tronic $Co_2(CO)_8$.[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 $FeCo(CO)_8^-$ ion will have a structure similar to $Co_2(CO)_8$ and will be quite different from the isoelectronic species $Fe_2(CO)_8^{2-}$ which is presumed to have a simple metal–metal bond.[20]

There are no bands present in the spectra of the $MM'(CO)_9^-$ 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 $Fe_2(CO)_9$,[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 $MnCo(CO)_9$ in which bridging carbonyls also appear to be absent.[22]

If a simple metal–metal bond exists in the $MM'(CO)_9^-$ 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 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.

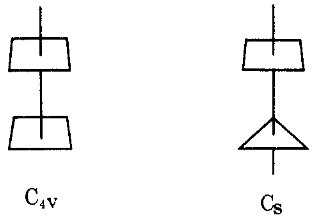

Figure 1.—Proposed structures for the $MM'(CO)_9^-$ ions.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DAAH01-67-C-0655.

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

By J. K. Ruff

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Anions of the type $M(CO)_5I^-$ (where M = Cr, Mo, or W) react with excess $M(CO)_6$ or $M'(CO)_6$ under photolytic conditions to form dinuclear anions of the type $M_2(CO)_{10}I^-$ or $MM'(CO)_{10}I^-$. 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 $Cr_2(CO)_{10}^{2-}$ 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 $M(CO)_5X^-$ 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 $Na_2Cr_2(CO)_{10}$ gave $NaCr(CO)_5I$, $Cr(CO)_5I$, or $Cr_2(CO)_{10}I$.[6,7] Furthermore, it was found that the last species could be reduced to the anion $Cr_2(CO)_{10}I^-$,[8] which is apparently identical with those reported in this study.

Since it has recently been demonstrated that anionic

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Table I

Analytical Data for the Compounds Prepared

Anion	Yield, %	Mp, °C	Analyses, % Calcd C	H	N	X	M	Found C	H	N	X	M
$Cr(CO)_5ICr(CO)_5^-$	54	109–110	52.8	2.86	1.33	12.1	9.9	52.8	2.79	1.37	12.3	9.7
$Cr(CO)_5BrCr(CO)_5^-$	35	98–99	55.1	2.99	1.40	8.0	10.4	55.2	2.96	1.34	8.2	10.6
$Cr(CO)_5IW(CO)_5^-$	50	118–120	46.8	2.54	1.19	10.8	Cr, 4.4	46.4	2.78	1.30	10.6	4.3
$Cr(CO)_5BrW(CO)_5^-$	18	101–103	48.7	2.65	1.23	7.1	Cr, 4.6	48.7	2.79	1.27	7.2	4.7
$Cr(CO)_5IMo(CO)_5^-$	27	111–113 dec	50.5	2.75	1.28	11.6	Cr, 4.8	50.3	2.66	1.37	11.3	4.5
$W(CO)_5IW(CO)_5^-$	43	114–116	42.1	2.28	1.07	9.7		41.9	2.28	1.12	10.0	
$W(CO)_5BrW(CO)_5^-$	28	112–114 dec	43.6	2.37	1.11	6.3		44.1	2.52	1.25	6.3	
$Mo(CO)_5IMo(CO)_5^-$	17	113–115 dec	48.6	2.64	1.23	11.2		49.0	2.91	1.31	11.2	
$Cr(CO)_5ClCr(CO)_5^-$	43	91–93	57.5	3.13	1.46	3.71	10.9	57.7	3.35	1.47	3.85	10.7
$Cr(CO)_5I^-$	75	168–170	57.5	3.50	1.63	14.8		57.2	3.75	1.54	14.9	
$Cr(CO)_5Br^-$	62	173–175	60.8	3.70	1.63	9.9		61.2	3.94	1.77	9.7	
$W(CO)_5I^-$	85	172–174	49.8	3.03	1.42	12.8		50.0	3.09	1.44	12.5	
$W(CO)_5Br^-$	70	184–186	52.3	3.18	1.49	8.5		51.9	3.08	1.53	8.7	

derivatives of the group VI metal carbonyls can be prepared by photolytic activation,[1,9] this method was adapted to the halide ions. A reinvestigation of the reaction of iodine with the dinuclear metal carbonyl anions $M_2(CO)_{10}^{2-}$ was also made.

