C_{2v} symmetry. Molecules of **3** possess crystallographic C_s-m symmetry in the solid but their Fe_3P_2 cores do not approximate C_{2v} symmetry. The Fe–P bonds to basal iron atoms Fe_1 and Fe_3 in **1** are equivalent and have an average value of 2.216 (5, 8, 17, 8) Å[19,20] which is quite similar to the 2.198 (1, 20, 21, 4)-Å average for the corresponding Fe–P bonds in **3**. The Fe_1–P and Fe_3–P bonds in **3** are not equivalent because they are trans to ligands with considerably different π-acceptor properties: Fe_1 had acetonitrile ligands trans to the two cis bridging phosphorus atoms and Fe_3 has a carbonyl ligand trans to them. Thus, the cis phosphorus atoms in **3** are competing with carbonyl ligands on Fe_3 and acetonitrile ligands on Fe_1 for back-donation of electron density from the same metal orbital. The observed 0.039-Å shortening of the Fe_1–P bonds in **3** relative to the Fe_3–P bonds is thus consistent with carbonyl being the better π-acceptor ligand. The presence of two relatively poor π-acceptor acetonitrile ligands on Fe_1 should also make it electron rich relative to Fe_3 and could explain the 0.032-Å shortening of the Fe_1–C_{11} bond relative to Fe_3–C_{31} through enhanced metal→ligand π bonding. Such an enhancement of metal–ligand π bonding for C_{11} could explain the 0.089-Å elongation of the Fe_1–Fe_2 bonds in **3** relative to Fe_2–Fe_3. The Fe_1–Fe_2 and Fe_2–Fe_3 bonds are equivalent in **1**[19] and have an average value of 2.717 (3, 1, 3, 4) Å[20] which is comparable to the 2.727 (1, 45, 49, 4)-Å average value in **3**. Similar effects have been observed in other metal cluster molecules containing acetonitrile and carbonyl ligands bonded to the same metal.[2a,c,21]

The remainder of the bond lengths and angles for **3** are unexceptional.[22] Note that the Fe–N bonds to the nitrile ligand average to 1.973 (4, 6, 6, 2) Å, which is close to the 2.00-Å sum of the respective covalent radii, and that the nitrile C–N bonds in **3** average to 1.118 (6) Å which compares with a range of 1.11 (2)–1.25 (4) Å established for terminally bonded acetonitrile in other metal complexes.[1c,4] Consistent with the weak character of the iron–nitrile bond, no elongation of the nitrile bond was detectable: the 1.118 (6) Å distance in the complexed nitrile is essentially indistinguishable from the 1.158 (2) Å value for free alkyl cyanides.[23]

Listed in Table VI are M–N and N–C distances and the M–N–C bond angles in nitrile derivatives of cluster molecules. The significant features of these parameters are the nearly linear M–N–C angles for terminally bound nitrile ligands and the close correspondence (within experimental error) in N–C distances between the free nitrile and the bound nitrile (terminally bound). However, in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}NCCH_2CH_2CH_3)$ where both the nitrogen and the carbon atoms of the NC group are bonded to metal atoms, the N–C distance is significantly increased (1.260 (30) Å vs. 1.118 (6) Å for free alkyl cyanides).

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Registry No. **1**, 38903-71-8; **2** (R = CH_3), 86372-86-3; **2** (R = C_2H_5), 86372-87-4; **3** (R = CH_3), 86372-88-5; **3** (R = C_2H_5), 86372-89-6; **4**, 58092-22-1; **5**, 86372-90-9; $Fe_3(PC_6H_5)_2(CO)_8[P(OCH_3)_3]$ (isomer 1), 86420-08-8; $Fe_3(PC_6H_5)_2(CO)_8[P(OCH_3)_3]$ (isomer 2), 86420-09-9; $Fe_3(PC_6H_5)_2(CO)_8[As(C_6H_5)_3]$ (isomer 1), 86372-92-1; $Fe_3(PC_6H_5)_2(CO)_8[As(C_6H_5)_3]$ (isomer 2), 86420-10-2; $Fe_3(PC_6H_5)_2(CO)_8[P(C_6H_5)_3]$ (isomer 1), 86372-93-2; $Fe_3(PC_6H_5)_2(CO)_8[P(C_6H_5)_3]$ (isomer 2), 86420-11-3; $Fe_3(PC_6H_5)_2(CO)_8(PF_3)$ (isomer 1), 86372-94-3; $Fe_3(PC_6H_5)_2(CO)_8(PF_3)$ (isomer 2), 86373-01-5; $Fe_3(PC_6H_5)_2(CO)_8(PF_3)$ (isomer 3), 86420-12-4; $Fe_3(PHC_6H_5)_2(CO)_6$, 39049-79-1; $Fe_3(PC_6H_5)_2(CO)_7[P(OCH_3)_3]_2$, 86391-87-9; $Co_4(PC_6H_5)_2(CO)_9[P(OCH_3)_3]$, 86372-99-8; $Co_4(PC_6H_5)_2(CO)_8[P(OCH_3)_3]_2$, 86373-00-4; $Co_4(PC_6H_5)_2(CO)_9[P(C_6H_5)_3]$, 86372-91-0; $Fe_3(PC_6H_5)_2(^{13}CO)_9$, 86372-95-4; $Fe_3(PC_6H_5)_2(^{13}CO)_8(NCC_2H_5)$, 86372-96-5; $Fe_3(PC_6H_5)_2(^{13}CO)_7(NCCH_3)_2$, 86372-97-6; $Fe_3(PC_6H_5)_2(^{13}CO)_8[P(OCH_3)_3]$, 86372-98-7; $N_{92}Fe(CO)_4$, 14878-31-0; $Na_2Fe_2(CO)_8$, 64913-30-0; $Co_2(CO)_8$, 10210-68-1; Fe, 7439-89-6; Co, 7440-48-4; $C_6H_5PCl_2$, 644-97-3; CH_3CN, 75-05-8; $NCCH_2CH_3$, 107-12-0; $P(OMe)_3$, 121-45-9; $As(C_6H_5)_3$, 603-32-7; $P(C_6H_5)_3$, 603-35-0; PF_3, 7783-55-3; HCl, 7647-01-0; ^{13}CO, 1641-69-6; iron pentacarbonyl, 13463-40-6.

