240

^a Conditions: 0.18 mmol of $W(CO)_6$, 2.5 mL of H₂O diluted to 100 mL with methanol, 155 °C, 20 h, 0.31-L reactor; 0 psi of CO implies 250 psi of N₂; t_{H_2} = mol of H₂/mol of $W(CO)_6$.

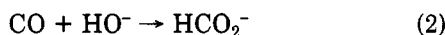
context, intermediates with metal to oxygen to carbon bonding, rather than metal to carbon, are of particular interest. Although formyl (1) intermediates have captured much interest within the catalytic community, the analogous formate (2) species have received little attention. Basically 2 is a formyl group chemisorbed on a metal oxide.



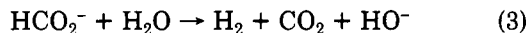
We have previously reported some evidence implicating the formate complexes $(CO)_5MO_2CH^-$ in the homogeneous WGSR



catalyzed by the group 6 metal carbonyls.⁷ Table I summarizes some results employing $W(CO)_6$ as the catalyst for eq 1 at 155 °C. Clearly base promotes the reaction. Entries 2, 3, and 4 demonstrate the pronounced effect of carbon monoxide pressure on activity: as the pressure is reduced, activity increases markedly. Entries 3, 5, and 6 suggest that the nature of the base has little bearing on activity. This is reasonable, since CO readily reacts with hydroxide to form the formate ion in solution

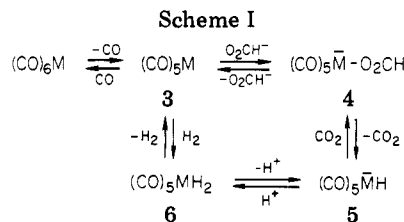


In fact very basic solutions (>pH 14) are leveled to pH 9–10, usually during the reactor warm-up period. Entry 7 demonstrates that the formate ion, in the absence of CO, may be decomposed to H₂ and CO₂ (eq 3). In fact, the yield of hydrogen corresponds to about 85% of the formate added.

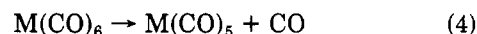


Generally the yields of CO₂ are lower than those of H₂. Although significant amounts of CO₂ may dissolve in the H₂O/CH₃OH solvent system, solution basicity may be an important factor. Entries 6 and 7 show less CO₂ observed in the absence of CO pressure, suggesting a competition between the two gases for Brønsted basicity. The experiments with K₂CO₃ show that as CO pressure is increased, larger fractions of carbon dioxide are expelled from the solution. Molybdenum and chromium carbonyls display very similar activities for eq 1 and a similar activity dependence on pressure.

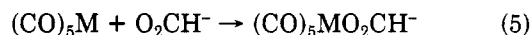
The activity dependence on CO pressure could be attributed to a dissociative mechanism, i.e., one that ne-



cessitates loss of a carbonyl ligand as a kinetically limiting step:



Once formed, the coordinately unsaturated $M(CO)_5$ species might be expected to react with formate (from eq 2) in solution to form a formate complex:



For a test of the validity of this hypothesis, chromium carbonyl (1.0 g) was photolyzed at ambient temperature in a solution (285 mL) of methanol and hexamethylphosphoramide. A 450-W Hg lamp with Vycor filter was employed in a quartz well, cooled with water. Argon was bubbled through the solution to promote gas evolution. Because of the low solubility of $Cr(CO)_6$, several photolyzing cycles were necessary to effect nearly complete conversion to the coordinately unsaturated species (eq 4). At this point, only CO and Ar were present in the gas phase. Most of the CO was swept from the system by purging with argon. After the system was allowed to cool to 30 °C in the absence of light, a solution of tetraethylammonium formate in methanol–water was added. After about 2 min, small streams of bubbles were vigorously evolved from the solution. The gases were collected and were found to contain principally Ar and H₂ with a small quantity of CO₂.

Similar experiments at ambient temperature were carried out with $Mo(CO)_6$ and $W(CO)_6$, but no appreciable H₂ was observed. In the case of the latter, the IR spectrum indicated unreacted $W(CO)_6$ along with a broad absorbance at 1910 cm⁻¹.