Experimental Section

Materials.—The group VI metal carbonyls were obtained from Alfa Inorganics, Inc. The dinuclear carbonyl anions, $M_2(CO)_{10}^{2-}$, were prepared and isolated as described previously.[10]

Preparation of $[(C_6H_5)_3P]_2NM_2(CO)_{10}X$ (where M = Cr, Mo, or W and X = I, Br or Cl).—The preparation of all of the symmetrical derivatives was carried out in an analogous fashion. The analytical data are presented in Table I. A typical example is given below. A mixture containing 0.82 g of $[(C_6H_5)_3P]_2NI$ and 1.0 g of $Cr(CO)_6$ in 50 ml of THF was irradiated until approximately 75 cm^3 of gas had been evolved. The solvent was removed from the mixture under reduced pressure. The residue was extracted once with 25 ml of ether and an additional 25 ml of ether was then added to the filtered extract. The product, 0.70 g, crystallized upon the addition of pentane. The solid product was extracted with 15–20 ml of ether and an additional 20 ml of ether was added to the filtered extract. The recrystallized product was obtained by adding pentane.

Preparation of $[(C_6H_5)_3P]NMM'(CO)_{10}X$.—All of the examples reported were prepared in the same manner. For example, a mixture of 0.83 g of $[(C_6H_5)_3P]_2NCr(CO)_5I$ and 0.6 g of $W(CO)_6$ in 50 ml of THF was irradiated until approximately 40–45 cm^3 of gas was evolved. The reaction mixture was worked up as described above for the symmetrical derivatives and gave 0.57 g of product.

Preparation of $[(C_6H_5)_3P]_2NM(CO)_5X$.—All of the preparations were carried out in an analogous manner. A mixture of $[(C_6H_5)_3P]_2NI$, 1.42 g, and $Cr(CO)_6$, 0.50 g, in 50 ml of CH_2Cl_2 was irradiated until 50 cm^3 of gas had been evolved. The mixture was concentrated to approximately 20 ml, and 80 ml of ether was added. The solid that precipitated was unreacted iodide. After filtering the mixture, pentane was added to the filtrate. A 0.77-g sample of $[(C_6H_5)_3P]_2NCr(CO)_5I$ was obtained.

The Reaction of I_2 with $[[(C_6H_5)_3P]_2N]_2Cr_2(CO)_{10}$.—A. Iodine, 0.255 g in 20 ml of CH_2Cl_2, was added dropwise to a solution of 1.47 g of $[[(C_6H_5)_3P]_2N]_2Cr_2(CO)_{10}$, in 60 ml of CH_2Cl_2 at 0°. After the addition was complete, the mixture was filtered and the solvent was removed at reduced pressure. The residue was dissolved in 20 ml of CH_2Cl_2, and 80 ml of ether was added. The mixture was filtered, and pentane was added to the filtrate. A 1.29-g sample of $[(C_6H_5)_3P]_2NCr(CO)_5I$ was obtained. When the reaction was run using bromine instead of iodine, a temperature of $-20°$ was employed. Table I presents the analytical data for the compounds prepared by this reaction.

B. The above procedure was repeated using 1.45 g of $[[(C_6H_5)_3P]_2N]_2Cr_2(CO)_{10}$ and 0.380 g of I_2. After the reaction was complete, the mixture was filtered and the solvent was removed under vacuum. The residue was extracted with 25 ml of ether. Addition of pentane to the extract resulted in the crystallization of 0.31 g of $[(C_6H_5)_3P]_2NCr_2(CO)_{10}I$. The residue from the extraction was dissolved in 20 ml of CH_2Cl_2. Ether, 80 ml, was added. A 0.42-g sample of $[(C_6H_5)_3P]_2NI_3$ precipitated. *Anal.* Calcd for $[(C_6H_5)_3P]_2NI_3$: C, 46.7; H, 3.25; N, 1.49; I, 42.0. Found: C, 47.1; H, 3.26; N, 1.52; I, 41.5. Pentane was added to the filtrate and a 0.65-g sample of $[(C_6H_5)_3P]_2NCr(CO)_5I$ was obtained.

