

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
REDSTONE RESEARCH LABORATORIES, HUNTSVILLE, ALABAMA 35807The Chemistry of the Dinuclear Carbonyl Anions. II. Mixed-Metal Derivatives¹

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The reaction of the carbonyl anion $\text{Mn}(\text{CO})_5^-$ or $\text{Co}(\text{CO})_4^-$ with $\text{Fe}(\text{CO})_5$ produces the new anion $\text{FeMn}(\text{CO})_9^-$ or $\text{FeCo}(\text{CO})_8^-$. The reaction of the carbonyl anions $\text{M}_2(\text{CO})_{10}^{2-}$ ($\text{M} = \text{Cr}$ or W) with either $\text{Co}_2(\text{CO})_8$ or $\text{Mn}_2(\text{CO})_{10}$ produces the mixed-metal dinuclear anion $\text{MCo}(\text{CO})_9^-$ or $\text{MMn}(\text{CO})_{10}^-$. Some reactions of the anion $\text{Fe}_2(\text{CO})_8^{2-}$ are also discussed.

Although a number of dinuclear metal carbonyl anions have been known for some time²⁻⁴ (e.g., $\text{Fe}_2(\text{CO})_8^{2-}$, $\text{Ni}_2(\text{CO})_6^{2-}$, and $\text{M}_2(\text{CO})_{10}^{2-}$ where $\text{M} = \text{Cr}$, Mo , or W), no dinuclear species that contained different metals were known until recently. Graham reported that the reaction between either the $\text{Mn}(\text{CO})_5^-$ or $\text{Re}(\text{CO})_5^-$ ion and a group VI hexacarbonyl at 170° produced the anionic dinuclear species $\text{MnM}(\text{CO})_{10}^-$ or $\text{ReM}(\text{CO})_{10}^-$ (where $\text{M} = \text{Cr}$, Mo , or W).⁵ He postulated that the mononuclear ions were behaving as Lewis bases and displacing carbon monoxide from the group VI metal. Alternately the reaction between Lewis bases and the metal hexacarbonyls can be carried out photochemically at ambient temperature.⁶ Therefore, a study of the reaction of several mononuclear carbonyl anions with $\text{Fe}(\text{CO})_5$ or $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}$, Mo , or W) under photolytic conditions was initiated. In addition, it was found that the dinuclear anions $\text{M}_2(\text{CO})_{10}^{2-}$ were valuable reagents for the preparation of dinuclear anions containing different metals.

Experimental Section

All of the manipulations described in this section except the weighing of reactants were performed under a nitrogen atmosphere since solutions of both the reactants and products were susceptible to oxidation. However, in the solid state decomposition of the products was observed only after several weeks. The iron-containing dinuclear species were more reactive toward oxygen than the others.

Materials.—The metal carbonyls $\text{Mn}_2(\text{CO})_{10}$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Fe}(\text{CO})_5$, and $\text{Co}_2(\text{CO})_8$ were obtained from Alfa Inorganics. The simple anions⁷⁻⁹ $\text{Co}(\text{CO})_4^-$, $\text{Mn}(\text{CO})_5^-$, and $\text{HFe}(\text{CO})_4^-$ were prepared by the literature methods and isolated as crystalline solids by use of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCl}$ as the counterion.¹⁰ The dinuclear carbonyl anions $\text{M}_2(\text{CO})_{10}^{2-}$ (where $\text{M} = \text{Cr}$, Mo , or W) were prepared as described previously.

Preparation of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFeCo}(\text{CO})_8^-$.—A mixture of 0.35 ml (2.62 mmol) of $\text{Fe}(\text{CO})_5$ and 0.71 g (1.00 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$ in 50 ml of dry tetrahydrofuran (THF) was irradiated with a GE AH4 floodlamp until 35 cm³ (at STP) of gas was evolved. The mixture was filtered under nitrogen and the solvent was removed from the filtrate under vacuum at ambient temperature. The residue was extracted with 75 ml of ether. Pentane was added to the extract to crystallize the

product. A 0.32-g sample of the red product was obtained; mp $100\text{--}102^\circ$ (rapid heating). Decomposition of the product commenced at approximately $75\text{--}80^\circ$ and it did not melt when a slow heating rate was used.