For minimization of side reactions, direct photolysis of $W(CO)_6$ (1 g) with tetrabutylammonium formate (0.85 g containing about 0.1 g of H₂O) in methanol was attempted. The solution quickly assumed a yellow color, and the IR displayed a decrease in the 1975-cm⁻¹ peak of $W(CO)_6$ with concomitant growth of the peak at 1910 cm⁻¹. Although the photolysis proceeded quickly, the sluggish dissolution properties of the carbonyl necessitated a 6.5-h reaction time for nearly complete loss of $W(CO)_6$. The clear, deep yellow solution afforded an IR spectrum (2060 (w), 1910 (s), 1840 (mw), 1605 (mbr) cm⁻¹) in accord with that reported for $(CO)_5WO_2CH^-$.⁸⁻¹⁰

Removal of the solvent from the photolysis solution yielded a viscous, yellow oil displaying the same IR, although somewhat broadened. Heating a solution of the formate complex in a sealed tube at 100 °C resulted in the liberation of H₂, CO, and CO₂ with the fate of the metal dependent on the solvent. In air, a methanol solution of the formate complex is cleanly converted to a mixture of $HW_2(CO)_{10}^-$ and $W(CO)_6$.

We believe the above results are in accord with the mechanism presented in Scheme I. Thermally or photolytically promoted loss of CO from the metal carbonyl

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results in the formation of the coordinately unsaturated 3. The photolysis experiments indicate that 3 reacts readily with formate, which in turn is rapidly formed from the reaction of CO with hydroxide, to yield the formate complex 4. The chromium formate complex readily loses CO₂ to form 5 at ambient temperature, while the tungsten formate may be readily isolated and decarboxylates slowly and may be isolated, in accord with the results recently reported by the Darensbourg group.¹⁰ Protonation of 5 has been reported to yield H₂.¹⁰

Studies of other homogeneous WGS systems have pointed toward associative mechanisms.^{7,11} The similarities between the heterogeneous WGS and the homogeneous WGS catalyzed by the group 6 metal carbonyls are worthy of note.

Registry No. Formate, 71-47-6.

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Reaction of Lithium Dimethylcuprate with C₆H₆Mn(CO)₃⁺. Observation of Methyl Group Migration from Manganese to the Arene Ring in C₆H₆(CO)₂Mn-CH₃[†]

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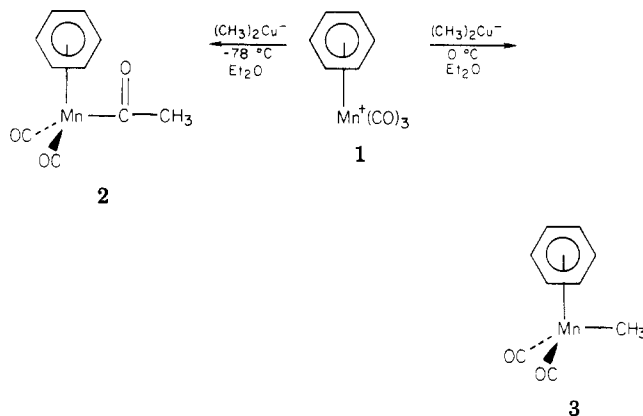
Received August 31, 1982

Summary: C₆H₆(CO)₂Mn-CH₃, prepared by the reaction of lithium dimethylcuprate with C₆H₆Mn(CO)₃⁺, yields 6-*endo*-C₆H₆(CH₃)Mn(CO)₂(PPh₃) via intramolecular methyl migration to the arene ring in the presence of triphenylphosphine.

The reaction of (arene)manganese tricarbonyl cations with nucleophiles normally results in exo attack at the ring and formation of the corresponding 6-*exo*-substituted cyclohexadienylmanganese tricarbonyl complexes.¹⁻³ In the reaction of the unsubstituted cation C₆H₆Mn(CO)₃⁺, 1, with lithium aluminum hydride, a minor side product, C₆H₆(CO)₂Mn-CH₃, 3 (0.6%), can be observed, apparently formed from hydride reduction of coordinated CO.¹ Yields of the dicarbonyl methyl complexes rise as the ring is progressively alkylated. Thus, hydride reduction of the C₆Me₆Mn(CO)₃⁺ system yields ca. 8% C₆Me₆(CO)₂Mn-CH₃.¹ A similar trend is noted for addition of methyl-lithium. Reaction of C₆H₆Mn(CO)₃⁺ with CH₃Li yields solely (6-*exo*-methylcyclohexadienyl)manganese tricarbonyl;^{1,2a} however, for C₆Me₆Mn(CO)₃⁺ the acyl complex C₆Me₆(CO)₂Mn-COCH₃ is formed in ca. 33% yield as the only isolated product.¹