The procedure described in section A was repeated using a 1.54-g sample of $[[(C_6H_5)_3P]_2N]_2Cr_2(CO)_{10}$ and 0.535 g of I_2. The work-up of the reaction mixture was the same as described in section B. This yielded a 0.63-g sample of $[(C_6H_5)_3P]_2NCr_2(CO)_{10}I$ and a 0.84-g sample of $[(C_6H_5)_3P]_2NI_3$. Less than 0.1 g of $[(C_6H_5)_3P]_2NCr(CO)_5I$ was obtained.

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

Conductivity Measurements.—The conductivity of all of the compounds prepared was determined on solutions approximately 10^{-3} *M* in nitromethane using equipment previously described.[11] In addition, the conductivity of the salt $[(C_6H_5)_3P]_2NCr_2(CO)_{10}I$ was determined as a function of concentration in nitromethane solution. The specific conductivity of the nitromethane employed as solvent was 5.47×10^{-7}. The anion, concentration (*M*), and molar conductance (cm^2/ohm equiv) are: $Cr_2(CO)_{10}I^-$, 1.078×10^{-3}, 68.0; $Cr_2(CO)_{10}Br^-$, 1.062×10^{-3}, 71.6; $Cr_2(CO)_{10}Cl^-$, 1.002, 71.1; $W_2(CO)_{10}Br^-$, 0.986×10^{-3}, 71.9; $W_2(CO)_{10}I^-$, 1.036×10^{-3}, 68.2; $Mo_2(CO)_{10}I^-$, 0.992×10^{-3}, 73.0; $CrW(CO)_{10}I^-$, 1.036, 68.5; $CrW(CO)_{10}Br^-$, 1.002×10^{-3}, 70.3; $CrMo(CO)_{10}I^-$, 1.000×10^{-3}, 70.3. The molar concentration and molar conductance of the $Cr_2(CO)_{10}I^-$ ion are: 8.625×10^{-3}, 58.9; 4.313×10^{-3}, 63.0; 2.156×10^{-3}, 65.8; 1.078×10^{-3}, 68.0. A plot of Λ *vs.* $\sqrt{C}$ gives a value of the equivalent conductance at infinite dilution of 72.8 and the slope of a plot of $\Lambda_\infty = \Lambda_c$ *vs.* $\sqrt{C}$ is 153.

Results and Discussion

The reaction between halide ions and the group VI metal carbonyls was found to occur stepwise when carried out under photolytic activation. The first step involved the formation of mononuclear anions of the type prepared by Fischer[4] and Wilkinson.[3] The

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TABLE II
CARBONYL STRETCHING FREQUENCIES OF THE COMPLEX CARBONYL HALIDE ANIONS

Anions	CO str freq, cm^{-1}
$Cr_2(CO)_{10}I^-$	2066 w, 2050 m, 1973 w, 1940 vs, 1918 s, 1877 s, 1857 m, sh
$Cr_2(CO)_{10}Br^-$	2073 vw, sh, 2060 w, 1974 m, 1943 vs, 1919 s, 1871 s, 1855 m, sh
$Cr_2(CO)_{10}Cl^-$	2069 vw, sh, 2057 w, 1974 m, 1942 v, 1917 s, 1867 s, 1850 m, sh
$Mo_2(CO)_{10}I^-$	2070 vw, sh, 2058 w, 1976 m, 1943 vs, 1921 s, 1871 s, 1856 m, sh
$W_2(CO)_{10}I^-$	2073 vw, sh, 2062 w, 1972 w, 1939 vs, 1914 s, 1872 s, 1851 m, sh
$W_2(CO)_{10}Br^-$	2074 vw, sh, 2063 w, 1971 m, 1937 vs, 1912 s, 1867 m, 1846 m, sh
$CrW(CO)_{10}I^-$	2071 vw, sh, 2062 vw, sh, 2058 w, 1978 w, sh, 1972 m, sh, 1939 vs, 1914 s, 1874 s, 1850 m, sh
$CrW(CO)_{10}Br^-$	2073 vw, sh, 2058 w, 1996 w, sh, 1972 m, sh, 1939 vs, 1913 vs, 1858 s, 1849 m, sh
$CrMo(CO)_{10}I^-$	2072 vw, sh, 2061 vw, sh, 2054 w, 1974 m, 1943 vs, 1918 s, 1875 s, 1857 m, sh

