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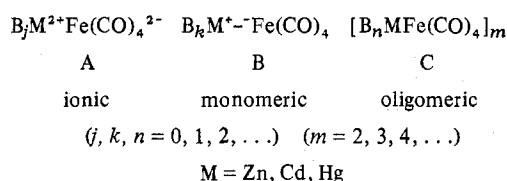
Chemical and Structural Relationships among the Oligomeric Compounds MFe(CO)₄ (M = Zn, Cd, Hg), PbFe(CO)₄, AgCo(CO)₄, and Their Base Adducts

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The synthesis and characterization of the following new metal-metal bonded complexes are reported: (py)₃ZnFe(CO)₄, (NH₃)(2,2'-bpy)ZnFe(CO)₄, (2,2':6',2''-tpy)CdFe(CO)₄, (2,2',2''-tren)CdFe(CO)₄, (2,2'-bpy)ZnFe(CO)₄, (4,4'-bpy)-CdFe(CO)₄, and (4-C₆H₅C₃H₄N)CdFe(CO)₄. Proper ligational strategy thus allows the isolation of several types of compounds which differ from the previously known B₂CdFe(CO)₄ and (NH₃)₃ZnFe(CO)₄ patterns. It is also possible to manipulate the degree of association of these species by control of the group 2B metal ion coordination sphere. Thus the first four of the new compounds listed are tentatively assigned monomeric structures, while the latter three are assigned oligomeric structures. The present studies also reveal that AgCo(CO)₄ is isomorphous with [CdFe(CO)₄]₄ and that (py)₂CdFe(CO)₄ exists as a trimer in the solid state. The complex (2,2'-bpy)AgCo(CO)₄ is found to be at most partly associated in noncoordinating solvents. In the solid state, PbFe(CO)₄ is associated.

It has been known for some time that the metal-metal bonded oligomer [CdFe(CO)₄]_n³ forms adducts, B₂CdFe(CO)₄, with a wide variety of Lewis bases, B.^{3,4} Until very recently there has been no structural information available for any of these materials. Diffraction studies have now shown that [CdFe(CO)₄]_n is a tetramer (n = 4) with approximately D_{4h} symmetry^{5a} and that (2,2'-bpy)CdFe(CO)₄, bpy = bipyridyl, is a trimer with approximately D_{3h} symmetry.^{5b} The molecular geometries of these compounds are illustrated in Figure 1. The structures of [CdFe(CO)₄]₄ adducts with other Lewis bases remain largely undefined. The compound [HgFe(CO)₄]₄ is also known^{6,7} and is isomorphous with [CdFe(CO)₄]₄,^{5a} but no base adducts have been isolated. In comparison to the results for cadmium and mercury, the only reported zinc-containing derivative, B₃ZnFe(CO)₄ where B = NH₃,⁷ contains three molecules of base. Unlike the cadmium diammine, (NH₃)₂CdFe(CO)₄, the zinc triammine does not readily lose ammonia on heating in vacuo.⁴ A number of structural types are conceivable for the above Lewis base adducts, viz., A-C. In isoelectronic group 1B metal-transition



metal carbonyl chemistry an analogous range of possibilities exists for the compounds AgCo(CO)₄ and B_nAgCo(CO)₄.⁸ Likewise, little is known about the related group 4B derivative PbFe(CO)₄.⁹

From the above discussion it can be seen that the relationships between stable oligomeric structures as well as allowed structural interconversions in group 2B and 1B metal-transition metal compounds depend on ligands and metals in a way that has not been investigated in depth. The details of, and reasons for, such relationships are of importance to studies of metal-metal bonding in general and to the challenge of preparing infinite metal atom arrays in particular. In this article we report on the synthesis of several new types of group 2B metal-transition metal complexes and discuss, on the basis of physical measurements, possible chemical and structural relationships in the B_nMFe(CO)₄ (M = Zn, Cd, Hg), AgCo(CO)₄, B_nAgCo(CO)₄, and PbFe(CO)₄ classes of molecules.

Experimental Section

All operations involving metal carbonyls were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled under nitrogen im-

mediately prior to use. Elemental analyses were performed by Miss H. Beck, Northwestern University Analytical Services Laboratory, Dornis and Kolbe Analytical Laboratories, or Schwarzkopf Analytical Laboratories. Osmometric molecular weight determinations were also carried out by Miss H. Beck using a Mechrolab Model 302 instrument.

Mercury Tetracarbonyliron, [HgFe(CO)₄]₄. This compound was prepared by the procedure of Brauer¹⁰ and was dried overnight under high vacuum. The infrared spectrum of a Nujol mull was identical with that reported previously.¹¹

Thallium Tetracarbonylcobalt, TlCo(CO)₄. This was prepared from thallium metal and Co₂(CO)₈ as described by Robinson et al.^{12a} The infrared spectral parameters were identical with those previously reported^{12b} and are consistent with the structure found by x-ray structural determination.^{12a}

Lead Tetracarbonyliron, PbFe(CO)₄. This very air-sensitive black compound was prepared by the method of Krumholz and Brill.⁹

Diamminecadmium Tetracarbonyliron, (NH₃)₂CdFe(CO)₄. This compound was synthesized by the procedure of Feigl and Krumholz³ and was dried overnight under high vacuum. Infrared spectral parameters were identical with those previously reported.^{5a}

Cadmium Tetracarbonyliron, [CdFe(CO)₄]₄, and Bis(pyridine)-cadmium Tetracarbonyliron, (py)₂CdFe(CO)₄. These were prepared from (NH₃)₂CdFe(CO)₄ according to our previous procedures.^{5a}

(2,2',2''-Triaminotriethylamine)cadmium Tetracarbonyliron, (tren)CdFe(CO)₄. To a suspension of 1.40 g (4.45 mmol) of (NH₃)₂CdFe(CO)₄ in 40 mL of diethyl ether under nitrogen was added an excess (1.0 mL) of 2,2',2''-triaminotriethylamine with stirring. After 3 h, stirring was discontinued and the solid product was allowed to settle. The supernatant was removed and the product was washed three times with 25-mL portions of diethyl ether and dried in vacuo overnight. The compound is only very slightly soluble in most organic solvents. Crystalline material could best be obtained by a controlled ligand replacement in which a solution of 2,2',2''-triaminotriethylamine is slowly reacted with (2,2'-bpy)CdFe(CO)₄.⁵

Anal. Calcd for C₁₀H₁₈CdFeN₄O₄: C, 28.16; H, 4.25; N, 13.14. Found: C, 27.84; H, 4.31; N, 12.93.

Complete infrared data (Nujol mull): 3364 (m), 3310 (w), 3212 (m), 3126 (sh), 1948 (s), 1857 (s), 1815 (sh), 1798 (vs, br), 1583 (s), 1314 (m), 1268 (w), 1107 (w), 1094 (w), 1065 (s), 1037 (s), 1000 (m), 973 (m), 883 (m), 855 (w), 734 (w), 716 (w), 626 (s) cm⁻¹.