Anal. Calcd for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFeCo}(\text{CO})_8$: C, 60.2; H, 3.42; N, 1.60; Fe, 6.30; Co, 6.52; O, 14.6. Found: C, 60.4; H, 3.44; N, 1.65; Fe, 6.17; Co, 6.70; O, 14.2.

Preparation of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFeMn}(\text{CO})_9^-$.—A mixture of 0.40 ml (2.99 mmol) of $\text{Fe}(\text{CO})_5$ and 0.75 g (1.02 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NMn}(\text{CO})_5$ in 50 ml of THF was treated as described above. Upon addition of pentane to the ether extract, a 0.27-g sample of dark red product was obtained; mp $134\text{--}135^\circ$. Decomposition began at approximately $120\text{--}125^\circ$.

Anal. Calcd for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NFeMn}(\text{CO})_9$: C, 60.0; H, 3.33; N, 1.55; Fe, 6.2; Mn, 6.1; O, 16.0. Found: C, 59.8; H, 3.36; N, 1.59; Fe, 6.4; Mn, 6.0; O, 15.5.

Preparation of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NMCo}(\text{CO})_9^-$ ($\text{M} = \text{Cr}$ or W).—A. The preparations of both the chromium and the tungsten derivatives were carried out in an analogous manner except a reaction temperature of -10° was used in the former case. To 1.71 g (0.99 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}_2\text{W}_2(\text{CO})_{10}$ in 50 ml of THF at 0° 0.5 g (1.46 mmol) of $\text{Co}_2(\text{CO})_8$ was added. The reaction mixture was stirred for 0.5 hr and then the solvent was removed at 0° under vacuum. The solid residue was extracted three times with 25-ml portions of ether. Pentane was added to the combined ether extracts to crystallize the product. A 0.75-g sample of product was obtained; mp $111\text{--}113^\circ$ with decomposition when a fast heating rate was used. Decomposition occurred below this temperature and no melting was observed until $185\text{--}187^\circ$ (the melting point of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$ when a slow heating rate was employed. When a 1.4-g sample of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}_2\text{Cr}_2(\text{CO})_{10}$ was treated in the same way, a 0.41-g sample of product was obtained; mp $73\text{--}75^\circ$ dec. Both of the products were orange.

Anal. Calcd for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCoCr}(\text{CO})_9$: C, 60.0; H, 3.33; N, 1.55; Co, 6.5; Cr, 5.8. Found: C, 59.7; H, 3.30; N, 1.62; Co, 6.4; Cr, 5.3. Calcd for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NWCo}(\text{CO})_9$: C, 52.3; H, 2.90; N, 1.36; Co, 5.7; W, 17.8. Found: C, 52.2; H, 2.98; N, 1.40; Co, 5.8; W, 17.0.

B. A mixture of 1.0 g (2.83 mmol) of $\text{W}(\text{CO})_6$ and 1.41 g (1.99 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$ in 40 ml of THF was irradiated until 55 cm³ (at STP) of gas was evolved. The solution was filtered and the solvent was removed under vacuum. The solid residue was extracted three times with 25-ml portions of ether. Pentane was added to the ether extracts to crystallize the product. A 0.35-g sample of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NWCo}(\text{CO})_9$, which was identical with that prepared above, was obtained.

Preparation of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NMnM}(\text{CO})_{10}$ (where $\text{M} = \text{Cr}$, Mo , or W).—The preparation was performed in an analogous manner for the chromium, molybdenum, and tungsten derivatives. For example, a mixture of 0.73 g (0.50 mmol) of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}_2\text{Cr}_2(\text{CO})_{10}$ and 0.21 g (0.54 mmol) of $\text{Mn}_2(\text{CO})_{10}$ in 25 ml of THF was refluxed for 10 min. The reaction mixture was filtered and the solvent was removed under vacuum. The residue was dissolved in 10 ml of CH_2Cl_2 . Then 50 ml of ether was added and finally pentane was added to crystallize the product. A 0.79-g sample of $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NMnCr}(\text{CO})_{10}$ was obtained. Following the same procedure resulted in the isolation of 0.71 g