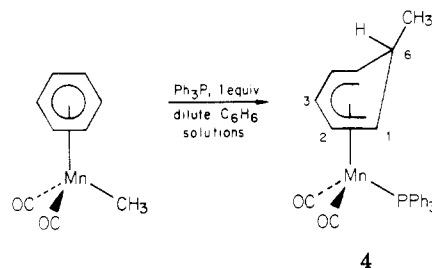
We wish to report that, in contrast to methyl lithium, reaction of lithium dimethylcuprate with the parent, un-

substituted cation, 1, results exclusively in products which are apparently derived from attack at CO and not from exo methyl addition to the ring. Treatment of 1 at -78 °C in ether with 2.5 equiv of Me₂CuLi followed by rapid workup gives the acyl complex C₆H₆(CO)₂Mn-COCH₃, 2, in 45% yield.⁴ The same reaction carried out at 0 °C gives



the methyl complex C₆H₆(CO)₂Mn-CH₃, 3, in 42% yield.⁵ The latter complex, 3, presumably results from initial formation of the acyl species 2 followed by decarbonylation; however, the manner in which decarbonylation occurs is not known.⁶

The dimethylcuprate reaction thus provides an easy and viable synthetic entry into the alkyl and acyl complexes 2 and 3, which are analogues of the exhaustively studied alkyl and acyl derivatives Fp-CH₃ and Fp-COCH₃ (Fp = Cp(CO)₂Fe). Initial results indicate that interesting differences in the chemistry of these manganese and iron analogues can be observed. Treatment of Fp-CH₃ with phosphines invariably results in CO insertion and formation of acyls Cp(CO)(L)Fe-COCH₃ (L = phosphine).⁷ In contrast, treatment of 3 (0.04 M) with 1 equiv of (C₆H₅)₃P in refluxing benzene (80 °C) for 5 days (t_{1/2} ca. 30 h) results in intramolecular migration of the methyl group to the arene and formation of (*endo*-methylcyclohexadienyl)manganese dicarbonyl triphenylphosphine, 4 (68% yield). The spectral properties are completely in accord with structure 4, and the *endo* stereochemistry is confirmed by the observed J_{6x,1} = J_{6x,5} = 0 vicinal coupling constant.⁸



[†] Dedicated to the memory of Rowland Pettit. His enthusiasm for chemistry and elegant, incisive work established standards of dedication and excellence for all of us who knew him.

(1) Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* 1976-1977, 15, 258.

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(3) Attack of amines and alcohols have been noted to occur at carbonyl; see for example: (a) Angelici, R. J.; Blacik, L. *J. Inorg. Chem.* 1972, 11, 1754. (b) Walker, P. J. C.; Mawby, R. *J. Inorg. Chim. Acta* 1973, 7, 621.

(4) Spectral properties of this species are similar to those of other acyl complexes previously reported:¹ ¹H NMR (C₆D₆) δ 2.60 (3 H, br s), 4.52 (6 H, s); IR (ν_{CO}, diethyl ether) 1965 (s), 1915 (s), 1630 (m) cm⁻¹.

(5) Spectral properties: ¹H NMR (C₆D₆) δ 0.17 (3 H, s), 4.40 (6 H, s); IR (ν_{CO}, isopentane) 1975 (s), 1930 (s) cm⁻¹; high-resolution mass spectrum, calculated 203.9983, found 203.9988. Anal. Calcd for C₉H₈MnO₂: C, 52.96; H, 4.44; Mn, 26.92. Found: C, 52.99; H, 4.51; Mn, 26.84.

(6) In some reactions carried out at 0 °C contamination of 3 by 2 was observed. If a sample of pure 2 is stirred in ether at 25 °C, it does not yield 3; thus, decarbonylation is not strictly a thermal process. If 2 is irradiated for 0.5 h, a 3:1 ratio of 2 to 3 is observed by ¹H NMR spectroscopy. However, prolonged irradiation results in total decomposition.

(7) See, for example: (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* 1974, 96, 2814. (b) Brunner, H.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 616. (c) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* 1966, 5, 889.