Attempted Preparation of Bis(2,2'-bipyridyl)cadmium Tetracarbonyliron, (2,2'-bpy)₂CdFe(CO)₄. To 50 mL of deoxygenated aqueous ammonia was added 1.3 mL of Fe(CO)₅ (0.010 mol) under nitrogen and the resulting mixture was stirred overnight. To this solution of HFe(CO)₄⁻⁴ was added 50 mL of a deoxygenated aqueous solution containing 2.67 g (0.01 mol) of cadmium acetate dihydrate and 3.12 g (0.02 mol) of 2,2'-bipyridyl at 0 °C. This resulted in the precipitation of a yellow-orange solid which was filtered, washed with three 20-mL portions of deoxygenated water followed by three 20-mL portions of diethyl ether, and dried in vacuo. Elemental analysis (C, H, N), infrared spectroscopy, and x-ray powder diffraction identified the product as [(2,2'-bpy)CdFe(CO)₄]₃.⁵

(2,2':6',2''-Terpyridyl)cadmium Tetracarbonyliron, (tpy)CdFe(CO)₄. A slight excess of 2,2':6',2''-terpyridyl (0.20 g, 0.86 mmol) was dissolved in 10 mL of acetone and added dropwise to 0.20 g (0.71 mmol) of [CdFe(CO)₄]₄ in 25 mL of acetone under nitrogen with

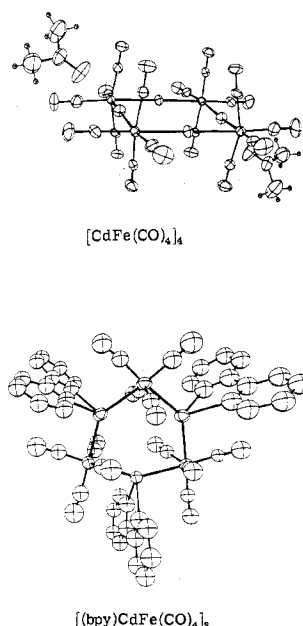


Figure 1. Perspective views of $[\text{CdFe}(\text{CO})_4]_4$ (from ref 5a) and $[(2,2'\text{-bpy})\text{CdFe}(\text{CO})_4]_3$ (from ref 5b).

stirring. A reddish orange precipitate immediately formed, and after 2 h of stirring, the supernatant was removed. The solid product was then washed with three 25-mL portions of acetone and dried in vacuo. The product so obtained smolders in air and is nearly insoluble in most organic solvents, except pyridine. Crystalline materials, significantly more air-resistant, may be obtained by slow diffusion of the reacting species through a medium glass frit.

Anal.¹³ Calcd for $\text{C}_{19}\text{H}_{11}\text{CdFeN}_3\text{O}_4$: C, 44.44; H, 2.16; N, 8.18; Cd, 21.89; Fe, 10.87. Found: C, 42.30; H, 2.48; N, 8.59; Cd, 22.32; Fe, 11.20.

Complete infrared data (Nujol mull): 1985 (sh), 1973 (s), 1887 (s), 1872 (sh), 1850 (sh), 1593 (m), 1579 (w), 1573 (w), 1563 (w), 1433 (sh), 1419 (sh), 1306 (w), 1241 (w), 1186 (w), 1162 (w), 1155 (w), 998 (w), 754 (s), 645 (m), 622 (s) cm^{-1} .

(4,4'-Bipyridyl)cadmium Tetracarbonyliron, (4,4'-bpy)CdFe(CO)₄. This compound was prepared by stirring stoichiometric amounts of 4,4'-bipyridyl dihydrate (0.50 g, 2.6 mmol) and $[\text{CdFe}(\text{CO})_4]_4$ (0.73 g, 2.6 mmol) in 30 mL of acetone under nitrogen for 1 day. The bright yellow precipitate which had formed immediately was then filtered from the supernatant, washed with several 10-mL portions of acetone, followed by several 20-mL portions of ether, and dried in vacuo.

Anal. Calcd for $\text{C}_{14}\text{H}_8\text{CdFeN}_2\text{O}_4$: C, 38.52; H, 1.86; N, 6.42. Found: C, 37.83; H, 1.58; N, 6.03.

Complete infrared data (Nujol mull): 1977 (s), 1904 (s), 1892 (s, sh), 1604 (m), 1534 (w), 1491 (sh), 1414 (m), 1317 (w), 1219 (m), 1215 (m), 1062 (m), 1042 (w), 997 (m), 847 (w), 799 (m), 606 (s) cm^{-1} .

(4-Phenylpyridine)cadmium Tetracarbonyliron, (4-C₆H₅C₃H₄N)CdFe(CO)₄. To 0.33 g (1.18 mmol) of $[\text{CdFe}(\text{CO})_4]_4$ in 30 mL of acetone at -78°C under nitrogen was added 0.15 g (0.97 mmol) of 4-phenylpyridine with stirring. The solution was allowed to reach room temperature over a period of several hours and was then stirred 2 h more. The volume of the solution was next reduced by half, 50 mL of pentane was added, and the solution was cooled to -78°C , producing a yellow mixture of crystals and microcrystalline powder. The supernatant was removed and the solid was washed twice with 20-mL portions of diethyl ether and thoroughly dried in vacuo. The product was next taken up in a minimum volume of methylene chloride and filtered from any residue (unreacted $[\text{CdFe}(\text{CO})_4]_4$). An equal volume of pentane was added to the filtrate at -78°C , producing a beautiful lemon yellow microcrystalline solid. After removal of solvent, the somewhat air-sensitive product was dried in vacuo for 1 h.

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{CdFeNO}_4$: C, 41.28; H, 2.31; N, 3.21. Found: C, 40.87; H, 2.31; N, 3.33.

Complete infrared data (Nujol mull): 2000 (s), 1990 (sh), 1941 (sh), 1933 (sh), 1914 (s), 1907 (sh), 1891 (s), 1868 (sh), 1840 (m), 1806 (m), 1606 (m), 1546 (w), 1483 (sh), 1412 (m), 1219 (m), 1063

(m), 1040 (w), 1017 (w), 1003 (m), 912 (w), 827 (w), 756 (m), 748 (sh), 724 (w), 690 (w), 605 (s) cm^{-1} .

Tris(pyridine)zinc Tetracarbonyliron, (py)₃ZnFe(CO)₄. The compound $(\text{NH}_3)_3\text{ZnFe}(\text{CO})_4$, prepared as previously described,^{4,8} was dissolved in an excess of deoxygenated pyridine under nitrogen. After evolution of NH_3 was complete, a nitrogen flow was passed over the solution for 1 h. Addition of ten volumes of pentane produced an oil, which solidified on cooling to -20°C . The supernatant was removed, and the yellow-brown solid crushed to a powder. After washing with three 30-mL portions of diethyl ether, a bright yellow solid remained, which was dried in vacuo 1 h.

Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{FeN}_3\text{O}_4\text{Zn}$: C, 48.50; H, 3.21; N, 8.93. Found: C, 48.50; H, 3.20; N, 8.33.

Complete infrared data (Nujol mull): 1974 (s), 1954 (s), 1879 (s, vbr), 1821 (s, vbr), 1796 (sh), 1603 (m), 1485 (sh), 1445 (sh), 1213 (m), 1153 (m), 1064 (m), 1036 (m), 1006 (m), 752 (m), 693 (s), 618 (s) cm^{-1} .

(Ammine)(2,2'-bipyridyl)zinc Tetracarbonyliron, (NH₃)(2,2'-bpy)ZnFe(CO)₄. To 50 mL of aqueous ammonia was added 1.3 mL (0.01 mol) of $\text{Fe}(\text{CO})_5$ under nitrogen. After allowing this mixture to stir overnight (producing $\text{HFe}(\text{CO})_4^-$),⁴ 50 mL of a deoxygenated aqueous solution containing 2.20 g (0.01 mol) of zinc acetate dihydrate and 1.56 g (0.01 mol) of 2,2'-bipyridyl was added at 0°C , causing a red-violet solid to appear. After 1 h, the supernatant was removed and the solid was washed with three 30-mL portions of water, followed by three 30-mL portions of diethyl ether. The slightly air-sensitive product was then dried in vacuo 1 h.

Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{FeN}_3\text{O}_4\text{Zn}$: C, 41.37; H, 2.73; N, 10.34. Found: C, 40.53; H, 2.63; N, 9.85.