(1) Part I: J. K. Ruff, *Inorg. Chem.*, **6**, 2080 (1967).(2) W. Hieber and N. Kahlen, *Chem. Ber.*, **91**, 2223, 2234 (1958).(3) W. Hieber, W. Kroder, and E. Zahn, *Z. Naturforsch.*, **15b**, 325 (1960).(4) R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).(5) A. Anders and W. A. G. Graham, *ibid.*, **89**, 539 (1967).(6) W. Strohmer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 730 (1960).(7) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).(8) W. Hieber and G. Wagner, *Z. Naturforsch.*, **12b**, 478 (1957).(9) W. Hieber and F. Leutert, *Z. Anorg. Allgem. Chem.*, **204**, 145 (1932).(10) R. Appel and A. Huass, *ibid.*, **311**, 290 (1961).

of $[(C_6H_5)_3P]_2NMnMo(CO)_{10}$ and 0.89 g of $[(C_6H_5)_3P]_2NMnW(CO)_{10}$ when 0.79 g of $[(C_6H_5)_3P]_2N]_2Mo_2(CO)_{10}$ and 0.91 g of $[(C_6H_5)_3P]_2N]_2W_2(CO)_{10}$ were used, respectively. The infrared spectra of these compounds in the CO stretching region were identical (to within $\pm 2\text{ cm}^{-1}$) with the literature values.⁵

Anal. Calcd for $[(C_6H_5)_3P]_2N]_2CrMn(CO)_{10}$: C, 59.7; H, 3.24; N, 1.51. Found: C, 59.3; H, 3.01; N, 1.42. Calcd for $[(C_6H_5)_3P]_2NMnMo(CO)_{10}$: C, 57.0; H, 3.10; N, 1.44. Found: C, 56.5; H, 3.08; N, 1.31. Calcd for $[(C_6H_5)_3P]_2NMnW(CO)_{10}$: C, 52.3; H, 2.84; N, 1.32. Found: C, 52.1; H, 2.79; N, 1.20.

Preparation of $[(C_6H_5)_3P]_2N]_2Fe_2(CO)_8$.—A mixture of 0.70 ml (5.24 mmol) of $Fe(CO)_5$ and 25 g of 1% sodium amalgam in 50 ml of THF was irradiated with a GE AH-4 floodlamp for 4 hr. The mixture was decanted off the amalgam under nitrogen and 2.0 g (3.48 mmol) of $[(C_6H_5)_3P]_2NCl$ in 75 ml of CH_2Cl_2 was added. Then the mixture was filtered and the solvent was removed under vacuum. The residue was dissolved in 35 ml of CH_2Cl_2 and 30 ml of ethyl acetate was added. Upon cooling a 1.91-g sample of dark brown product was obtained; mp 183–185°.

Anal. Calcd for $[(C_6H_5)_3P]_2N]_2Fe_2(CO)_8$: C, 68.0; H, 4.25; N, 1.98; Fe, 7.93. Found: C, 67.9; H, 4.22; N, 1.91; Fe, 7.87.

Preparation of $[(C_6H_5)_3P]_2N]Fe_2Mn(CO)_{12}$.—A. To a solution of $Na_2Fe(CO)_8$, prepared as described above, 1.0 g (2.55 mmol) of $Mn_2(CO)_{10}$ was added. The mixture was heated at 40° for 1 hr and then 2.5 g (4.35 mmol) of $[(C_6H_5)_3P]_2NCl$ in 100 ml of methylene chloride was added. The mixture was filtered and the solvent was removed from the filtrate under vacuum. The residue was extracted three times with a 10:40 CH_2Cl_2 -ether mixture. Pentane was added to the combined extracts. A 0.83-g sample of dark blue product was obtained. The residual solid left after extraction was recrystallized from CH_2Cl_2 and ether. A 1.21-g sample of $[(C_6H_5)_3P]_2NMn(CO)_8$ (contaminated with a small amount of the chloride) was obtained.

B. A mixture of 1.6 g (4.39 mmol) of $Fe_2(CO)_9$ and 1.4 g (1.91 mmol) of $[(C_6H_5)_3P]_2NMn(CO)_8$ in 50 ml of THF was refluxed for 2 hr. The solution was filtered and the solvent was removed under vacuum. The residue was washed with 25 ml of ether and the washings were discarded. It was then recrystallized from CH_2Cl_2 and ether. A 1.10-g sample of product was obtained; mp 171–173°. The infrared spectrum of the compound in THF was identical (within $\pm 3\text{ cm}^{-1}$) with the spectrum reported in the literature.¹¹

Anal. Calcd for $[(C_6H_5)_3P]_2N]Fe_2Mn(CO)_{12}$: C, 55.4; H, 2.88; N, 1.34; Fe, 10.8. Found: C, 55.6; H, 2.89; N, 1.42; Fe, 10.1.

