

ciable structural influences. In (2,2':6',2''-terpyridyl)Cd-[Mn(CO)₅]₂,³⁷ O...O contacts of 3.035 Å were observed. The two Cd-Mn distances differed and were perhaps a bit long at 2.760 (4) and 2.799 (5) Å. In the rather more ionic Na₂Fe(CO)₄·^{3/2}(dioxane) structure,³⁸ one can observe an essentially dimeric, planar [NaFe(CO)₄]₂ cluster (see Figure 5, ref 37). In this cluster, both short O...O contacts (3.02 Å) and long Na-Fe bond distances (3.086 Å) were reported, somewhat analogous to the present situation.

The present study indicates that the axial carbonyl oxygen-oxygen repulsions present in these ring systems are apparently not capable of destabilizing ring structures sufficiently to result in chain formation. The very severe distortions which are found in this structure seemingly point out a marked reluctance of these species to form polymers. Hence, the

(37) W. Clegg and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 90 (1973).
 (38) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976).

prospects of preparing such polymers, in the present systems at least, may be expected to be a difficult task. It is, however, somewhat encouraging that virtually insoluble species such as [(bpy)ZnFe(CO)₄]₂ can be crystallized and characterized by proper manipulations.

Acknowledgment. R.D.E wishes to express his gratitude for partial support of this research through grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from a Pennwalt Corp. Grant of Research Corp., and from the University of Utah Research Committee. We also wish to thank Professor R. W. Parry for use of his infrared spectrometer.

Registry No. (NH₃)₃ZnFe(CO)₄, 45048-25-7; [ZnFe(CO)₄]₄, 73513-02-7; [(bpy)ZnFe(CO)₄]₂, 66027-70-1.

Supplementary Material Available: A listing of root-mean-square amplitudes of vibration (Table II) and the structure amplitude table (19 pages.) Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
 University of Utah, Salt Lake City, Utah 84112

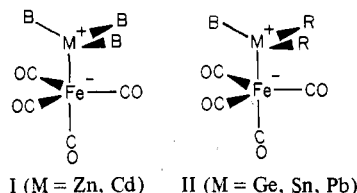
Synthesis and Characterization of Lewis Base Adducts of Ethylgallium Tetracarbonyliron, B_n(C₂H₅)GaFe(CO)₄ (B = Lewis Base)

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Received October 23, 1979

The syntheses and complete characterization of various base adducts of ethylgallium tetracarbonyliron are reported. With nitrogenous bases, monomeric complexes incorporating two base molecules are isolated, while with THF (tetrahydrofuran), a dimeric complex incorporating one donor THF molecule for each gallium atom is obtained. Infrared spectral evidence is also presented which indicates a similar associated base-free complex also exists. The nature of these compounds is discussed and compared with other related metal-metal bonded complexes.

A number of metal-metal bonded compounds have been reported which can be looked upon as being derived from Fe(CO)₄²⁻ interacting with either a B_nM²⁺ (B = Lewis base; n = 0-3 and M = Zn, Cd or n = 0 and M = Hg)¹ or B_nR₂M²⁺ (R = alkyl; n = 0, 1; M = Ge, Sn, Pb)² species. In general, the B₃MFe(CO)₄ (M = Zn, Cd) and (B)₂R₂MFe(CO)₄ (M = Ge, Sn, Pb) complexes are monomeric, with four-coordinate metal M and a five-coordinate (TBP) iron, as in I and II. In



the other cases, a monomeric complex would impose a coordination number less than 4 on the metal M, and as a result, each metal M and each iron atom form a second metal-metal bond, resulting in each case so far in the formation of a cyclic ring structure containing cis-disubstituted octahedrally coordinated iron (e.g., [(C₂H₅)₂GeFe(CO)₄]₂, [(bpy)CdFe(CO)₄]₃, [CdFe(CO)₄]₄ (bpy = 2,2'-bipyridyl)), although a chain structure is also possible.