Complete infrared data (Nujol mull): 3367 (m), 3346 (m), 3276 (w), 1975 (m), 1947 (s), 1914 (m), 1832 (s, vbr), 1788 (s, br), 1605 (m), 1596 (m), 1491 (sh), 1443 (sh), 1315 (m), 1204 (m), 1173 (w), 1157 (m), 1036 (w), 1020 (m), 1012 (sh), 834 (w, br), 760 (s), 726 (m), 643 (m), 625 (s) cm^{-1} .

(2,2'-Bipyridyl)zinc Tetracarbonyliron, (2,2'-bpy)ZnFe(CO)₄. By maintaining $(\text{NH}_3)(2,2'\text{-bpy})\text{ZnFe}(\text{CO})_4$ at 75°C in vacuo for 3 days, the desired compound, of red-violet color, was obtained.

Anal. Calcd for $\text{C}_{14}\text{H}_8\text{FeN}_2\text{O}_4\text{Zn}$: C, 43.18; H, 2.07; N, 7.19. Found: C, 43.52; H, 2.28; N, 7.07.

Complete infrared data (Nujol mull): 2031 (w), 1975 (s), 1914 (s), 1881 (sh), 1866 (s), 1605 (m), 1597 (m), 1440 (sh), 1321 (m), 1258 (w), 1244 (w), 1172 (m), 1158 (m), 1060 (w), 1041 (m), 1015 (m), 1006 (sh), 760 (s), 727 (m), 715 (sh), 644 (m), 623 (s), 615 (sh) cm^{-1} .

Silver Tetracarbonylcobalt, AgCo(CO)₄. This was prepared by a variation of the method of Schubert,¹⁴ wherein an ammoniacal aqueous AgNO_3 solution is reacted with aqueous $\text{NaCo}(\text{CO})_4$ ¹⁵ under nitrogen. The yellow precipitate was then filtered, washed with pentane to remove $\text{Co}_2(\text{CO})_8$, taken up in acetone, and filtered through a fine frit (to remove metallic silver). Addition of water to the filtrate caused precipitation of the compound. If necessary, the acetone/water recrystallization was repeated several times to complete the removal of silver (which, along with $\text{Co}_2(\text{CO})_8$, causes rapid catalytic decomposition of the compound).^{7,15} After removal of the supernatant, the solid compound was further washed with pentane, dried quickly (1 h) in vacuo, and stored in darkness at -20°C to avoid decomposition.

Infrared data (Nujol mull): 2069 (s), 2034 (s), 2008 (s), 1993 (s), 1961 (s, br), 1937 (s) cm^{-1} .

(2,2'-Bipyridyl)silver Tetracarbonylcobalt, (2,2'-bpy)AgCo(CO)₄. This compound was prepared by a modification of the procedure of Hieber, et al.^{8,16} The addition of 0.46 g (2.95 mmol) of 2,2'-bipyridyl to a freshly prepared solution of $\text{AgCo}(\text{CO})_4$ in ethanol (from the addition of 0.57 g (2.95 mmol) of $\text{NaCo}(\text{CO})_4$ in 30 mL of ethanol to 0.50 g (2.95 mmol) of AgNO_3 in 30 mL of ethanol) produced the desired compound. After stirring the mixture under nitrogen for 30 min, the solvent was removed in vacuo. The compound was then quickly extracted with a large volume of methylene chloride and the resulting solution was filtered and reduced in volume under high vacuum. Addition of several volumes of pentane at -20°C resulted in precipitation of the compound as a bright yellow solid.

Anal. Calcd for $\text{C}_{14}\text{H}_8\text{AgCoN}_2\text{O}_4$: C, 38.65; H, 1.85; N, 6.44. Found: C, 37.67; H, 1.80; N, 6.17.

Complete infrared data (Nujol mull): 2014 (s), 1967 (s), 1938 (s), 1910 (s), 1595 (sh), 1590 (m), 1566 (w), 1483 (sh), 1473 (sh), 1435 (sh), 1314 (m), 1303 (w), 1252 (w), 1240 (w), 1204 (w), 1169

(m), 1152 (m), 1097 (w), 1055 (w), 1036 (w), 1004 (m), 999 (sh), 747 (s), 730 (m), 635 (mw), 613 (w) cm⁻¹.

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer 267 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. Solutions were prepared in Schlenk apparatus and were transferred to matched NaCl cells as described previously.¹⁷ All spectra were calibrated with polystyrene.

X-ray Powder Diffraction Studies. X-ray powder diffraction patterns were recorded photographically on a Picker 6147 x-ray diffractometer using filtered Cu K α radiation. Samples were sealed in 0.5-mm glass capillaries under nitrogen and rotated during exposure.

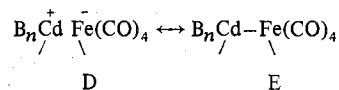
Unit Cell and Space Group Determination of Bis(pyridine)cadmium Tetracarbonyliron, (py)₂CdFe(CO)₄. The compound was crystallized by very slow cooling of a hot saturated solution in pyridine/mesitylene (1:4), yielding large, well-formed crystals. Elemental analysis of the single crystals proved them to be identical with that of the starting compound.¹⁸

A suitable single crystal was mounted under nitrogen in a glass capillary. Microscopic examination revealed no evidence of twinning. Oscillation, Weissenberg, and precession photographs, using filtered Cu K α or Mo K α radiation, revealed an orthorhombic unit cell, $a = 12.42 \text{ \AA}$, $b = 22.62 \text{ \AA}$, $c = 17.04 \text{ \AA}$, and $V = 4788 \text{ \AA}^3$. Systematic absences were observed for reflections of the type $hk0$, $h + k$ odd, $h0l$, l odd, and $0kl$, k odd. These absences are uniquely consistent with space group No. 60, D_{2h}^{14} - $Pbcn$.¹⁹ The observed density, 1.82 g/cm³ in a 1,4-dibromobutane/methylene bromide mixture, agrees with the calculated value of 1.82 g/cm³ for $Z = 12$. Since there are eight general positions in the unit cell, this means that, barring the unlikely of extreme disorder, the unit cell contains four trimeric units, which lie on twofold axes (e.g., along $0, y, 1/4$).

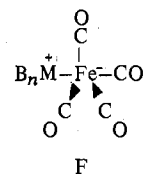
Results

Group 2B Compounds. Previously reported group 2B metal-tetracarbonyliron complexes have been of the stoichiometry MFe(CO)₄ (where M = Cd,³ Hg^{6,7}), B₂MFe(CO)₄ (where M = Cd and B = NH₃,³ pyridine,³ γ -picoline;⁴ B₂ = 2,2'-bipyridyl,⁴ 1,10-phenanthroline,⁴ ethylenediamine⁴), as well as B₃MFe(CO)₄ (where M = Zn and B = NH₃).⁷ The scope of complexes which can be synthesized is expanded in the present work. By carefully controlling the stoichiometry, reaction conditions, and the nature of the ligands, we have obtained the following new types of compounds: BCdFe(CO)₄, from a low-temperature reaction of B = 4-C₆H₅C₃H₄N with excess [CdFe(CO)₄]₄, (4,4'-bpy)CdFe(CO)₄, which may be polymeric by virtue of bridging nitrogenous ligands, B₃CdFe(CO)₄, by using the tridentate ligand 2,2':6',2''-terpyridyl (tpy), possibly B₄CdFe(CO)₄ by using the potentially tetradentate ligand 2,2',2''-triaminotriethylamine (tren),²⁰ and finally B₂ZnFe(CO)₄, by careful removal of NH₃ from (NH₃)(2,2'-bpy)ZnFe(CO)₄ in vacuo. Attempts to stabilize the B₄CdFe(CO)₄ species (2,2'-bpy)₂CdFe(CO)₄ by coordination of the base on cadmium prior to reaction with HFe(CO)₄⁻ led simply to loss of the excess base and isolation of [(2,2'-bpy)CdFe(CO)₄]₃. Attempts to prepare base adducts of [HgFe(CO)₄]₄ using mono- or bidentate nitrogen donor ligands also failed, as determined by x-ray powder diffraction, infrared spectroscopy, and elemental analysis. Synthetic procedures and analytical data are compiled in the Experimental Section.