Reaction of $[(C_6H_5)_3P]_2N]HFe(CO)_4$ and $Fe(CO)_5$.—A mixture of 0.70 ml (5.24 mmol) of $Fe(CO)_5$ and 1.43 g (2.02 mmol) of $[(C_6H_5)_3P]_2N]HFe(CO)_4$ in 25 ml of THF was irradiated with a GE AH-4 floodlamp until 60 cm^3 (at STP) was evolved. The mixture was filtered and the solvent was removed under vacuum. The residue was extracted with two portions of 75 ml of ether. Pentane was added to the extract to crystallize the product. A 0.22-g sample of the red $[(C_6H_5)_3P]_2N]HFe_3(CO)_{11}$ was obtained; mp 145–147°. The H^1 nmr spectrum in CH_2Cl_2 solution contained a peak at +12.1 ppm from TMS.

Anal. Calcd for $[(C_6H_5)_3P]_2N]HFe_3(CO)_{11}$: C, 55.6; H, 3.05; N, 1.43; Fe, 16.5. Found: C, 55.4; H, 3.11; N, 1.38; Fe, 16.3.

Thermal Decomposition of $[(C_6H_5)_3P]_2MCo(CO)_9$ (M = Cr or W).—The thermal decomposition of both the chromium and tungsten salts was carried out in the same manner. A 1.22-g (1.18 mmol) sample of $[(C_6H_5)_3P]_2WCo(CO)_9^-$ was placed in a cold-finger-equipped sublimator and the system was evacuated. Then a 100° oil bath was raised around the sample. Almost immediately a white sublimate appeared on the cold finger. After 15 min the system was opened to a manometer. No pressure increase was observed. The white sublimate (0.36 g, 1.01 mmol) was identified as $W(CO)_6$ by its infrared spectrum. The residue was dissolved in 10 ml of CH_2Cl_2 and the mixture

was filtered. The dark deposit on the filter plate was discarded. Ether, 40 ml, was added to the filtrate. On standing, a 0.67-g (0.95-mmol) sample of $[(C_6H_5)_3P]_2N]Co(CO)_4$ was obtained. It was identified by its infrared spectrum and melting point.

Infrared Spectra.—The infrared spectra were obtained on solutions of approximately 0.010 g/ml of the compounds in CH_2Cl_2 unless otherwise noted. The instrument, a Perkin-Elmer Model 521 spectrometer, was calibrated with indene. Table I tabulates the bands observed in the carbonyl region.

TABLE I
INFRARED SPECTRA OF THE DINUCLEAR CARBONYL ANIONS IN THE CO STRETCHING REGION

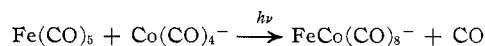
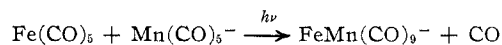
Compound	cm^{-1}
$FeCo(CO)_8^-$	2056 w, 1989 m, 1953 s, 1895 w, 1776 m
$FeMn(CO)_9^-$	2066 w, 2024 w, 1968 vs, 1937 m, sh, 1870 m
$WCo(CO)_9^-$	2062 w, 2012 m, 1940 vs, 1912 w, sh, 1864 m
$CrCo(CO)_9^-$ ^a	2055 w, 2000 w, 1936 vs, 1910 w, sh, 1864 m, 1854 m

^a Spectrum taken as a Nujol mull.

Conductivity Measurements.—Only two of the new salts were stable enough in solution to permit the determination of their conductivity in nitromethane solutions. The equipment employed has already been described.¹² The specific conductivity of the nitromethane used was 5.47×10^{-7} . The anion concentration (M) and molar conductance ($cm^2/ohm\ equiv$) are: for $FeCo(CO)_8^-$, 1.003×10^{-3} , 67.3; for $FeMn(CO)_9^-$, 1.002×10^{-3} , 68.7.