Supplementary Material Available: Crystal structure analysis report, Tables II and III, positional and thermal parameters for non-hydrogen atoms and refined hydrogen atom positions for **3**, and structure factor tables (24 pages). Ordering information is given on any current masthead page.

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[21] (a) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Oxton, I. A.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 289. (b) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2119.

[22] There were no intermolecular contacts significantly less than the corresponding van der Waals values.

[23] "Interatomic Distances 1960-65"; Crystallographic Data Centre: Cambridge, **1972**; Vol. A1, p 52.

[24] Raithby, P. R., private communication.

The Role of Acetyl Complexes in the Cobalt-Catalyzed Homologation of Methanol

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It is shown that stoichiometric hydrogenation of $MeCOCo(CO)_3PMePh_2$ in methanol yields a product distribution similar to that obtained during the homologation of methanol catalyzed by $[Co(CO)_3PMePh_2]_2$. The result suggests that the acetyl compound is an intermediate during the catalytic reaction.

Introduction

Much of the current interest in transition-metal-catalyzed reactions of synthesis gas is derived from the impending need to find new processes for the conversion of coal to feedstocks for the organic chemical industry.[1,2] Of great potential importance[3,4] is the alcohol homologation reaction, in which an alcohol, RCH_2OH, is converted to its next higher homologue, i.e., eq 1. This cobalt carbonyl catalyzed reaction was first reported in 1949[5] but elicited

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[1] Falbe, J., Ed. "New Syntheses with Carbon Monoxide"; Springer-Verlag: New York, 1980.

[2] Falbe, J., Ed. Chemical Feedstocks from Coal; Wiley: New York, 1982.

[3] Bahrmann, H.; Cornils, B., ref 1, p 226.

[4] Cornils, B.; Rottig, W., ref 2, p 477.

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$$RCH_2OH + CO + 2H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2OH + H_2O \quad (1)$$

little general interest over the next 30 years.[3,6] Little is therefore known mechanistically about the reaction, and there are considerable differences of opinion about the mechanism in the literature,[3,6] even for as simple a substrate as methanol. Slocum[6b] has eloquently argued for the series of steps shown in eq 2–7 for methanol homologation.

$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4 \quad (2)$$

$$HCo(CO)_4 + MeOH \rightarrow MeOH_2^+ + Co(CO)_4^- \quad (3)$$

$$MeOH_2^+ + Co(CO)_4^- \rightarrow MeCo(CO)_4 + H_2O \quad (4)$$

$$MeCo(CO)_4 + CO \rightarrow MeCOCo(CO)_4 \quad (5)$$

$$MeCOCo(CO)_4 + H_2 \rightarrow MeCHO + HCo(CO)_4 \quad (6a)$$

$$\text{or } MeCOCo(CO)_4 + HCo(CO)_4 \rightarrow MeCHO + Co_2(CO)_8 \quad (6b)$$

$$MeCHO + H_2 \rightarrow MeCH_2OH \quad (7)$$

Most of these steps have precedent in the relatively well-understood olefin hydroformylation catalysis by cobalt carbonyls,[7-9] but several controversial issues remain. For instance step 4, in which a cobalt–carbon bond is formed following methanol protonation by the strong acid $HCo(CO)_4$,[10,11] has not been demonstrated as a stoichiometric reaction although the product is a known compound.[12] Furthermore while the role of iodide ion as a cocatalyst is probably to be rationalized in terms of formation of the good alkylating agent methyl iodide,[6] the role of tertiary phosphines as catalyst modifiers is not at all clear.[6c] In fact the presence of a tertiary phosphine in a cobalt homologation system would probably result in the formation of weak acids of the type $HCo(CO)_3PR_3$ (R = alkyl, aryl) as intermediates,[13] and step 3 would not be feasible. The relative importance of the two routes, (6a) and (6b), by which the acetyl compound $MeCOCo(CO)_4$ may be cleaved, still seems to be somewhat controversial,[14] and only one relevant but brief study of the cleavage step in a phosphine-containing system has appeared in the literature.[15] Finally, of course, even the significance of the hydroformylation sequence as a basis of discussion of the homologation reaction may be suspect, as the solvent systems used for the two types of catalysis are often quite different; many of the mechanistic studies carried out on hydroformylation have utilized nonpolar solvents, while methanol homologation is, of course, best carried out in methanol.