From our previous work in group 2B^{5,21} and group 4B^{22,23} metal-transition metal chemistry as well from established electron density-CO force constant relationships in metal carbonyl vibrational spectroscopy,^{5,24} it is possible to draw a number of qualitative structural inferences about the new Fe(CO)₄ derivatives from band positions, splittings, and intensities in the infrared spectra. In particular, progressive coordination of Lewis base molecules to the main group metal is expected to weaken or destroy metal-metal bonding.^{5,23,25} Furthermore, the accompanying base stabilization of ionic resonance hybrids such as D is predicted to result in a lowering of C-O stretching frequencies due to increased population of C-O π^* orbitals and decreased C-O bond order. Whether

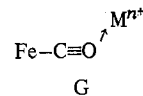


a particular B_nMFe(CO)₄ species is or is not oligomeric can be investigated by comparing spectra in the solid state^{24f} or in noncoordinating solvents with those obtained in coordinating solvents (e.g., pyridine). Base-induced metal-metal bond fracture by the coordinating solvent will result in a shift of the $\nu_{\text{C-O}}$ absorptions to lower energy. Upon full cleavage to bimetallic units, the band pattern generally simplifies and is characteristic of the C_{3v} local symmetry (2A₁, 1E modes) of the monomer, F.⁵ Such structures have been identified for



isoelectronic R₂(B)M'Fe(CO)₄^{23,25a} and X₃M'Fe(CO)₄⁻²⁶ derivatives (M' = group 4B metal), (py)₃CdFe(CO)₄ (shown to be monomeric in solution),⁵ HFe(CO)₄⁻²⁷ and RFe(CO)₄⁻ (R = *n*-C₃H₇).²⁸ Cleavage of all metal-metal bonds to yield an ionic structure, A, would displace the C-O vibrational frequencies to the region of Na₂Fe(CO)₄, i.e., 1720 cm⁻¹ in [(cryptate)Na]₂Fe(CO)₄,^{28a} 1730 cm⁻¹ in DMF,²⁹ and 1761 cm⁻¹ as a Nujol mull.²⁷ As will be seen, the above vibrational spectroscopic information can be supplemented by x-ray powder diffraction studies in the solid and molecular weight measurements in solution. Detailed metrical data, however, will only come from complete single-crystal diffraction studies.

Solid-state infrared spectra in the C-O stretching region of representative group 2B metal-transition metal derivatives are shown in Figure 2. Numerical data are summarized in Table I along with solution molecular weights. It can be seen that increasing the number as well as the basicity of donor molecules coordinated to the group 2B metal generally leads to a lowering of the carbonyl stretching frequencies. Also, zinc complexes have lower energy C-O stretching transitions than cadmium analogues. These trends reflect increasing polarity of metal-metal bonding and negative charge buildup on the Fe(CO)₄ fragment. The lowest C-O stretching frequencies are observed for the B₃MFe(CO)₄ complexes. The energies of the carbonyl stretching absorptions in the latter compounds shift very little on dissolution in coordinating solvents. Furthermore, solution spectra (Figure 3) are in good agreement with the approximately C_{3v} structure F.^{5,24} These observations viewed in light of the molecular weight data and the saturation of the M²⁺ coordination sphere strongly suggest monomeric structures.³⁰ The complex (tren)CdFe(CO)₄ possesses the lowest energy $\nu_{\text{C-O}}$ absorptions of any of the molecules examined. Though the energies and the molecular symmetry as revealed by the band multiplicity are not compatible with a purely ionic structure, it is possible that tetradentate Cd²⁺ coordination by the tren ligand may be placing additional negative charge on the tetracarbonyliron moiety. In none of the compounds studied was the characteristic C-O band position of a species with an isocarbonyl interaction,³¹ G, observed. A strong transition in the infrared



spectrum of (tren)CdFe(CO)₄ at 1583 cm⁻¹ can be assigned to an NH₂ deformation;³² in the free ligand this band occurs at 1592 cm⁻¹.

The B₂MFe(CO)₄ molecules all appear to be associated to some degree. We have already shown [(2,2'-bpy)CdFe(CO)₄]₃

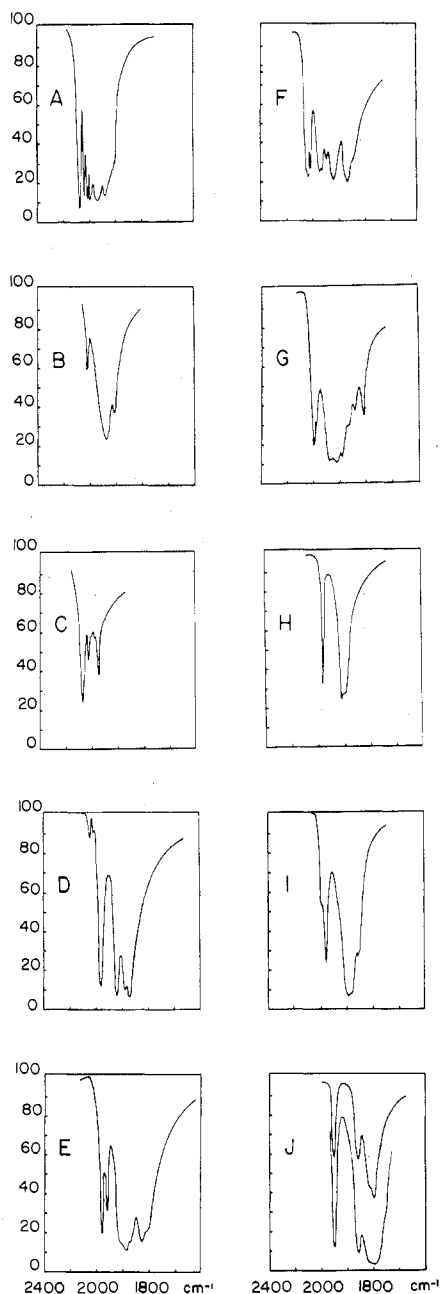


Figure 2. Nujol mull infrared spectra of various metal carbonyl complexes: (A) $[\text{AgCo}(\text{CO})_4]_4$, (B) $\text{TlCo}(\text{CO})_4$, (C) $\text{PbFe}(\text{CO})_4$, (D) $(2, 2'\text{-bpy})\text{ZnFe}(\text{CO})_4$, (E) $(\text{py})_3\text{ZnFe}(\text{CO})_4$, (F) $[\text{CdFe}(\text{CO})_4]_4$, (G) $(4\text{-C}_6\text{H}_5\text{C}_2\text{H}_4\text{N})\text{CdFe}(\text{CO})_4$, (H) $(4,4'\text{-bpy})\text{CdFe}(\text{CO})_4$, (I) $(\text{tpy})\text{CdFe}(\text{CO})_4$, (J) $(\text{tren})\text{CdFe}(\text{CO})_4$.