Results and Discussion

Although it has been recognized for several years that mononuclear carbonyl anions such as $Mn(CO)_5^-$ or $Re(CO)_5^-$ can function as a Lewis base toward a few select Lewis acids¹³ it was not until recently that their ability to function as a ligand toward a neutral metal carbonyl moiety was apparently demonstrated.⁵ This concept has now been extended to include the $Co(CO)_4^-$ ion. Thus, when a solution containing $Fe(CO)_5$ and either of the above two ions was irradiated, carbon monoxide was evolved and the mixed-metal dinuclear anions were formed in low to moderate yields



When the reactions were carried out thermally, no dinuclear species could be isolated. In fact, the reaction of the $Mn(CO)_5^-$ ion with $Fe(CO)_5$ in diglyme has been reported to yield a trinuclear species, $Fe_2Mn(CO)_{12}^-$.¹¹ This may, in part, be due to the relatively low thermal stability of the dinuclear ions. However, further reaction of these species with excess $Fe(CO)_5$ must also be considered likely. When an attempt was made to extend this reaction to include the $HFe(CO)_4^-$ ion, the desired product, $HFe_2(CO)_8^-$, was not isolated. Instead, the $HFe_3(CO)_{11}^-$ anion was formed in low yield. This material was identified by analysis and by comparison with an authentic sample of $(C_2H_5)_3NH-HFe_3(CO)_{11}$.¹⁴

In order to determine if the $Co(CO)_4^-$ anion could also function as a base toward the group VI metal

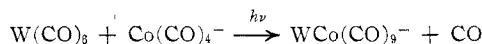
(11) U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).

(12) J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963).

(13) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 361 (1964).

(14) J. R. Case and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960).

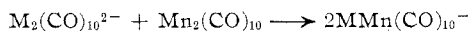
carbonyls, mixtures of $\text{W}(\text{CO})_6$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$ were irradiated. Only small amounts of the desired dinuclear metal carbonyl anion, $\text{WCo}(\text{CO})_9^-$, were isolated. No product could be obtained when either of the two other group VI metal carbonyls were used in this type of reaction



However, an alternate route to some of these derivatives was found. This is based on the reaction of the dianion $\text{W}_2(\text{CO})_{10}^{2-}$ or $\text{Cr}_2(\text{CO})_{10}^{2-}$ with $\text{Co}_2(\text{CO})_8$. The reaction proceeded readily at 0° in THF and the mixed species were formed in low yield. Unfortunately, it was not possible to obtain an analytically pure sample of the molybdenum derivative by this method since it appeared to be quite unstable. The equation

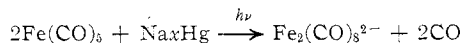


is only approximate since large amounts of the $\text{Co}(\text{CO})_4^-$ anion were also produced. This reaction could easily be extended to produce the known mixed-metal dinuclear metal carbonyl anions $\text{MMn}(\text{CO})_{10}^-$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$)⁵

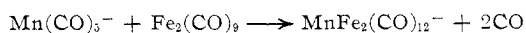


The reaction proceeded rapidly at 50° and almost quantitative yields of the products were isolated.

Since the dinuclear anions of the group VI metals appear to be useful reagents in the preparation of mixed-metal derivatives, it was of interest to explore similar reactions using the $\text{Fe}_2(\text{CO})_8^{2-}$ anion. Although the preparation of this anion has been accomplished by several methods,¹⁵ it is easily prepared in a manner analogous to that reported for the $\text{M}_2(\text{CO})_{10}^{2-}$ anions (where $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$)⁴



Both $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$ reacted with the $\text{Fe}_2(\text{CO})_8^{2-}$ anion in solution at or below ambient temperature. However, no dinuclear species could be isolated. Instead, the $\text{Co}_2(\text{CO})_8$ was converted to the $\text{Co}(\text{CO})_4^-$ ion in good yield. The fate of the iron carbonyl moiety is not known, although evidence for the presence of other products was found by infrared spectroscopy. The reaction involving $\text{Mn}_2(\text{CO})_{10}$ was also complex. However, it was possible to isolate in moderate yield both the known trinuclear species $\text{Fe}_2\text{Mn}(\text{CO})_{12}^-$ ¹¹ and the $\text{Mn}(\text{CO})_5^-$ ion. A much higher yield of the trinuclear species was obtained in the reaction of the $\text{Mn}(\text{CO})_5^-$ ion with $\text{Fe}_2(\text{CO})_8$ ¹⁶

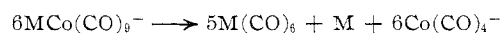


Since both of the two systems involving the $\text{Fe}_2(\text{CO})_8^{2-}$ ion are complex, speculation on the exact mechanism of the observed reactions seems unwarranted. It is apparent, however, that the $\text{Fe}_2(\text{CO})_8^{2-}$ ion is a better reducing agent than either of the ions

$\text{Mn}(\text{CO})_5^-$ or $\text{Co}(\text{CO})_4^-$. It is possible that the other species observed in these systems may arise from the reaction of these mononuclear ions with an iron carbonyl moiety formed by oxidation.