It can be noted that the group 4B metals Ge, Sn, and Pb do not differ very substantially in their preference for base adduct molecules, generally the preferred value of n being 0.^{2d} However, in the group 2B series, a value of n = 3 is favored for zinc, n = 2 for cadmium, and n = 0 for mercury (where the Lewis base generally contains a nitrogen donor atom).^{1b-j} To date, no intermediate group 3B species of the general type B_nRMFe(CO)₄ (M = Ga, In, Tl) have been reported, although various other complexes are known in which these metals form typical single bonds to Co(CO)₄,³ Mn(CO)₅,⁴ (C₅H₅)Fe(CO)₂,⁵ etc.⁶ It was therefore of interest to attempt the

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- (2) Some of many examples: (a) R. M. Sweet, C. J. Fritchie, Jr., and R. A. Schunn, *Inorg. Chem.*, **6**, 749 (1967); (b) J.-C. Zimmer and M. Huber, *C. R. Acad. Sci., Ser. C*, **267**, 1685 (1968); (c) C. J. Gilmore and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1387 (1972); (d) T. J. Marks and A. R. Newman, *J. Am. Chem. Soc.*, **95**, 769 (1973); (e) P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 2097 (1975); (f) G. W. Grynkewich and T. J. Marks, *Inorg. Chem.*, **15**, 1307 (1976); (g) others may be found referenced in the above articles or else in the recent review: A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organomet. Chem.*, **108**, 47 (1976).

- (3) (a) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1586 (1966); (b) W. R. Robinson and D. P. Schussler, *ibid.*, **12**, 848 (1973); (c) S. E. Pedersen, W. R. Robinson, and D. P. Schussler, *J. Chem. Soc., Chem. Commun.*, 805 (1974); (d) T. B. Brill and D. C. Miller, *Inorg. Chem.*, **15**, 2553 (1976).
- (4) (a) J. Hoyano, D. J. Patmore, and W. A. G. Graham, *Inorg. Nucl. Chem. Lett.*, **4**, 201 (1968); (b) A. T. T. Hsieh and M. J. Mays, *J. Organomet. Chem.*, **22**, 29 (1970); (c) A. T. T. Hsieh and M. J. Mays, *Chem. Commun.*, 1234 (1971); (d) A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 516 (1972); (e) H.-J. Haupt and F. Newmann, *J. Organomet. Chem.*, **50**, 63 (1973); (f) H. Preut and H.-J. Haupt, *Chem. Ber.*, **107**, 2860 (1974); (g) H.-J. Haupt, W. Wolfes, and H. Preut, *Inorg. Chem.*, **15**, 2920 (1976).
- (5) (a) A. T. T. Hsieh and M. J. Mays, *Inorg. Nucl. Chem. Lett.*, **7**, 223 (1971); (b) A. T. T. Hsieh and M. J. Mays, *J. Organomet. Chem.*, **37**, 9 (1972); (c) J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, and R. E. Hughes, *Inorg. Chem.*, **18**, 1097 (1979).

preparation of such compounds and to determine the general preferences exhibited by gallium, indium, and thallium for supplemental Lewis base coordination and to determine the type of ring or chain structure adopted by associated species. In addition, the recent crystallization and diffraction study of [(bpy)ZnFe(CO)₄]₂ has pointed out what appear to be the key factors in determining the extent of association (dimeric, trimeric, etc.) in these systems and on this basis has allowed prediction of the extent of association for most possible types of these complexes.⁷ The syntheses of the new B_nRGaFe(CO)₄ compounds reported herein thus also offer an opportunity to test some of these predictions.

Experimental Section

All operations involving metal carbonyls and organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately prior to use. Aqueous solutions were deoxygenated under a nitrogen stream. Elemental analyses were performed by Dornis and Kolbe Analytical Laboratories or Galbraith Laboratories. Osmometric molecular weight determinations were carried out by Galbraith Laboratories.

Spectroscopic Studies. Infrared spectra were recorded with a Beckman IR-20 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. Solutions were prepared in a Schlenk apparatus and syringed into matched NaCl cells under nitrogen. All spectra were calibrated with polystyrene. Nuclear magnetic resonance spectra were recorded on a Varian XL-100 spectrometer.