It seemed clear, therefore, that further work was needed to ascertain the possible importance of the putative intermediates $MeCo(CO)_3L$ and $MeCOCo(CO)_3L$ (L = CO, tertiary phosphine). As the tetracarbonyl compounds are rather thermally unstable,[13] we decided to synthesize the compounds $[Co(CO)_3PMePh_2]_2$, $HCo(CO)_3PMePh_2$, and $MeCOCo(CO)_3PMePh_2$ in order to assess their possible roles in methanol homologation. To this end, we have determined the product distributions obtained on treating the acetyl compound with both $HCo(CO)_3PMePh_2$ and with hydrogen and have compared the resulting product distributions with those obtained on using $[Co(CO)_3PMePh_2]_2$ as a homologation catalyst. The results strongly suggest the validity of a sequence of steps similar to that illustrated in (2)–(7).

Experimental Section

Most ^1H NMR spectra were run on a Bruker HX 60 spectrometer and some on a Bruker CXP 200 spectrometer; all ^{13}C and ^{31}P spectra were run on the latter instrument. IR spectra were recorded on a Beckman IR 4240 spectrometer and GC analyses on a Hewlett-Packard 5880A with FI and TC detectors and either a 4 m × 2 mm Porapak Q packed column or a J. & W. Scientific 30 m × 0.25 m Carbowax 20 capillary column. GC–MS studies were carried out by using a Finnigan Model 1020 automated spectrometer and assisted by a computerized Finnigan NBS Library compilation.

High-pressure reactions were carried out in a 300-mL Parr mini reactor as described below; other syntheses were performed under nitrogen. Elemental analyses were done by Canadian Microanalytical Services Ltd., Vancouver.

The compounds $[Co(CO)_3PPh_3]_2$ (I) and $[Co(CO)_3PMePh_2]_2$ (II) were prepared as in the literature[16] by treating $Co_2(CO)_8$ (Strem) with the corresponding phosphines in benzene. The synthesis of the $PMePh_2$ derivative has not been previously described in detail, but it was found that the dark reddish brown compound could be readily recrystallized from methylene chloride–petroleum ether (bp 40–60 °C). It is air-stable in the solid but mildly air-sensitive in solution: IR (CS_2) 2046 (w), 1973 (m), 1955 (s), 1930 (m), 1897 (w), cm^{-1}; ^1H NMR (C_6D_6) δ 1.66 (m, see Discussion, MeP); 6.9–7.5 (m, Ph); ^{31}P NMR (C_6H_6) δ 50.4. The compound $MeCo(CO)_3PPh_3$ (III) was prepared by treating $Na[Co(CO)_3PPh_3]$ with methyl iodide,[11b] while $MeCOCo(CO)_3PPh_3$ (IV) was prepared by treating $K[Co(CO)_4]$[17] with methyl iodide in the presence of a stoichimetric amount of PPh_3 at 0 °C.[18] These two compounds exhibit methyl proton chemical shifts ($CDCl_3$) at δ 0.97 (d, J(PH) = 2.0 Hz) and 2.80 (d, J(PH) = 1.0 Hz), respectively.

Tricarbonylmethyl(methyldiphenylphosphine)cobalt(I), $MeCo(CO)_3PMePh_2$ (V). This new compound was prepared by stirring $[Co(CO)_3PMePh_2]_2$ (2.0 g, 2.9×10^{-3} mol) in 200 mL of tetrahydrofuran with 20 mL of 5% sodium amalgam for 5 h. The amalgam was removed, the solution of $Na[Co(CO)_3PMePh_2]$ was cooled to −78 °C, and methyl iodide (1.0 mL, 1.6×10^{-2} mol) was added. The mixture was stirred for 1 h, and the solvent was removed under reduced pressure to give a dark, gummy solid. Extraction at room temperature with ethyl ether gave an orange-yellow solution; removal of the ether gave the product as an air-sensitive oil, identified by NMR spectroscopy and by its reaction with carbon monoxide to give the better characterized acetyl derivative (see below): ^1H NMR (C_6D_6) δ 0.93 (d, J(PH) = 1.7 Hz, MeCo), 1.27 (d, J(PH) = 8.5 Hz, MeP).

Acetyltricarbonyl(methyldiphenylphosphine)cobalt(I), $MeCOCo(CO)_3PMePh_2$ (VI). A solution of $[Co(CO)_3PMePh_2]_2$

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[5] Wender, I.; Orchin, M.; Levine, R. *J. Am. Chem. Soc.* **1949**, *71*, 4160.

[6] For general reviews, see: (a) Piacenti, F.; Bianchi, M., In "Organic Syntheses via Metal Carbonyls"; and Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 1. (b) Slocum, D. W., In "Catalysis in Organic Synthesis"; Jones, W. H., Ed.; Academic Press: New York, 1980; p 245; (c) Pretzer, W. R.; Kobylinski, T. P. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 58.

[7] Pino, P.; Piacenti, F.; Bianchi, M., In "Organic Syntheses via Metal Carbonyls"; Wender, I., and Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 43.

[8] Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1.

[9] Cornils, B., ref 1, p 1.

[10] Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717.

[11] (a) Hieber, W.; Hubel, W. *Z. Elektrochem.* **1953**, *57*, 235. (b) Hieber, W.; Lindner, E. *Chem. Ber.* **1961**, *94*, 1417. (c) Hieber, W.; Duchatsch, H. *Ibid.* **1965**, *98*, 2933.

[12] Hieber, W.; Vohler, O.; Braun, G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1958**, *13B*, 192.

[13] Kemmitt, R. D. W.; Russell, D. R., In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., and Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 5, p 1.

[14] Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

[15] Piacenti, F.; Bianchi, M.; Benedetti, E. *Chim. Ind. (Milan)* **1967**, *49*, 245.