to be trimeric in the solid state and in noncoordinating solvents.⁵ The space group and unit cell parameters of $(\text{py})_2\text{CdFe}(\text{CO})_4$ also suggest a trimeric structure in the crystal (see Experimental Section for details). On the basis of infrared spectral and molecular weight studies, this compound is known to exist in pyridine solution as monomeric $(\text{py})_3\text{CdFe}(\text{CO})_4$.^{5a} X-ray powder diffraction studies revealed that $(2,2'\text{-bpy})\text{ZnFe}(\text{CO})_4$ and $(2,2'\text{-bpy})\text{CdFe}(\text{CO})_4$ are not isomorphous. The exact structure of the Zn compound remains undetermined; however, the similarity of the $\nu_{\text{C-O}}$ multiplicities and energies to those of the Cd analogue strongly suggest an associated structure. This compound is insufficiently soluble for solution molecular weight determination. The $\text{BCdFe}(\text{CO})_4$ compound $(4\text{-C}_6\text{H}_5\text{C}_2\text{H}_4\text{N})\text{CdFe}(\text{CO})_4$ is found to be dimeric in benzene (Table I). Though a similar structure could be adopted by $(4,4'\text{-bpy})\text{CdFe}(\text{CO})_4$, the very low solubility of this complex along with the lower C–O stretching

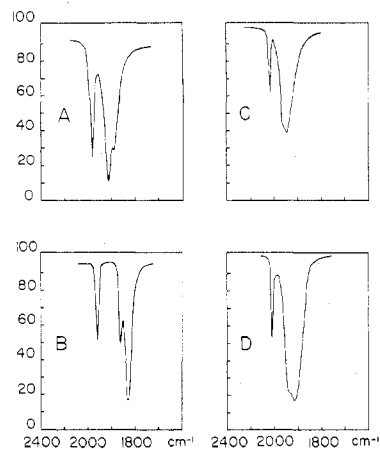


Figure 3. Solution infrared spectra for various monomeric metal-metal bonded carbonyls: (A) $(\text{tpy})\text{CdFe}(\text{CO})_4$ in pyridine, (B) $(\text{py})_3\text{ZnFe}(\text{CO})_4$ in pyridine, (C) $(2,2'\text{-bpy})\text{AgCo}(\text{CO})_4$ in CH_2Cl_2 , (D) $(2,2'\text{-bpy})\text{AgCo}(\text{CO})_4$ in pyridine.

frequencies suggests an oligomeric bpy cross-linked structure with both nitrogen atoms involved in Cd^{2+} coordination (to different cadmium ions).

Silver and Lead Complexes. A number of structural similarities exist between isoelectronic pairs of group 2B and group 4B metal-transition metal complexes. For example, the $\text{B}_3\text{MFe}(\text{CO})_4$ and $\text{R}_2(\text{B})\text{M}'\text{Fe}(\text{CO})_4$ ^{23,25a} ($\text{M}' = \text{Si, Ge, Sn, Pb}$) compounds are largely monomeric, while $\text{B}_2\text{CdFe}(\text{CO})_4$ and $\text{R}_2\text{M}'\text{Fe}(\text{CO})_4$ ³³ compounds are, in the absence of overwhelming steric factors, associated. These similarities motivated the examination of relationships among similar compounds involving group 4B (divalent), group 3B, and group 1B metal ions. For example, the structures of $\text{AgCo}(\text{CO})_4$ ¹⁴ and $\text{PbFe}(\text{CO})_4$ ⁹ are unknown, while those of their respective isoelectronic analogues, $[\text{CdFe}(\text{CO})_4]_4$ ^{5a} and $\text{TlCo}(\text{CO})_4$ ¹² are known. The solid-state infrared spectra of $\text{PbFe}(\text{CO})_4$ and $\text{TlCo}(\text{CO})_4$ are compared in Figure 2 and are seen to be rather dissimilar. The spectrum of $\text{PbFe}(\text{CO})_4$ resembles that of an oligomeric structure; i.e., the bands are shifted very much to high frequency, coming near those of $[\text{CdFe}(\text{CO})_4]_4$ and $\text{Fe}(\text{CO})_4\text{Cl}_2$ (Table I), whereas the spectrum of the more ionic^{12a} $\text{TlCo}(\text{CO})_4$ is closer to that of $\text{NaCo}(\text{CO})_4$ (Table I, Figure 2). In agreement with these observations, x-ray powder patterns reveal that these compounds are not isomorphous. Efforts to cleave $\text{PbFe}(\text{CO})_4$ with a variety of Lewis bases were unsuccessful.

In contrast to the Pb, Tl results, the infrared spectra of $\text{AgCo}(\text{CO})_4$ and $[\text{CdFe}(\text{CO})_4]_4$ are qualitatively rather similar (Figure 2), although the C–O stretching transitions of $\text{AgCo}(\text{CO})_4$ occur at somewhat higher energy, in accord with the lower formal negative charge on the $\text{Co}(\text{CO})_4^-$ fragment as compared to the $\text{Fe}(\text{CO})_4^{2-}$ fragment.²⁴ Thus the compounds may be composed of similar oligomeric units. Indeed, x-ray powder diffraction data (Table II) show them to be isomorphous. These results strongly argue that in $\text{AgCo}(\text{CO})_4$, the metal atoms are also arrayed in an approximately planar, centrosymmetric eight-membered ring. Unlike $[\text{CdFe}(\text{CO})_4]_4$, $[\text{AgCo}(\text{CO})_4]_4$ is particularly prone to thermal decomposition, yielding Ag and $\text{Co}_2(\text{CO})_8$. The decomposition is catalyzed so greatly by even traces of Ag that various attempts to crystallize the compound by a reversible homolytic metal-metal bond cleavage cycle have so far been fruitless.

The compounds $(2,2'\text{-bpy})\text{AgCo}(\text{CO})_4$ and $[(2,2'\text{-bpy})\text{CdFe}(\text{CO})_4]_3$ were also investigated for a possible structural relationship. The Nujol mull and solution infrared spectra of these compounds (Table I and Figure 3) are not particularly similar, and the solid compounds, each recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$, are not isomorphous by x-ray powder dif-

Table I. Comparison of Infrared-Active C-O Stretching Frequencies in Related Metal Carbonyl Complexes^a

Compound	Phase	ν_{CO} , cm ⁻¹	Mol wt ^b	Solvent
[CdFe(CO) ₄] ₄	Nujol mull	2032 s, 2012 m, 1972 ms, 1961 ms, 1946 m, 1920 s, br, 1867 s, br, 1840 w, sh		
PbFe(CO) ₄	Nujol mull	2049 s, 2006 m, 1990 w, sh, 1978 w, sh, 1964 ms		
[(4-C ₆ H ₅ C ₅ H ₄)CdFe(CO) ₄] ₂	Nujol mull	2000 s, 1990 sh, 1941 sh, 1933 sh, 1914 s, 1907 sh, 1891 s, 1868 sh, 1840 m, 1806 m		
[(4-C ₆ H ₅ C ₅ H ₄ N)CdFe(CO) ₄] ₂	CH ₂ Cl ₂	1992 m, 1927 s, br	819 (873)	Benzene
[(2,2'-bpy)CdFe(CO) ₄] ₃ ^c	Benzene	1982 vs, 1922 s, 1894 ms, 1879 sh	1344 (1308)	Benzene
(py) ₃ CdFe(CO) ₄ ^c	Pyridine	1976 s, 1908 vs, 1886 sh	320 (280) ^c	Pyridine
(tpy)CdFe(CO) ₄	Nujol mull	1985 sh, 1973 s, 1887 s, 1872 sh, 1850 sh		
(tpy)CdFe(CO) ₄	Pyridine	1977 s, 1907 vs, 1888 sh		
(tren)CdFe(CO) ₄	Nujol mull	1948 s, 1857 s, 1815 sh, 1798 vs, br		
(4,4'-bpy)CdFe(CO) ₄	Nujol mull	1977 s, 1904 s, 1892 s, sh		
(2,2'-bpy)ZnFe(CO) ₄	Nujol mull	1975 s, 1914 s, 1881 sh, 1866 s		
(NH ₃)(2,2'-bpy)ZnFe(CO) ₄	Nujol mull	1975 m, 1947 s, 1914 m, 1832 s, 1788 s		
(NH ₃) ₃ ZnFe(CO) ₄	Nujol mull	1994 m, 1943 s		
(py) ₃ ZnFe(CO) ₄	Nujol mull	1974 s, 1954 s, 1879 s, br, 1821 s, 1796 sh		
(py) ₃ ZnFe(CO) ₄	Pyridine	1954 ms, 1857 ms, 1823 s	487 (470)	Pyridine
[Et ₄ N]HFe(CO) ₄ ^d	Nujol mull	2008 mw, 1910 sh, 1848 s, br		
Na ₂ Fe(CO) ₄ ^{24a}	Nujol mull	1761 s		
Na ₂ Fe(CO) ₄ ^{24b}	DMF	1730 s		
[(cryptate)Na] ₂ Fe(CO) ₄ ^e	KBr	1720 s		
Fe(CO) ₄ Cl ₂ ^f	C ₆ Cl ₆	2164 w, 2124 s, 2108 m, 2084 s		
[AgCo(CO) ₄] ₄	Nujol mull	2069 s, 2034 s, 2008 s, 1993 s, 1961 s, br, 1937 s		
TiCo(CO) ₄	Nujol mull	2020 mw, 1931 vs, 1900 m, sh	376 (375) ^g	Benzene ^g
(2,2'-bpy)AgCo(CO) ₄	Nujol mull	2014 s, 1967 s, 1938 s, 1910 s		
(2,2'-bpy)AgCo(CO) ₄	CH ₂ Cl ₂	2023 ms, 1954 sh, 1940 s, br	603 (435)	CH ₂ Cl ₂
(2,2'-bpy)AgCo(CO) ₄	Pyridine	2011 ms, 1930 sh, 1910 s, br		
(o-triars)AgCo(CO) ₄ ^h	CHCl ₃	2037 s, 1953 sh, 1923 s	778 (730) ^h	Benzene
NaCo(CO) ₄ ⁱ	DMF	1892 s		
Co(CO) ₄ Cl ^j	Acetone	2120 m, 2068 m, 2046 s, br		