Sodium Tetracarbonylferrate, Na₂Fe(CO)₄. An improvement of previously known methods⁸ was used to prepare Na₂Fe(CO)₄. To 323 g of a 1% sodium amalgam (140 mmol of sodium) were added 1–2 g of benzophenone and 300 mL of THF (tetrahydrofuran) under nitrogen. While this was being rapidly stirred magnetically, Fe(CO)₅ (12.5 mL, 93.5 mmol) was added dropwise with an addition funnel, and the rate of addition was controlled such that the solution maintained at least a light blue color. If the color became discharged, the addition was stopped and was not resumed again until the reappearance of the blue color. A small amount of red material (Fe₂(CO)₉)⁹ was deposited on the sides of the flask during the addition. This was washed into the reaction mixture by vigorously swirling the flask. Upon completion of the addition, the mixture was stirred for 1 h and as much of the residual mercury as possible removed carefully by syringe. The mixture was then decanted under nitrogen onto a coarse frit and collected by filtration under nitrogen while the residual mercury was left behind. The resulting pure white and pyrophoric product was washed with several small portions of THF, followed by several portions of ether, and dried in vacuo. The procedure may easily be scaled up to much larger quantities, with yields readily in excess of 90%.

Ethylgallium Diiodide, [(C₂H₅)GaI₂]₂. A simplified modification of a reported procedure¹⁰ was used for this preparation. To 4.2 g (60.3 mmol) of gallium metal and 7.62 g (30.0 mmol) iodine in a dry flask under nitrogen was added 100 g of iodoethane. The mixture was stirred at 0 °C for 5 min and then allowed to warm to room temperature. After being stirred for 7 days, the solution was filtered under nitrogen, and the solvent was removed in vacuo. The resulting yellow solid was sufficiently pure for further use. If desired, the product could be recrystallized by dissolving it in a minimum volume of toluene and adding 2 volumes of hexane. After the mixture was cooled to –78 °C overnight, the supernatant was removed by syringe, and the ex-

remely hygroscopic off-white product was washed with pentane and dried under a nitrogen stream.

(Tetrahydrofuran)ethylgallium Tetracarbonyliron, (THF)(C₂H₅)GaFe(CO)₄. To a slurry of 1.63 g (7.62 mmol) of Na₂Fe(CO)₄ in 50 mL of THF at –78 °C was added 2.64 g (7.49 mmol) of EtGaI₂ in 20 mL, also at –78 °C. The mixture was allowed to warm to room temperature after addition was complete. After 8 h of stirring, the solvent was removed, and the resulting orange product was dissolved in 60 mL of dichloromethane. The solution was immediately filtered, and the solvent was quickly removed under vacuum. The resulting orange to reddish brown product was washed with small portions of diethyl ether until the product remained as a fine yellow air- and light-sensitive powder. It was then recrystallized by dissolution in THF and precipitation with excess pentane. A good deal of care must be exercised in the preparation of this compound, or else so much ether will be required to remove the dark brown impurity that most, if not all, of the compound will also be extracted: complete infrared data (Nujol mull) 2085 sh, 2030 sh, 2009 s, 1962 sh, 1949 sh, 1926 vs, 1350 m, 1253 w, 1173 w, 1044 m, 1023 ms, 915 w, 930 w, 903 ms, br, 683 w, sh, 645 s, 613 s cm⁻¹.

Anal. Calcd for C₁₀H₁₃FeGaO₅: C, 35.45; H, 3.87. Found: C, 35.43; H, 3.83.

(Tetramethylethylenediamine)ethylgallium Tetracarbonyliron, (TMEDA)(C₂H₅)GaFe(CO)₄. To 2.0 g (7.5 mmol) of (THF)(C₂H₅)GaFe(CO)₄ in a minimum amount of THF was added 4 mL (26.5 mmol) of TMEDA. The solution immediately turned tan. The light tan product was precipitated by the addition of 3 volumes of pentane to the reaction mixture, after which the solvent was removed by syringe. After being washed with several small quantities of ether, the product was dried in vacuo: complete infrared data (Nujol mull) 1983 s, 1890 sh, 1850 vs, br, 1376 m, 1232 mw, 1189 mw, 1159 w, 1113 mw, 1097 w, 1067 w, 1048 w, 1034 m, 1008 ms, 993 m, 957 w, 942 ms, 919 w, 837 mw, 793 ms, 755 mw, 715 w, 619 s cm⁻¹; NMR (C₆D₆) δ 2.30 (s, 6 H), ca. 1.93 (complex multiplet, 4 H), 1.75 (s, 6 H), 1.45 (t, 3 H), 0.40 (q, 2 H). Anal. Calcd for C₈H₂₁N₂FeGaO₄: C, 36.64; H, 5.53; N, 7.32. Found: C, 36.79; H, 5.53; N, 7.39.