second step involved the reaction of this mononuclear anion with an activated carbonyl moiety.

$$M(CO)_6 + I^- \xrightarrow{h\nu} M(CO)_5I^- + CO$$

$$M(CO)_5I^- + M(CO)_6 \xrightarrow{h\nu} M_2(CO)_{10}I^- + CO$$

By choosing the appropriate conditions, it was possible to isolate either type of anion in moderate to good yield. A slight excess of halide ion and a completely miscible system favored the formation of the mononuclear anion while a large excess of metal carbonyl and the use of a solvent, such as THF (tetrahydrofuran), in which the halide salt was only partially soluble, favored the formation of the dinuclear species. The use of THF has the added benefit of stabilizing the activated carbonyl species by complex formation (*e.g.*, $Cr(CO)_5 \cdot THF$).[12] There was no evidence for the formation of disubstituted metal carbonyl derivatives (*e.g.*, $M(CO)_4I_2^{2-}$) when either $Cr(CO)_6$ or $W(CO)_6$ was employed. No attempt was made to prepare the mononuclear molybdenum derivatives *via* the photolytic method.

Dinuclear metal carbonyl halide anions containing different metals could be prepared by photolysis of a mixture of the mononuclear derivative of one metal carbonyl with another metal hexacarbonyl

$$Cr(CO)_5I^- + W(CO)_6 \xrightarrow[THF]{h\nu} CrW(CO)_{10}I^-$$

The yields obtained in this reaction were similar to those obtained for the symmetrical derivatives. Furthermore, the same product was obtained regardless of which metal was incorporated in the mononuclear anionic species if the other metal was used as the hexacarbonyl [*e.g.*, the same product as shown in the above equation was obtained from the reaction of $W(CO)_5I^-$ and $Cr(CO)_6$].

The halogen-containing dinuclear metal carbonyl anions form salts which in the solid state are stable in air, although in solution they undergo very slow oxidation. These salts are soluble in polar organic solvents such as CH_3NO_2, THF, ether, and CH_2Cl_2. They vary in color from red to yellow. All of the chromium-containing derivatives are orange except for $[(C_6H_5)_3P]_2NCr_2(CO)_{10}I$ which is red. The molybdenum and tungsten derivatives are yellow. There is a marked difference in stability and/or ease of preparation of these materials. The stability decreases from the iodide to the chloride as might be expected and from chromium to tungsten to molybdenum. Thus, it was not possible to prepare the $Mo_2(CO)_{10}Br^-$, $Mo_2(CO)_{10}Cl^-$, or $W_2(CO)_{10}Cl^-$ ion, and the $W_2(CO)_{10}Br^-$ ion was difficult to obtain in high yield or purity because of contamination with the mononuclear ion $W(CO)_5Br^-$. Proton nmr measurements showed that no hydridic hydrogen or paramagnetic impurities were present in the compounds. The molar conductivity of approximately 10^{-3} *M* nitromethane solutions was in the range attributed to 1:1 electrolytes.[13] The conductivity of the $Cr_2(CO)_{10}I^-$ ion was also determined as a function of concentration and a plot of $\Lambda_\infty - \Lambda_c$ *vs.* $\sqrt{C}$ gave a straight line with a slope of 153 which further supports the formulation of these materials as 1:1 electrolytes.[13] The infrared spectra in the carbonyl stretching region for the salts are summarized in Table II.