[16] (a) Manning, A. R. *J. Chem. Soc. A* **1968**, 1135. (b) Manning, A. R.; Miller, J. R. *Ibid.* **1970**, 3352.

[17] Steinhardt, P. C.; Gladfelter, W. L.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 332.

[18] Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499.

(4.0 g, 5.8×10^{-3} mol) in 100 mL of tetrahydrofuran was stirred with 20 mL of 5% sodium amalgam for 5 h. The amalgam was removed, methyl iodide (2.2 mL, 3.5×10^{-2} mol) was added, and the solution was stirred for 2 h as carbon monoxide was bubbled through it. The solvent was then removed under reduced pressure, the residue was extracted with ethyl ether, the yellow ether solution was concentrated to approximately 10 mL, and approximately 10 mL of *n*-hexane was added to induce crystallization of the product as a yellow powder in 70–90% yield: IR (c-C_6H_{12}) 2049 (w) 1984 (s), 1962 (s), 1691 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 1.42 (d, J(PH) = 8.1 Hz, MeP), 2.63 (d, J(PH) = 0.9 Hz, MeCO), 7–7.3 (m, Ph); ^{31}P NMR (C_6H_6) δ 33.4; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 19.7 (d, J(PC) = 27.7 Hz, MeP), 51.5 (d, J(PC) = 27.7 Hz, MeCO), 130.6 (d, J(PC) = 9.1 Hz, $C_{3,5}$), 132.2 (s, C_4), 133.3 (d, J(PC) = 11.1 Hz, $C_{2,6}$), 137.4 (d, J(PC) = 42.8 Hz, C_1), 201.4 (br, terminal CO). Anal. Calcd for $C_{18}H_{16}CoO_4P$: C, 55.98; H, 4.18. Found: C, 55.86; H, 4.90.

Carbon-13 labeled $MeCOCo(CO)_3PMePh_2$ was prepared similarly by using 5% enriched methyl iodide (purchased as 60% enriched material from MSD Isotopes): ^1H NMR (C_6D_6) $^1J(C{-}H_3)$ = 124.1 Hz.

Tricarbonylhydrido(methyldiphenylphosphine)cobalt(I), $HCo(CO)_3PMePh_2$ (VII). A solution of $Na[Co(CO)_3PMePh_2]$ was prepared as above from 2.0 g of $[Co(CO)_3PMePh_2]_2$, cooled to −35 °C, and, under an atmosphere of hydrogen, treated with 2.5 mL of 85% phosphoric acid in 10 mL of water. The solution was stirred for 10 min, brought up to −10 °C, and quickly taken to dryness under reduced pressure. Hydrogen was readmitted to the flask, the solid residue was extracted with a 1:2 ethyl ether–water mixture, the water layer was frozen, the yellow ether layer was decanted, and the ether was removed under reduced pressure. At this point, the residue was oily and appeared to contain traces of water. It was therefore dissolved in 1:1 ethyl ether–petroleum ether (bp 40–60 °C), whereupon precipitation of the product (dark brown) in 30% yield was observed. The hydride is thermally labile and could not be recrystallized satisfactorily. The presence of the expected hydride resonance in the ^1H NMR spectrum, however, verified the structure: IR (Et_2O) 1979 (w), 1958 (s) cm^{-1}; ^1H NMR (C_6D_6) δ −10.4 (d, J(PH) = 50 Hz, HCo), 1.52 (d, J(PH) = 8.5 Hz, MeP), 7.2 (m, Ph); ^{31}P NMR (C_6D_6) δ 41.0.

Low-Pressure Reactions of III, V, and VI. A solution of III in $CDCl_3$ was treated with carbon monoxide for 20 min. The ^1H NMR spectrum showed that the III had been quantitatively converted to IV. A similar study of V in C_6D_6 showed that the corresponding conversion to VI was about 50% completed after 10 min and quantitative after 30 min. In contrast, a solution of VI in C_6D_6 showed essentially no reaction (^1H NMR, IR) with hydrogen at 1 atm after 24 h.

High-Pressure Hydrogenation Reactions of VI. The reactions generally involved solutions of VI (approximately 0.5 g, approximately 1.3×10^{-3} mol) in 25.0 mL of solvent (toluene or methanol) containing 16.0 μL (1.23×10^{-4} mol) of *n*-hexane as GC standard. The solutions were placed in the Parr mini reactor (glass liner), and the reactor was first flushed and then pressured with hydrogen to 35 atm. In most cases, the reactor was heated to the desired temperature, a process which took from 7 to 12 min according to the internal temperature control device. The reactor was then cooled in a dry ice–2-propanol bath to below −60 °C and opened. An aliquot (approximately 2 mL) of the solution was removed and vacuum distilled to dryness, and the distillate was analyzed by GC and/or GC–MS. Selected residues from the distillations were also analyzed by using combinations of IR, ^1H NMR, and ^{31}P NMR spectroscopy. A blank run was also carried out in toluene under nitrogen.

Hydrogenation of VI enriched in carbon-13 at the acetyl position was carried out similarly by using benzene-d_6 and methanol as solvents. In these cases, the distillates were also analyzed by ^1H and/or ^{13}C NMR spectroscopy.

Miscellaneous Reactions. In some cases, a cobalt mirror formed on the glass liner of the reactor, leading to the possibility of heterogeneously catalyzed reactions. Treatment of acetaldehyde in toluene with 35 atm of hydrogen in the presence of such a mirror at 75 °C for 11 min resulted in no reaction. Similarly the attempted reaction of acetaldehyde (3.6×10^{3} g, 8.1×10^{-5} mol) with VII (0.056 g, 1.6×10^{-4} mol) in toluene at room temperature for 20 h led to 91% recovery of the acetaldehyde. An IR spectrum of the residue showed it to be $[Co(CO)_3PMePh_2]_2$.