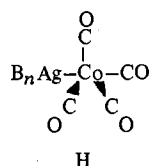
^a Key: m = medium; s = strong; sh = shoulder; br = broad; w = weak; v = very. ^b Value in parentheses is that calculated for the formula unit shown in the left-hand column. ^c Reference 5. ^d Reference 27. ^e Reference 28a. ^f K. Noack, *Helv. Chim. Acta*, 45, 1847 (1962). ^g S. R. Pedersen and W. R. Robinson, *Inorg. Chem.*, 14, 2360 (1975). ^h Reference 35. ⁱ W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, 87, 2563 (1965). ^j M. Pankowsky and M. Bigorgne, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 264, 1382 (1967).

Table II. X-Ray Powder Diffraction Data for [CdFe(CO)₄]₄ and [AgCo(CO)₄]₄^{a,b}

[CdFe(CO) ₄] ₄		[AgCo(CO) ₄] ₄	
9.61 s	4.08 mw	9.83 s	4.11 m
8.67 w	2.88 s	8.89 m	2.94 s
6.07 s		6.33 s	2.67 m
4.85 s	2.48 s	5.14 s, 4.91 mw	2.49 s

^a Calculated *d* spacings in Å; Cu K α radiation. ^b Relative line intensities: s = strong, m = medium, w = weak.

fraction. The infrared spectrum of (2,2'-bpy)AgCo(CO)₄ in CH₂Cl₂ (Figure 3) is essentially that expected for a monomeric D_{3h} structure such as H.^{24,34} Furthermore, the compound is



found to be at most only partially associated in methylene chloride solution by osmometry (Table I). Relatively small shifts of the C-O stretching transitions are observed in pyridine solution (Table I, Figure 3) indicating a similar structure in this medium, with possible weak coordination of an additional

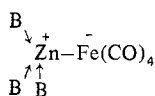
molecule of base. The related compound (o-triars)AgCo(CO)₄ (o-triars = bis(o-dimethylarsinophenyl)methylarsine) is known to be monomeric in solution and exhibits a similar infrared spectrum³⁵ (Table I).

Discussion

The results of these studies have shown that B_nMFe(CO)₄ complexes (for M = Zn or Cd) other than those normally favored by typical monodentate ligands in the solid state can be isolated using an appropriate ligational strategy. Thus, not only have solution-state structures (e.g., monomeric B₃CdFe(CO)₄⁵) been stabilized in the solid state but also structures previously unknown in either phase have been obtained (e.g., B₂ZnFe(CO)₄ and BCdFe(CO)₄). The solid-state structures of these and isoelectronic species thus far observed fall into three categories of aggregation: ionic (A), monomeric (B), and oligomeric (C). Through this series the iron coordination number ranges from 4 to 6. The ionic mode has already been established in [(cryptate)Na]₂Fe(CO)₄³⁶ and to some extent in isoelectronic TiCo(CO)₄¹² while (B)-R₂M'Fe(CO)₄^{23,25a} B₃CdFe(CO)₄⁵ and (o-triars)AgCo(CO)₄³⁵ are known to be monomeric. Similarly, oligomeric structures have been demonstrated for [CdFe(CO)₄]₄⁵ B₂CdFe(CO)₄⁵ and R₂M'Fe(CO)₄ species³³ with normal R groups. The present studies have shown that B₂ZnFe(CO)₄ (B₂ = 2,2'-bpy), BCdFe(CO)₄ (B = 4-C₆H₅C₅H₄N), and

$\text{AgCo}(\text{CO})_4$ are most likely oligomeric, while $\text{B}_3\text{ZnFe}(\text{CO})_4$ ($\text{B} = \text{py}$, $\text{B}_3 = (\text{NH}_3)(2,2'\text{-bpy})$), $\text{B}_n\text{AgCo}(\text{CO})_4$ ($\text{B}_n = (2,2'\text{-bpy})$), and $\text{B}_3\text{CdFe}(\text{CO})_4$ ($\text{B}_3 = \text{tpy}$, tren) are most likely monomeric, or only very weakly associated.

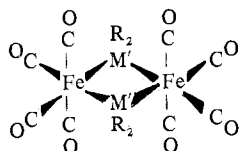
Two key factors in determining which structure is favored for a given complex seem to be the formal positive charge on, and the electronegativity of, the main group metal. For example, in comparing the isoelectronic $\text{B}_2\text{AgCo}(\text{CO})_4$ and $\text{B}_2\text{CdFe}(\text{CO})_4$ complexes, the oligomeric nature of the latter species plausibly derives from the greater difficulty in separating ions of formal charge ± 2 as compared to ± 1 in the former complexes. Within group 2B, the most common compounds of zinc are monomeric with three base molecules ($\text{B}_3\text{ZnFe}(\text{CO})_4$) and those of cadmium are oligomeric in the solid state with two base molecules ($\text{B}_2\text{CdFe}(\text{CO})_4$), while $[\text{HgFe}(\text{CO})_4]_4$ does not form base adducts. This trend reflects the propensity of the harder and more acidic main group metals to be coordinated by the nitrogen donor ligands, which are harder than the $\text{Fe}(\text{CO})_4$ moiety. Alternatively, it could be said that zinc, being the most electropositive group 2B metal, is most capable of stabilizing the positive charge resulting from resonance hybrid I. Species of the type



I

$\text{B}_3\text{CdFe}(\text{CO})_4$ are generally observed only when very large excesses of B are present (e.g., in pyridine solutions) or when certain polydentate ligands are present. However, even though zinc displays a strong preference for bonding to the harder nitrogen donors in monomeric complexes, we have prepared the $(2,2'\text{-bpy})\text{ZnFe}(\text{CO})_4$ oligomer from the $(\text{NH}_3)(2,2'\text{-bpy})\text{ZnFe}(\text{CO})_4$ monomer by taking advantage of the greater volatility of NH_3 . Our inability to isolate base adducts of $[\text{HgFe}(\text{CO})_4]_4$ parallels previous work on $\text{M}[\text{Co}(\text{CO})_4]_2$ compounds ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$).³⁷ The marked tendency for mercury to retain two-coordination has often been attributed to a high 6s–6p promotional energy.³⁸