The reaction of iodine with $Na_2Cr_2(CO)_{10}$, in addition to giving the $Cr(CO)_5I^-$ ion, was reported to give two neutral compounds: $Cr(CO)_5I$ (blue) and $Cr_2(CO)_{10}I$ (red).[6,7] This reaction was claimed to be stepwise, *e.g.*

$$Cr_2(CO)_{10}^{2-} \xrightarrow{I_2} 2Cr(CO)_5I^- \xrightarrow{0.5I_2} Cr_2(CO)_{10}I \xrightarrow{0.5I_2} 2Cr(CO)_5I$$

and the product distribution was said to depend only on the ratio of iodine to the metal carbonyl anion. Furthermore, the reduction of the neutral dinuclear derivative produced above with sodium amalgam produced an anionic dinuclear species, $Cr_2(CO)_{10}I^-$.[8] Since this anion is apparently identical with one of the anions prepared in this study, the reaction discussed above was repeated. However, the bis(triphenylphosphine)imminium salt of the chromium carbonyl anion was employed instead of the sodium salt. Thus, a completely miscible system could be employed. The course of the reaction under these conditions was found, in part, to be different. The initial step was confirmed not only for iodine, but also for bromine and for the analogous tungsten carbonyl dianion with either iodine or bromine

$$M_2(CO)_{10}^{2-} + X_2 \longrightarrow 2M(CO)_5X^-$$

where M = Cr or W and X = Br or I. However, the succeeding reactions were not observed. Instead only one reaction occurred for iodine to anion ratios between 1 and 2

$$2Cr(CO)_5I^- + I_2 \longrightarrow Cr_2(CO)_{10}I^- + I_3^-$$

No evidence was found for the formation of any neutral species in this system. The reason for the differences

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is not obvious, but it may result from the use of a different solvent system in which the neutral species would be expected to be soluble.

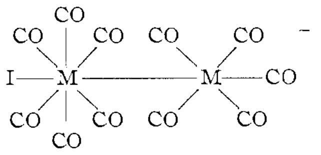
The chromium iodide derivative was found to react with triphenylphosphine at ambient temperature to regenerate the monoanion.

$$Cr_2(CO)_{10}I^- + (C_6H_5)_3P \longrightarrow Cr(CO)_5I^- + Cr(CO)_5P(C_6H_5)_3$$

Reactions of the mononuclear anions $M(CO)_5I^-$ (where M = Mo or W) with iodine or bromine have also been reported.[14,15] However, no evidence was obtained for the formation of a dinuclear species when the reaction was carried out in CCl_4. Instead the heptacoordinated species $M(CO)_4X_3^-$ was formed.

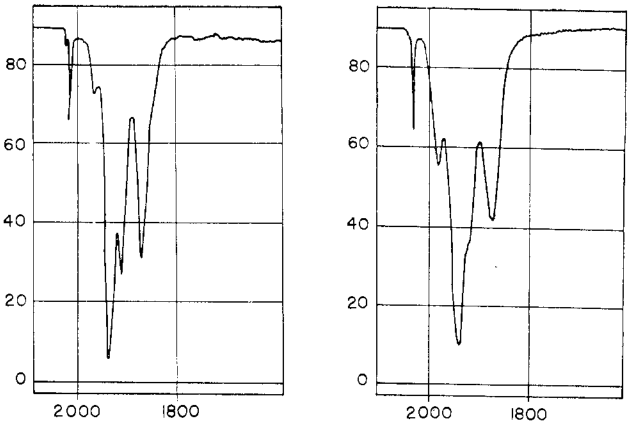
Several structures are possible for the anions prepared in this investigation. The infrared spectra of these anions rule out the presence of bridging carbonyl groups since there are no bands in the 1800–1700-cm^{-1} region of the infrared spectra. Therefore, only structures which contain either a metal–metal bond or a bridging halogen need be considered. Of these two possibilities, the latter is preferred (a) because each chromium would attain a rare gas configuration and (b) because of the method of preparation. It has been shown that the group VI metal hexacarbonyls are decomposed by ultraviolet light to an $M(CO)_5$ species which is a Lewis acid.[12] The iodide ion is sufficiently basic to form a complex with this moiety producing the monoanion $Cr(CO)_5I^-$.