A reaction of VI and VII in methanol was also attempted. The hydride was generated by treating a solution of $Na[Co(CO)_3PMePh_2]$ in methanol with phosphoric acid at −30 °C. An approximately equimolar amount of VI was added, and the reaction mixture was stirred for 3 h at −30 °C and then for 24 h at room temperature, during which time it turned from gray to orange in color. Periodically the organic products were monitored by GC and the organometallic by IR spectroscopy.

Catalytic Methanol Homologation. A solution of II (1.0 g), methyl iodide (0.09 mL), and *n*-hexane (1.0 mL) in 45.0 mL of methanol was pressured to 63 atm with 1:1 hydrogen–carbon monoxide. The reactor was heated to 125 °C, attaining a pressure of 77 atm, and held at these conditions for 26 h. The reactor was then cooled and opened as described above, and the resulting orange yellow solution was analyzed for organic and cobalt-containing products in the usual manner.

Results and Discussion

Syntheses and Properties of Phosphine-Substituted Cobalt Carbonyl Compounds. The tetracarbonylcobalt compounds analogous to those studied here are very unstable thermally, generally decomposing below 0 °C.[13] Therefore, when this work was undertaken, it was decided to substitute a carbon monoxide by a tertiary phosphine because of both the expected increased stability[13] and the potential for chemistry different from that of the unsubstituted analogues; as mentioned in the Introduction, phosphines play an important role as catalyst modifiers in cobalt homologation systems. Although triphenylphosphine was originally chosen because the complexes $XCo(CO)_3PPh_3$ (X = H, Me, MeCO) were all known, it was soon discovered that the dimeric precursor to these compounds $[Co(CO)_3PPh_3]_2$ was too insoluble in all solvents for it to be convenient to work with. The methyldiphenylphosphine system, in contrast, proved to be a very useful alternate. Its compounds were found to be crystalline solids with good solubility properties. Also, as shown in the Experimental Section, the phosphine methyl resonances in the ^1H NMR spectra provided very useful criteria for the spectroscopic identification of species in solution.

The dimer II had been briefly mentioned in the literature[16] and was found to be reasonably air-stable as a crystalline solid. Its ^1H NMR spectrum in the methyl region exhibits the multiplet structure characteristic of an $X_3AA'X_3'$ spin system[19] and was not analyzed in detail although the separation between the two most prominant peaks, 8.8 Hz, equals $^2J(PH) + {}^5J(PH')$. Compound II is readily cleaved in solution by sodium amalgam, although the resulting carbonylate species was not isolated. Methylation of the latter gave the corresponding methylcobalt compound V, which was not purified both because of its limited lifetime in solution (20–30 min at room temperature) and because it was only to be used as a precursor to VI. The proton chemical shift and proton–phosphorus coupling constant of the cobalt–methyl group are very similar to those of the triphenylphosphine analogue, however, and there can be little doubt about the identity of the compound.

Treatment of V with carbon monoxide readily gave the desired acetyl compound VI, as also occurs for the triphenylphosphine analogue III. Compound VI is quite stable thermally and was satisfactorily characterized by elemental analyses and spectroscopic means, including ^{13}C NMR spectroscopy. The ^{13}C NMR assignments were made in part on the basis of a labeling experiment, in part

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(19) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

on basis of precedents in the literature.[20-22] It is interesting to note that the acyl carbonyl carbon resonance was not observed, presumably because of extreme line broadening resulting from rapid relaxation by the quadrupolar metal atom. Similar effects have been observed for acetylmanganese compounds.[22]

The hydride complex VII was air-sensitive and thermally very labile even in the solid state. Samples maintained at −10 to −20 °C were found to have decomposed to the dimer II within a month, and solutions behaved similarly within hours even under 1 atm of hydrogen. Similar decomposition reactions have been observed for $HCo(CO)_3PBu_3$[23] and have been studied in detail for $HCo(CO)_4$.[10,24] The hydride could not, therefore, be purified satisfactorily, and the dark brown coloration of the material obtained is probably a result of small amounts of the deeply colored dimer II. Reactions of the hydride were generally carried out by reacting it in situ immediately after synthesis.

Reactions of the Acetyl Compound VI with Hydrogen and Hydride, VII. As mentioned in the Introduction, $MeCOCo(CO)_4$ may be cleaved by either hydrogen or $HCo(CO)_4$ to give aldehyde. Prior to the work reported here, the only report of similar reactions of a phosphine-containing system involved treatment of $MeCOCo(CO)_3PBu_3$ in pentane with both hydrogen (20 atm) and with $HCo(CO)_3PBu_3$.[15] No reaction of the acetyl compound with the hydride was observed in the temperature range −70 to +20 °C; the latter instead slowly decomposed to $[Co(CO)_3PBu_3]_2$. The hydrogenation reaction did result in cleavage of the acetyl compound, an IR study indicating completion of the reaction within 12 h with formation of acetaldehyde. Identification of the latter was confirmed by isolation of the 2,4-dinitrophenylhydrazone derivative, but neither the yield nor the presence of other products appear to have been determined.