After considering the factors which control stoichiometry and the extent of association of the complexes, it is next appropriate to discuss the extent of oligomerization in some of the specific cases. From the unit cell and space group determination of $(\text{py})_2\text{CdFe}(\text{CO})_4$ (see Experimental Section), we have found that this complex is trimeric in the solid state, as in the case of the related 2,2'-bipyridyl complex.^{5b} In contrast, the isoelectronic $\text{R}_2\text{SnFe}(\text{CO})_4$ compounds are dimeric³³ (structure J). The trimeric structures of $[(2,2'\text{-}$



J

$\text{bpy})\text{CdFe}(\text{CO})_4]_3$ and $[(\text{py})_2\text{CdFe}(\text{CO})_4]_3$ appear to reflect the preferred valence angles at the group 2B metal and at iron. The $\text{Fe}-\text{Cd}-\text{Fe}$ angles in the bipyridyl complex are in the range 138.81 (15)–148.40 (15)°,^{5b} while the $\text{Fe}-\text{Sn}-\text{Fe}$ angles in $[(\text{CH}_3)_2\text{SnFe}(\text{CO})_4]_2$ ^{33b} are 103.7 (4) and 102.6 (3)° and angles in $[(\eta^1\text{-C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$ ^{33a} are 102.04 (3)°. The larger angles in the Cd compound seem to reflect a preference for greater cadmium s character in the more covalent Cd–Fe bonds (as opposed to the weaker Cd–N coordinate bonds), while in the group 4B system the Sn–C and Sn–Fe bonds are more equal in covalency and the hybridization is expected to be more nearly tetrahedral. It should be noted, in support of relatively constant cadmium hybridization, that in the series

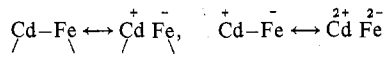
$\text{B}_n\text{Cd}[\text{Mn}(\text{CO})_5]_2$, $\text{B} = \text{terpyridyl}$,^{39a} diglyme,^{39b} 2,2'-bipyridyl,^{39c} and 1,10-phenanthroline,^{39c} the observed Mn–Cd–Mn angles are in the relatively narrow range of 128–136°. The larger $\text{Fe}-\text{Cd}-\text{Fe}$ angles in $\text{B}_2\text{CdFe}(\text{CO})_4$ species clearly favor a ring size larger than four members. In addition to factors involving the main group metal ion, it was noted in the discussion of the $[(2,2'\text{-bpy})\text{CdFe}(\text{CO})_4]_3$ structure^{5b} that the tetracarbonyliron coordination geometry was appreciably distorted from octahedral toward bicapped tetrahedral (the two cadmium atoms located at the capping vertices), with Cd–Fe–Cd angles ranging from 94.9 (1) to 102.2 (2)° and $\text{C}_{\text{axial}}-\text{Fe}-\text{C}_{\text{axial}}$ angles of 135.8 (15)–141.8 (15)°. This distortion was attributed to the large amount of electron density being released by the cadmium atom onto the $\text{Fe}(\text{CO})_4$ fragment. Such a distortion also destabilizes a four-membered ring both because the Cd–Fe–Cd angles would be too large and because close nonbonded contacts ($\sim 2 \text{ \AA}$) are predicted between axial carbonyl ligands on opposite iron atoms. In contrast, Sn–Fe–Sn angles in the two aforementioned group 4B compounds were reported to be 76.3 (4), 77.4 (3),^{33b} and 77.96 (2)°.^{33a} This contraction from the octahedral 90°⁴⁰ is clearly more compatible with a four-membered ring. Not surprisingly, infrared spectra in the C–O stretching region reveal less electron density on the iron in the group 4B than in the group 2B compounds.⁵ That the new group 2B compound $[(4\text{-C}_6\text{H}_5\text{C}_5\text{H}_4\text{N})\text{CdFe}(\text{CO})_4]_2$ is apparently dimeric in solution suggests that, to maintain a planar ring structure, the tetracarbonyliron valence angles must decrease markedly in response to the removal of a base molecule from cadmium, while the $\text{Fe}-\text{Cd}-\text{Fe}$ angles must decrease to less than 120°. A solid-state structure determination for this compound is clearly of interest.

Isoelectronic Relationships. In our studies on the two isoelectronic pairs, $\text{TlCo}(\text{CO})_4$ and $\text{PbFe}(\text{CO})_4$, and $[\text{AgCo}(\text{CO})_4]_4$ and $[\text{CdFe}(\text{CO})_4]_4$, the conclusions drawn on the basis of infrared spectroscopy and x-ray powder diffraction parallel other known relationships. Thus, the first pair are as different in their chemical and physical properties as they are in their spectroscopic ones. While $\text{TlCo}(\text{CO})_4$ is yellow, sublimable, and soluble in aromatic solvents,¹² $\text{PbFe}(\text{CO})_4$ is black, nonsublimable, insoluble in aromatic solvents, and only very slightly soluble in coordinating solvents.⁹ Both are very air-sensitive, however. In this case, the chemical and physical differences are likely related to the fact that while Pb(II) tends toward high coordination numbers involving a stereochemically active (hence, nonbonding) lone pair,⁴¹ in Tl(I) the lone pair (at or near room temperature, at least) is essentially spherical and hence metal-to-ligand σ antibonding which, along with the lower formal charge on thallium, tends to reduce the tendency to high coordination numbers.⁴²

The structural similarities of the second isoelectronic pair, $[\text{AgCo}(\text{CO})_4]_4$ and $[\text{CdFe}(\text{CO})_4]_4$ (both planar tetramers), fall in line with other chemical similarities. Both compounds are yellow, nonvolatile, and soluble in coordinating solvents (e.g., acetone) from which they can be precipitated by the addition of water (cf. reversible homolytic cleavage cycle)^{5,23a} and form bipyridyl adducts. The chemical similarities in this case seem to stem from the ability of the two isoelectronic main group metals, Ag(I) and Cd(II), to adopt either linear, two-coordinate sp complexes or higher (especially three or four) coordination numbers.⁴³ However, the formal difference in charge does manifest itself in the 2,2'-bipyridyl adducts, where the cadmium complex is oligomeric while the silver complex is only partially associated. It can also be noted that while many cis-octahedral $\text{Fe}(\text{CO})_4\text{X}_2$ complexes are known,⁴⁰ $[\text{AgCo}(\text{CO})_4]_4$ appears to be the first such cobalt complex.

Although $[\text{AgCo}(\text{CO})_4]_4$ and $[\text{CdFe}(\text{CO})_4]_4$ are isoelectronic and isostructural, some interesting differences do exist

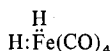
in their available resonance hybrids. Those of CdFe(CO)₄ and its base adducts involve (neglecting ligands)



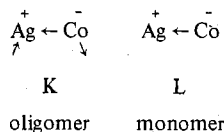
while the corresponding resonance structures for AgCo(CO)₄ and its base adducts are



For the silver-cobalt system, a much more convenient resonance formalism can be adopted, utilizing donation of lone pairs of electrons from the transition metal carbonyl to the main group metal. This is known in the related compounds (C₅H₅)Co(CO)₂·HgCl₂,^{44a} (C₅H₅)Co(olefin)₂·HgCl₂,^{44a} (C₅H₅)Rh(olefin)₂·HgCl₂,^{44a} Fe(CO)₅·HgCl₂,^{44b} and [(C₆H₅)(CH₃)₂P]₂Fe(CO)₃·HgCl₂,^{44c} as well as others.^{44d-h} Thus,



in forming the dianion, clearly has at least two electron pairs available, as does the isoelectronic Co(CO)₄⁻. Resonance structures K and L (neglecting ligands) can then be invoked in which the extent of lone pair donation is variable.