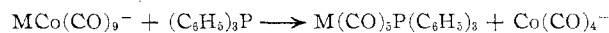
All of the new dinuclear metal carbonyl anions are crystalline solids which are relatively stable in air. The two ions $\text{CrCo}(\text{CO})_9^-$ and $\text{WCo}(\text{CO})_9^-$ are not stable in solution and are thus quite difficult to recrystallize. Therefore, conductivity and H^1 nmr measurements were obtained only on the $\text{FeCo}(\text{CO})_8^-$ and $\text{FeMn}(\text{CO})_9^-$ ions. The equivalent conductance for these ions was in the range expected for a 1:1 electrolyte in CH_3NO_2 solution.¹⁷ The H^1 nmr spectra of these indicated the absence of hydridic hydrogen and paramagnetic impurities.

The thermal stability of the new dinuclear anions is much lower than that found for either the $\text{M}_2(\text{CO})_{10}^{2-}$ or $\text{MMn}(\text{CO})_{10}^-$ ions (where $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$).^{4,5} The latter are stable above 150° while the former decompose near 100° . Little or no carbon monoxide was observed in the decomposition of either the $\text{CrCo}(\text{CO})_9^-$ or $\text{WCo}(\text{CO})_9^-$ ions



Both $\text{M}(\text{CO})_6$ and $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NCo}(\text{CO})_4$ could be isolated in high yield from the above decompositions. A dark deposit metallic in appearance was also formed. No quantitative investigation of the decomposition of the other two dinuclear metal carbonyl anions was carried out due to the limited amount of material available.

In addition to having a relatively low thermal stability, the $\text{CrCo}(\text{CO})_9^-$ ion and to a lesser extent the $\text{WCo}(\text{CO})_9^-$ ion is unstable in solution. In fact, it was not possible to obtain a reliable solution infrared spectrum of the former even in methylene chloride. The rate of decomposition appeared to increase with increasing basicity of the solvent. The only decomposition products that could be observed by infrared spectroscopy were $\text{Cr}(\text{CO})_6$ and the $\text{Co}(\text{CO})_4^-$ ion. Thus, the decomposition in solution may be similar to the thermal decomposition. The reaction of either of these ions with 1 equiv of $(\text{C}_6\text{H}_5)_3\text{P}$ at ambient temperature produced $\text{M}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ and the $\text{Co}(\text{CO})_4^-$ ion in high yield



where $\text{M} = \text{Cr}$ or W . No reaction was observed between $(\text{C}_6\text{H}_5)_3\text{P}$ and the $\text{FeMn}(\text{CO})_9^-$ or $\text{FeCo}(\text{CO})_8^-$ ion under similar conditions.

The infrared spectra in the carbonyl region of the new dinuclear metal carbonyl ions are summarized in Table I. One striking difference is apparent between the spectrum of the $\text{FeCo}(\text{CO})_8^-$ ion and the spectra of the others—the presence of a band in the region attributed to bridging carbonyls.¹⁸ The band at 1776 cm^{-1} in the $\text{FeCo}(\text{CO})_8^-$ ion is considerably lower than the band assigned to the bridging carbonyl groups in the isoelec-

(15) W. Hieber and R. Werner, *Chem. Ber.*, **90**, 1116 (1957).

(16) The $\text{Fe}_2(\text{CO})_8$ in this reaction may also be replaced with $\text{Fe}_3(\text{CO})_{12}$, but lower yields are obtained.