We find similar results for the attempted reaction of the acetyl compound VI with the hydride VII in the polar solvent methanol, GC and IR monitoring of the reaction indicating that conversion of VII to the dimeric II was the faster process. After several hours, when VII had essentially disappeared, VI began to react significantly with the solvent to produce methyl acetate, but this known[25] reaction was not pursued further. It seems clear, however, that reactions of type 6b are not important in phosphine-containing cobalt-catalyzed homologation systems.

In contrast, we find that although VI is inert to hydrogen at 1 atm, cleavage as in (6a) occurs rapidly at 35 atm both in a nonpolar solvent, toluene, and in methanol. Preliminary studies, in which solutions of VI were pressured to 35 atm and heated to 75 °C as rapidly as possible and then sampled through a liquid sampling valve at various times, showed that the reactions were complete by the time the first samples had been taken (35 min in toluene, 5 min in methanol). After these times, the products and yields in toluene (Porapak Q packed column) were acetaldehyde (9–12%), ethanol (28–36%), and ethylformate (approximately 21%). Only ethanol was definitely identified in the methanol reaction (40–45%) using the Porapak Q packed column and then only after the reactor was heated above room temperature. No ethanol was observed immediately after pressuring but before the reactor was heated.

The only cobalt-containing compound in the reaction mixtures was II, although ^{31}P NMR studies demonstrated the presence of some methyldiphenylphosphine oxide (δ 25.0 in benzene, δ 36.5 in methanol), presumably formed from adventitious traces of air in the system. Final solutions were always dark red-brown, the color of II, and there was never evidence of cobalt metal precipitation.

Although all the VI had reacted in both solvent systems, total yields of organic products never exceeded 79%. While the losses were possibly a result in part of the formation of low-boiling compounds such as methane and dimethyl ether, which were not analyzed for, we quickly realized that cooling the reactor to well below 0 °C was necessary before sampling in order not to partially lose even the higher boiling components such as acetaldehyde and n-hexane, the added internal standard. Subsequent procedures therefore involved cooling the reactor to −78 °C in an 2-propanol–dry ice bath, a tedious operation which made repeated sampling during a reaction impractical. Most runs to be described below therefore involved pressuring the reactor to 35 atm, heating to the desired temperature over 7–12 min, maintaining the temperature for a further 5 min, and then cooling. A change in analytical procedures was also made, a much more efficient Carbowax 20M capillary column being used for the GC analyses.

Hydrogenation of VI in toluene at 20 °C proceeded relatively slowly, producing after 6 h methanol (trace), acetaldehyde (approximately 18%), ethyl formate (approximately 30%), and ethanol (approximately 12%). Increasing the temperature (5-min runs) to 75, 100, 125, and 160 °C resulted in disappearance of the methanol, gradual disappearance of the acetaldehyde, and an increase in yield of ethanol (up to approximately 54% yield at 160 °C) as the temperature increased. The amounts of ethyl formate stayed relatively constant (20–30%), while overall yields of all organic products increased to 92 ± 7%. Above 100 °C, and especially at 160 °C, a cobalt mirror was evident on the glass liner, indicating decomposition of the cobalt complexes. In accord with this, small amounts of benzene were observed in the high-temperature runs, presumably resulting from hydrogenolysis of methyldiphenylphosphine. At lower temperatures, ^{31}P NMR spectroscopy showed that, as expected, the major cobalt-containing product was II.

Our results, coupled with those of other workers,[15] strongly suggest that the primary product from the hydrogenation of compounds of the type $MeCOCo(CO)_3L$ (L = tertiary phosphine) is acetaldehyde, presumably formed via an oxidative addition–reductive elimination process (eq 8 and 9).

$$MeCOCo(CO)_3L + H_2 \xrightarrow{-CO} MeCOCoH_2(CO)_2L \xrightarrow{+CO} MeCHO + HCo(CO)_3L \quad (8)$$

$$HCo(CO)_3L \rightarrow {}^1/_2[Co(CO)_3L]_2 + {}^1/_2H_2 \quad (9)$$

The observation in our system of a decrease in selectivity to acetaldehyde and an increase in selectivity to ethanol on going to higher temperatures and, hence, longer reaction times also supports the case for acetaldehyde as a precursor to ethanol as in (7). Similar conclusions have been reached for hydroformylation systems.[7-9] Blank runs showed that the cobalt metal formed at higher temperatures did *not* behave as a heterogeneous acetaldehyde hydrogenation catalyst and that thermal decomposition of VI at 100 °C

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(20) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: New York, 1979.

(21) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981.

(22) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.

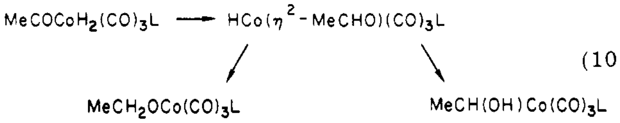
(23) Pregaglia, G. F.; Andreetta, A.; Gregorio, G.; Montrassi, G.; Ferrari, G. F. *Chem. Ind. (Milan)* **1972**, *54*, 405.

(24) Alemdaroğlu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsch. Chem.* **1976**, *107*, 1153.

(25) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 2779.

under 35 atm of nitrogen led to none of the organic products formed under hydrogen.

The mechanism of the conversion of acetaldehyde to ethanol is not known. Current thinking, applied to the phosphine-containing system, would have the cobalt(III) intermediate in (8) to rearrange to a η^2-acetaldehyde complex and then to either an α-hydroxyethyl or an ethoxy compound[7,8] (eq 10).