Concluding Remarks

In our synthetic, spectroscopic, and crystallographic studies on B_nMFe(CO)₄ and B_nM'Co(CO)₄ type compounds, we have found that the main group metal with attendant ligands plays a dominant role in determining the type of structure adopted and the resulting chemical and physical properties. Besides determining its own coordination sphere and tendency to form base adducts, the main group metal is primarily responsible for the extent of cation/anion association in these compounds, which encompasses ionic, monomeric, oligomeric, and possibly (but not presently) isocarbonyl structures. By suitable adaptation of the main group metal and the ligands chosen, we have shown that otherwise unfavored structures for a particular metal can be stabilized, thus potentially allowing for more detailed analysis of formerly unstable or solution-state structures. Such manipulations could also result in preferential stabilization of infinite metal chains and will be the subject of future investigations.

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Registry No. PbFe(CO)₄, 66119-72-0; (tren)CdFe(CO)₄, 66027-73-4; (NH₃)₂CdFe(CO)₄, 45000-79-1; (tpy)CdFe(CO)₄, 66027-75-6; [CdFe(CO)₄]₄, 62629-71-4; (4,4'-bpy)CdFe(CO)₄, 66027-72-3; (4-C₆H₅C₅H₄N)CdFe(CO)₄, 66057-00-9; (py)₃ZnFe(CO)₄, 66027-74-5; (NH₃)₃ZnFe(CO)₄, 45048-25-7; (NH₃)(2,2'-bpy)ZnFe(CO)₄, 66027-78-9; Fe(CO)₅, 13463-40-6; (2,2'-bpy)ZnFe(CO)₄, 66027-70-1; [AgCo(CO)₄]₄, 66057-01-0; (2,2'-bpy)AgCo(CO)₄, 66027-77-8; (py)₂CdFe(CO)₄, 66119-54-8.

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Reaction Mechanisms of Metal-Metal Bonded Carbonyls. 20.¹ Substitution and Fragmentation Reactions of Undecacarbonyl(triphenylphosphine)triruthenium and Decacarbonylbis(triphenylphosphine)triruthenium

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Kinetic studies are reported of reactions in decalin of the complexes $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$. At moderate temperatures (25–75 °C) they undergo substitution reactions with triphenylphosphine, but only $Ru_3(CO)_{10}(PPh_3)_2$ undergoes simple substitution with carbon monoxide. The retarding effect of CO on reactions with PPh_3 is quantitatively consistent with a simple CO-dissociative mechanism, but the considerable labilization, compared with $Ru_3(CO)_{12}$, caused by the presence of PPh_3 substituents suggests that a more complex mechanism may be operating. Equilibrium constants for the substitution reactions were determined and found to depend very little on temperature. At higher temperatures (130–170 °C) both complexes undergo fragmentation reactions leading to mononuclear complexes at rates that are independent of [CO] and $[PPh_3]$. The activation enthalpies for fragmentation of $Ru_3(CO)_{12-n}(PPh_3)_n$ ($n = 1, 2, \text{ or } 3$) increase dramatically with n with an almost compensating increase in ΔS^\ddagger . This trend can be rationalized in terms of steric effects operating in the proposed intermediates $Ru_2(CO)_{8-n}(PPh_3)_n$ ($n = 0, 1, \text{ or } 2$).

Introduction

Studies have been reported² of the kinetics of substitution reactions of $Ru_3(CO)_9(PPh_3)_3$ with carbon monoxide or tri-*n*-butylphosphine and of reaction with triphenylphosphine that leads mainly to fragmentation into monoruthenium complexes. The activation parameters for the last reaction, when it occurred at rates independent of both [CO] and $[PPh_3]$, were assigned to fragmentation into $Ru_2(CO)_6(PPh_3)_2$ and diamagnetic $Ru(CO)_3(PPh_3)$. Those for reaction with PPh_3 under argon (under conditions such that rates were independent of $[PPh_3]$), and with PBu_3 or CO, were assigned to the dissociative loss of CO and PPh_3 , respectively, although it was pointed out that dissociation could follow initial reversible formation of a reactive form of the complex. Activation parameters have also been obtained³ for what is believed to be fragmentation into $Ru_2(CO)_6(PPh_3)_2$ and paramagnetic $Ru(CO)_3(PPh_3)$. In an attempt to obtain a wider base for our mechanistic conclusions, and in order to obtain comparable kinetic parameters for related complexes with different numbers of PPh_3 ligands, we have studied substitution and fragmentation reactions of the incompletely substituted complexes $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_{11}(PPh_3)$.

Experimental Section

Chemicals were obtained and purified exactly as described in earlier papers in this series.^{2,4,5} The complexes $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$ were prepared *in situ* in decalin by reacting either $Ru_3(CO)_{12}$ or $Ru_3(CO)_9(PPh_3)_3$ in decalin at 80–120 °C under an atmosphere of CO and in the presence of appropriate concentrations

of PPh_3 . Thus, when decalin solutions that were ca. 10^{-3} M in $Ru_3(CO)_{12}$ and PPh_3 were heated under CO at 120 °C for 5 min, the solution became yellow and showed IR bands characteristic of $Ru_3(CO)_{11}(PPh_3)$ (Table I). The spectrum is closely similar to that reported for isolated $Ru_3(CO)_{11}(PPh_3)$ in cyclohexane,⁶ the main difference being the absence, in our samples, of the band of medium intensity at 1986 cm^{-1} . Weak bands characteristic of $Ru_3(CO)_{12}$ and $Ru(CO)_4(PPh_3)$ were also observed but the complex $Ru_3(CO)_{11}(PPh_3)$ was estimated to be $\geq 95\%$ pure.

A similar procedure, but with solutions ca. 5×10^{-3} M in PPh_3 , led to mixtures containing ca. 90% of the complex as $Ru_3(CO)_{10}(PPh_3)_2$, as judged by the IR spectrum, together with some $Ru_3(CO)_9(PPh_3)_3$. However, when decalin solutions that were ca. 10^{-3} M in $Ru_3(CO)_{12}$ and 2×10^{-3} M in PPh_3 were heated to 120 °C for 5 min under an atmosphere of CO a mixture of $Ru_3(CO)_{11}(PPh_3)$ and $Ru_3(CO)_{10}(PPh_3)_2$ was obtained. Replacement of the CO atmosphere by one of argon, followed by further heating at 75 °C for 5–10 min, led to solutions showing IR bands (Table I) attributable to $Ru_3(CO)_{10}(PPh_3)_2$ by comparison with spectra of other mono- and bis-substituted triruthenium carbonyls.^{4,6,7} $Ru_3(CO)_{10}(PPh_3)_2$ has not yet been isolated and characterized. No bands were observed characteristic of $Ru_3(CO)_{11}(PPh_3)$, $Ru_3(CO)_9(PPh_3)_3$, or any likely mononuclear complexes, and the solutions were therefore judged to contain virtually pure $Ru_3(CO)_{10}(PPh_3)_2$.

Solutions for kinetic studies were prepared as above in Schlenk tubes and sealed with rubber septum caps, and the concentrations of complex and PPh_3 were adjusted as required. The solutions were then degassed by repeated freeze-pump-thaw cycles, and the desired atmosphere was introduced above the solution through stainless steel tubing. The reaction tubes were then wrapped in aluminum foil and placed in a thermostated oil bath (± 0.1 °C), and samples were withdrawn at regular intervals through stainless steel tubing by