The iodide in this complex might still be sufficiently basic to react with another Lewis acid moiety. Thus, a halogen-bridged species would result. Recently methyl iodide has been reported to behave as a ligand toward rhodium to give the complex $[(C_6H_5)_3P]_2Rh(CH_3)(Cl)(ICH_3)$.[16] However, the possibility of a structure such as



cannot be completely eliminated since seven-coordinate halogen carbonyl derivatives are known for molybdenum and tungsten.[14,15,17–19] All of the known derivatives are mononuclear and many contain neutral organic bidentate ligands in addition to the halogen and carbonyl groups, so they are quite different from the anions prepared in this study. In addition, they are apparently less stable. Therefore it is probable that these anions are halogen bridged rather than metal–metal bonded.

If it is assumed that the halogen is bridged between the two, then the group VI metal anions might formally be considered to be related to the hydride-bridged dinuclear anions $M_2(CO)_{10}H^-$.[20] The latter anions have D_{4h} symmetry and thus the two metal atoms and presumably the hydride lie on a fourfold axis.[21] Since the hydride ion has only one pair of electrons the metal–hydride–metal bond is electron deficient. On the other hand, the halide ion has four pairs of electrons so that two bonding possibilities arise: (a) two pairs are involved in the metal–halogen–metal system or (b) only one pair of electrons is involved in an electron-deficient bond. The former would lead to a bent metal–halogen–metal bond because there are two bonding electron pairs and two nonbonding pairs. The latter case would result in a linear metal–halogen–metal bond and the symmetry would be either D_{4h} or D_{4d} when both metals are the same. Thus only three infrared carbonyl stretching frequencies would be expected. If the metal–halogen–metal bond were bent, the anion would have C_{2v} symmetry assuming the carbonyl groups are eclipsed and eight infrared-active carbonyl stretching frequencies would be predicted. If the dinuclear ions did not have a bridged structure, but one similar to that shown above containing the heptacoordinate metal, a similar number of infrared-active carbonyl bands would be expected so that it would not be possible to distinguish the two structures.



(a) (b)

Figure 1.—The infrared spectra of the $Cr_2(CO)_{10}I^-$ anion in (a) THF solution and (b) CH_2Cl_2 solution.

Since a large difference is expected in the number of carbonyl stretches between the bridged species having a bent or linear configuration, special attention was paid to the infrared spectra. In a recent study, Lindner and Behrens observed three bands in the spectrum of $Cr_2(CO)_{10}I$ and four bands in the spectrum of the $Cr_2(CO)_{10}I^-$ ion.[22] They concluded that both species had D_{4d} symmetry or that a linear metal–halogen–metal bridge existed. However, all of the infrared spectra of the dinuclear anions prepared in this investigation have the same appearance and consist of seven carbonyl bands for the compounds containing the same metal and eight, or in one case nine, bands for the anions containing different metals. The spectra re-

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ported in Table II were obtained on THF solutions while Lindner and Behrens used a methylene chloride solution of the anion. Figure 1 shows the infrared spectrum of the $Cr_2(CO)_{10}I^-$ ion taken on (a) a THF solution and (b) a CH_2Cl_2 solution. Obviously the resolution is poorer in the second case. Whether this is due to cation–anion interaction or to another solvent effect is not known. However, a similar loss in resolution has been observed in the solution infrared spectra of other metal carbonyl compounds when the solvent is changed.[23,24] The most likely impurity present in the anions prepared in this study is the mononuclear species. Therefore, the infrared spectra of mixtures of the $Cr(CO)_5I^-$ and $Cr_2(CO)_{10}I^-$ ions were obtained over the concentration range of 25–75% impurity. Only the bands at 2050 and 1918 cm^{-1} increased as the impurity was increased. A new band at 1858 cm^{-1} also appeared. Thus, the spectrum of the monoanion agrees closely with that observed by Lindner and Behrens.[20] However, the agreement between the spectra of the dinuclear species is not good even for the CH_2Cl_2 solution since the strongest reported by Lindner and Behrens is at 1940 cm^{-1}. Thus, it is not obvious whether the differences observed in the spectra are due to (a) a difference in the structure of the two anions or (b) a difference in resolution or other solvent effects.[23,24]