(10)

Addition of hydrogen to either product could result in the formation of ethanol, although our apparently unprecedented observation of ethyl formate probably requires reaction of the ethoxy compound (eq 11). The system

$$MeCH_2OCo(CO)_3L + CO \rightarrow MeCH_2OCOCo(CO)_3L \xrightarrow{H_2} HCO_2Et \quad (11)$$

undoubtedly involves a number of temperature-dependent rate and equilibrium constants, however, and it is unlikely that our results can be interpreted as favoring either of the alternatives of (10).

As mentioned above, the formation of ethyl formate was unexpected. This compound also proved to be very difficult to separate satisfactorily on a GC column from methyl acetate, even using the capillary column, and as the latter was an anticipated product,[6] an independent means of distinguishing the two isomeric compounds was required. A sample of VI enriched with carbon-13 to the extent of 5% at the acetyl methyl carbon was therefore prepared and hydrogenated in benzene-d_6 as above, in part to facilitate identification of the organic products by ^{13}C NMR spectroscopy and in part because of the intrinsic interest of such a study. The distribution of products, inorganic and organic, was essentially as observed in the toluene runs, and the ^{13}C NMR spectrum showed only the resonances expected for ethyl formate, ethanol, and acetaldehyde, enriched where expected on the basis of their anticipated modes of formation. There was no scrambling of the carbon atoms of any of of these products, results confirmed by GC-MS studies.

Hydrogenation reactions of VI in methanol gave a different distribution of products, although the individual yields were somewhat less reproducible, for reasons not yet clear. After 6 h at 35 atm and 20 °C, acetaldehyde (approximately 40%), ethanol (approximately 14%), and methyl acetate (approximately 5%) had formed, the last presumably via solvent attack on VI[25] because it was not formed at higher temperatures, where hydrogen cleavage was much more rapid. Several studies were carried out in the temperature range 75–160 °C (reaction times approximately 5 min), the general results being that while the ratio of acetaldehyde (and its dimethylacetal, 1,1-dimethoxyethane) to ethanol varied somewhat erratically between 1.2 and 2.3 at the lower temperatures, the ratio decreased dramatically to approximately 0.3 at 160 °C. At no time was ethyl formate observed, a result which cannot at present be unequivocally rationalized. It may be that the polar, protic solvent stabilizes the α-hydroxyethyl compound in (10) through hydrogen bonding to the alcohol group, but it is also possible that direct hydrogenation of the ethoxy compound becomes competitive in the more polar solvent. While ^{31}P NMR spectroscopy showed that the major organocobalt product was II, yields of organic products generally varied between 100 and 150%, suggesting utilization of some of the carbonyl groups of the added VI in order to effect partial homologation of the solvent. As before, cobalt metal precipitated during the higher temperature runs. The GC results were verified by a ^{13}C NMR study of the products from hydrogenation of II enriched at the acetyl methyl position, the labels in each case again appearing where expected (see above).

Table I. Homologation of Methanol Catalyzed by $[Co(CO)_3PMePh_2]_2$

product	yield,[a] %	turnover no.[b]
acetaldehyde	1.1	2.0
1,1-dimethoxyethane	5.9	11
methyl acetate	1.5	3.5
ethanol	0.6	1.1
total	9.1	17.6

[a] Based on starting methanol. [b] Per mole of cobalt.

Methanol Homologation Catalyzed by II. The final stage of this investigation involved determination of the products actually formed during methanol homologation catalyzed by II. If catalysis does occur essentially via the series of steps 1–10 and involving VI as an intermediate, then the products of the stoichiometric and catalytic reactions should be similar. Methanol solutions of II and a small amount of methyl iodide as promoter were treated with 77 atm of a 1:1 mixture of synthesis gas at 125 °C for 26 h. These conditions are milder than those necessary for high reaction rates,[6] but the reactor available was limited to approximately 95 atm. The restriction on the temperature arises from the desire to maintain homogeneous conditions during each run; it was found that, under the pressure of carbon monoxide which was used, higher temperatures would result in precipitation of cobalt metal.

The results of the homologation experiments are listed in Table I. The overall yields, based on available methanol, are low because the conditions used were far from optimum. However, the overall turnover number of 17.6 does show that the reactions were catalytic rather than stoichiometric.

The product selectivities initially seemed surprising given that, at the temperature used, VI would have been expected to give no methyl acetate but much more hydrogenation of acetaldehyde to ethanol. The differences are easily explained, however, if the reactions leading to the hydrogen cleavage of VI (as in (8)) and the hydrogenation of acetaldehyde require the dissociation of a coordinated carbon monoxide from the cobalt. The former condition is probably reasonable, as the hydrogen cleavage of $MeCOCo(CO)_4$ is inhibited by carbon monoxide in the nonpolar solvent *n*-heptane.[26] Thus methanol attack on VI could be much more competitive under a partial pressure of carbon monoxide than it is in the absence of added carbon monoxide. The hydrogenation of acetaldehyde would also be retarded by carbon monoxide if the assumption of the η^2-acetaldehyde complex in (10) is correct, both because the aldehyde might well be expected to be displaced by other good ligands and because hydrogen addition to the rearranged ethoxy and α-hydroxyethyl products may also require carbon monoxide dissociation.