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(18) Some care must be exercised in applying the empirical criteria for bridging carbonyls, especially in the case of charged species.

tronic $\text{Co}_2(\text{CO})_8$.¹⁹ This is undoubtedly due to the presence of the negative charge. No appreciable change in the intensity or position of this band was observed in different solvents such as THF, CH_3NO_2 , or CH_2Cl_2 or in the solid state, indicating that the bridges remain intact. Thus, it is likely that the $\text{FeCo}(\text{CO})_8^-$ ion will have a structure similar to $\text{Co}_2(\text{CO})_8$ and will be quite different from the isoelectronic species $\text{Fe}_2(\text{CO})_8^{2-}$ which is presumed to have a simple metal-metal bond.²⁰

There are no bands present in the spectra of the $\text{MM}'(\text{CO})_9^-$ ions that can be assigned to bridging carbonyls. They would be expected to be found below 1830 cm^{-1} , where the bridging carbonyl absorptions occur in the isoelectronic $\text{Fe}_2(\text{CO})_9$,²¹ owing to the negative charge on the ion. Thus, it must be concluded that a simple metal-metal bond exists in these three ions. A related case is the compound $\text{MnCo}(\text{CO})_9$ in which bridging carbonyls also appear to be absent.²²

If a simple metal-metal bond exists in the $\text{MM}'(\text{CO})_9^-$ ions, then the manganese or the group VI metal would be expected to be in an octahedral environment. The coordination of the iron or cobalt would be in the form of either a tetragonal pyramid or a trigonal bipyramid. The former configuration would result in an over-all symmetry for the ion of C_{4v} , while the latter

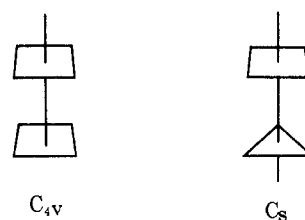


Figure 1.—Proposed structures for the $\text{MM}'(\text{CO})_9^-$ ions.

would result in C_s symmetry. (See Figure 1.) This would lead to the expectation of five ($3A'$ and $2E$) or nine ($6A'$ and $3A''$) infrared-active stretching frequencies in the carbonyl region, respectively, assuming that coupling of the carbonyl vibrations occurs across the metal-metal bond. If the coupling is negligible, local site symmetry will be sufficient to determine the number of active infrared frequencies, and either five or six infrared-active bands should be observed for the tetragonal-pyramid or the trigonal-bipyramid configuration, respectively. The observed spectra would tend to favor the C_{4v} symmetry of these ions. However, the structure with C_s symmetry cannot be completely eliminated since a lack of resolution or accidental degeneracy of some of the modes could easily result in the observed spectra.

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The Chemistry of the Dinuclear Carbonyl Anions. III.¹ Halogen-Bridged Anions

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Anions of the type $\text{M}(\text{CO})_5\text{I}^-$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) react with excess $\text{M}(\text{CO})_6$ or $\text{M}'(\text{CO})_6$ under photolytic conditions to form dinuclear anions of the type $\text{M}_2(\text{CO})_{10}\text{I}^-$ or $\text{MM}'(\text{CO})_{10}\text{I}^-$. Related chloride and bromide derivatives were prepared in several cases. The structures of these anions are discussed in terms of their infrared spectra. The reaction of the $\text{Cr}_2(\text{CO})_{10}^{2-}$ anion with iodine is also discussed.

Although the group VI metal carbonyls have been known to react with a large variety of neutral Lewis bases,² the use of anionic Lewis bases is more restricted. Wilkinson,³ Fischer,⁴ and their coworkers were the first to employ the halide ions as ligands for these carbonyls. This system was later expanded by Abel, Butler, and Reid.⁵ These workers reported that a variety of mononuclear derivatives of the type $\text{M}(\text{CO})_5-$

X^- could be prepared by the thermal reaction of the group VI metal hexacarbonyl and a relatively soluble form of halide ion such as the tetraethylammonium salts. Behrens and Schwab reported that the reaction of iodine with the salt $\text{Na}_2\text{Cr}_2(\text{CO})_{10}$ gave $\text{NaCr}(\text{CO})_5\text{I}$, $\text{Cr}(\text{CO})_5\text{I}$, or $\text{Cr}_2(\text{CO})_{10}\text{I}$.^{6,7} Furthermore, it was found that the last species could be reduced to the anion $\text{Cr}_2(\text{CO})_{10}\text{I}^-$,⁸ which is apparently identical with those reported in this study.

Since it has recently been demonstrated that anionic

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