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Transition Metal Complexes of Constrained Phosphite Esters. VI. Phosphorus–Metal Stretching Frequencies in Metal Carbonyl Complexes of Polycyclic Phosphites

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The far-infrared spectra of complexes of the forms $Ni(CO)_{4-x}L_x$ (x = 1, 2, 3, 4), $Fe(CO)_{5-x}L_x$ (x = 1, 2), and *cis*- and *trans*-$M(CO)_{6-x}L_x$ (x = 1, 2 and M = Cr, Mo, W) where L = $P(OCH_2)_3CCH_3$, $As(OCH_2)_3CCH_3$, or $N(C_2H_4)_3CH$ (quinuclidine) have been obtained and the absorption bands assigned to ligand vibrations, ν(M–C), δ(M–C–O), and ν(M–P), and bending modes of the general form δ(X–M–Y), where X and Y = C and C, C and P, C and N, or P and P. The preparations and characterization of the new complexes in this study are also given. Improved synthetic and purification techniques now allow an unambiguous assignment of the configurations from infrared data of the *cis* and *trans* group VI complexes of the type $M(CO)_4L_2$, where M = Cr, Mo, and W and L = $P(OCH_2)_3CCH_3$ or $P(OCH)_3(CH_2)_3$. The greater increase in ν(M–P) from the mono- to the corresponding disubstituted *trans*-octahedral carbonyl complexes of $P(OCH_2)_3CR$ (R = CH_3 or $(CH_2)_2CH_3$) compared to the *cis* isomers is tentatively interpreted in terms of the number of π metal orbitals common to both phosphorus ligands and the probable relative π-bonding powers of the carbonyl and phosphorus ligands. The opposite trends in ν(C–O) and ν(M–P) in $Ni(CO)_{4-x}L_x$ (L = PF_3 or $P(OCH_2)_3CCH_3$) upon stepwise substitution of the carbonyl groups are ascribed to the contrasting π-bonding abilities of these two ligands compared to those of a CO group.

Introduction

The degree of metal to phosphorus π bonding in transition metal carbonyl complexes containing phosphorus ligands and the influence of this mode of bonding on the carbonyl stretching frequencies have been interpreted to be significant[2] and of little or no significance.[3] The present systematic far-infrared study of a series of metal carbonyl complexes of the polycyclic phosphites $P(OCH_2)_3CR$ (where R = CH_3 or $(CH_2)_2CH_3$) permitted the assignment of the metal–phosphorus vibration ν(M–P). The trends in ν(M–P) on substitution of carbonyl groups in $Ni(CO)_4$ and $M(CO)_6$ (where M = Cr, Mo, and W) appear in all cases to be dominated by the π-bonding characteristics of the ligand.

Although the infrared modes associated with a ligand of the type $P(OR)_3$ in a complex will be more numerous and complicated than those of PF_3, for example, complexes containing a constrained ligand such as $P(OCH_2)_3CCH_3$ are more amenable to an infrared study since fewer bands are expected from the ligand on symmetry grounds. The ν(M–P) vibration(s) in the far-infrared spectra (70–800 cm^{-1}) of 15 metal carbonyl complexes of $P(OCH_2)_3CR$ (where R = CH_3 or $(CH_2)_2CH_3$) of the forms $Ni(CO)_{4-x}L_x$ (x = 1, 2, 3, 4), $Fe(CO)_{5-x}L_x$ (x = 1, 2), and $M(CO)_{6-x}L_x$ (x = 1, 2, and M = Cr, Mo, and W) were assigned by comparison of the spectra with that of *cis*-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$ in the case of the group VI complexes. The three *cis*-bis(phosphite) tetracarbonyl complexes of Cr, Mo, and W as

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[2] See for example F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references therein.

[3] See for example A. Loutellier and M. Bigorgne, *Bull. Soc. Chim. France*, 3186 (1965), and references therein.