Synopsis. Given the variety of products which can ensue from homologation reactions,[6] the correspondence found here between stoichiometric and catalytic reactions is good and may be taken as confirmatory evidence for the intermediacy of acyl species in the methanol homologation

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[26] Heck, R. F.; Breslow, D. S. "Actes 2^e Congr. Intern. Catalyse, Paris, 1960"; Edition Technip: Paris, 1961; p 671.

reaction. This generalization is probably true even for systems which use cobalt(II) salts as catalyst precursors,[6c] as the carbonylate anion $[Co(CO)_4]^-$ can be formed from such compounds even at low pressures of carbon monoxide.[27]

As mentioned above, it seems unlikely that the intermediate methyl compounds $MeCo(CO)_3L$ (L = tertiary phosphine) are formed via methanol protonation by the weak acids $HCo(CO)_3L$, but homologation by phosphine-containing cobalt systems are relatively slow in the absence of either iodide ion or compounds which will generate iodide.[6c] It thus seems much more likely that the reactive alkylating agent in these cases is methyl iodide, which reacts with the small equilibrium concentrations of carbonylate anion $[Co(CO)_3L]^-$ formed by partial dissociation of $HCo(CO)_3L$. Conversion of methyl to acetyl species by treatment of the former with carbon monoxide is certainly quite facile.

Another, relative minor contribution made here is confirmation that cleavage of the acetyl compounds $MeCOCo(CO)_3L$ to give C_2-containing products involves attack by molecular hydrogen rather than by hydrides, $HCo(CO)_3L$. Our carbon-13 labeling studies are also consistent with and extend carbon-14 studies reported in 1953 using the tetracarbonyl system[28] and tend to confirm the basic features of mechanism advocated by Slocum.[6b]

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Registry No. I, 24212-54-2; II, 31178-43-5; III, 14841-12-4; IV, 14054-68-3; V, 86196-53-4; VI, 86177-65-3; VII, 86177-66-4; methanol, 67-56-1.

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(27) Clark, R. J.; Whiddon, S. E.; Serfass, R. E. *J. Organomet. Chem.* **1968,** *11,* 637.

(28) Burns, G. R. *J. Am. Chem. Soc.* **1955,** *77,* 6615.

Cluster Synthesis. 4. The Role of Sulfido Ligands in the Synthesis of High Nuclearity Metal Carbonyl Cluster Compounds. The Synthesis of $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ and $Os_7(CO)_{20}(\mu_4\text{-}S)_2$ and the Crystal and Molecular Structure of $Os_7(CO)_{20}(\mu_4\text{-}S)_2$

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The cluster compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ has been found to react with $Os(CO)_5$ in the presence of UV irradiation to yield the cluster $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (40% yield), and $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ has been found to combine with $Os_3(CO)_{10}(NCMe)_2$ when refluxed in octane solvent for 2 h to yield the new cluster compound $Os_7(CO)_{20}(\mu_4\text{-}S)_2$, V (16% yield). Compound V has been characterized by a single-crystal X-ray diffraction analysis: space group $P2_12_12_1$, a = 11.205 (5) Å, b = 14.461 (6) Å, c = 21.246 (16) Å, V = 3443 (6) Å^3, M_r = 1955.7 g/cm^3, Z = 4, ρ_{calcd} = 3.77 g/cm^3. The structure was solved by direct methods. Full-matrix least-squares refinement on 2315 reflections ($F^2 \geq 3.0\sigma(F^2)$) yielded the final residuals R_F = 0.055 and R_{wF} = 0.044. The structure consists of a pentagonal-bipyramidal cluster of five osmium atoms and two tetracoordinate sulfido ligands. The two sulfido ligands which are not mutually bonded and three osmium atoms form the equatorial plane. Two $Os(CO)_4$ groups bridge adjacent apical–equatorial edges of the pentagonal bipyramid on opposite sites of the equatorial plane. Two of apical–equatorial metal–metal bonds in the cluster at 2.969 (2) and 2.963 (2) Å are significantly longer than the other four, range 2.893 (2)–2.905 (2) Å. The metal–metal bonds involving the $Os(CO)_4$ groups range from 2.801 (2) to 2.825 (2) Å. Compound V contains 20 linear terminal carbonyl ligands. The importance of sulfido ligands in the synthesis of high nuclearity metal carbonyl clusters is noted and discussed.

Introduction

Recent studies have shown that atoms derived from certain elements of the main groups can play an important role in the synthesis of heteronuclear transition-metal cluster compounds. Elements such as sulfur,[1–11] selenium,[11] phosphorus,[12,13] arsenic,[13,14] carbon,[15] nitrogen,[16] and even germanium[17] have been among the most useful of these.

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(1) (a) Marko, L. *Gazz. Chim. Ital.* **1979,** *109,* 247. (b) Vahrenkamp, J. *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 322.

(2) (a) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1979,** *18,* 531. (b) Vahrenkamp, H.; Wuchere, E. J. *Ibid.* **1981,** *20,* 680. (c) Day, V.; Lesch, D. A.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1982,** *104,* 1290.

(3) Stevenson, D. L.; Magnuson, V. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1967,** *89,* 3727.

(4) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1982,** *104,* 4115.

(5) Adams, R. D.; Dawoodi, Z.; Foust, D. *Organometallics* **1982,** *1,* 411.

(6) Adams, R. D.; Horváth, I. T.; Yang, L.-W. *J. Am. Chem. Soc.* **1983,** *105,* 1533.

(7) Adams, R. D.; Männig, D.; Segmüller, B. E. *Organometallics* **1983,** *2,* 149.

(8) Adams, R. D.; Foust, D. F.; Mathur, P.*Organometallics* **1983,** *2,* 990.

(9) Adams, R. D.; Horváth, I. T.; Mathur, P.; Segmüller, B. E. *Organometallics* **1983,** 2, 996.

(10) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L.-W. *Organometallics* **1983,** *2,* 144.