(2,2'-Bipyridyl)ethylgallium Tetracarbonyliron, (bpy)(C₂H₅)GaFe(CO)₄. This compound was prepared by the addition of excess 2,2'-bipyridine in a minimum volume of THF to (THF)(C₂H₅)GaFe(CO)₄ in a minimum volume of THF. After 1 h of stirring, 3 volumes of hexane were added to the solution, resulting in the precipitation of the compound as a reddish solid. The product was then isolated by filtration under nitrogen, washed with several portions of hexane and dried in vacuo: complete infrared data (Nujol mull) 3120 sh, 3116 sh, 3080 w, 3076 w, 1986 s, 1965 vs, br, 1605 ms, 1463 sh, 1447 s, 1377 ms, 1369 sh, 1320 w, 1164 w, sh, 1158 w, 1038 w, 773 ms, 733 ms, 627 s, 520 w cm⁻¹. Anal. Calcd for C₁₆H₁₃FeGaN₂O₄: C, 45.45; H, 3.10; N, 6.62; mol wt 423. Found: C, 45.29; H, 3.21; N, 6.77; mol wt 445 (CH₂Cl₂).

Bis(pyridine)ethylgallium Tetracarbonyliron, (py)₂(C₂H₅)GaFe(CO)₄. The bis(pyridine) adduct was prepared by dissolving (THF)(C₂H₅)GaFe(CO)₄ in a small volume of dry pyridine. After concentration of the solution by evaporation under a nitrogen stream, 3 volumes of pentane were added to precipitate the yellow crystalline product, which was isolated by filtration, washed with small quantities of pentane, and finally dried in vacuo: complete infrared data (Nujol mull) 1983 s, 1875 sh, 1847 vs, br, 1606 mw, 1220 w, sh, 1209 w, 1146 w, 1062 mw, 1041 mw, 1011 mw, 750 mw, 692 m, 623 s cm⁻¹. Anal. Calcd for C₁₆H₁₅FeGaN₂O₄: C, 45.23; H, 3.56; N, 6.59. Found: C, 43.32; H, 3.31; N, 6.11.

Attempted Preparation of Base-Free Ethylgallium Tetracarbonyliron, (C₂H₅)GaFe(CO)₄. To a slurry of 0.61 g (2.8 mmol) of Na₂Fe(CO)₄ in toluene was added 1.00 g (2.8 mmol) of (C₂H₅)GaI₂ in toluene at –78 °C. The mixture was allowed to warm to room temperature and after being stirred for 10 h was filtered. After concentration in vacuum, 3 volumes of pentane were added to the red-brown solution, and a very small amount of pale brownish product was isolated by filtration. The product was washed with two small portions of pentane and dried in vacuo: complete infrared data (Nujol mull) 2025 sh, 1995 vs, br, 797 w, 610 s cm⁻¹.

Results and Discussion

The reaction of iron pentacarbonyl with 1% sodium amalgam in the presence of the electron carrier, benzophenone, results in the convenient, high-yield preparation of pure, white, highly pyrophoric Na₂Fe(CO)₄. In our hands, this method

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 (7) R. J. Neustadt, T. H. Cymbaluk, R. D. Ernst, and F. W. Cagle, Jr., *Inorg. Chem.*, companion paper in this issue. For comparison an O_{ax}–O_{ax} separation of ca. 3.048 (4) Å is observed in [(bpy)ZnFe(CO)₄]₂ along with a Zn–Zn separation of 2.788 (1) Å and a rather acute Zn–Fe–Zn angle of 66.02 (2)°.
 (8) (a) Cooke, *J. Am. Chem. Soc.*, **92**, 6080 (1970); (b) R. G. Komoto, Ph.D. Thesis, Stanford University, Stanford, Calif., 1974; (c) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 2515 (1977).
 (9) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978).
 (10) M. Wilkinson and I. J. Worrall, *J. Organomet. Chem.*, **93**, 39 (1975).

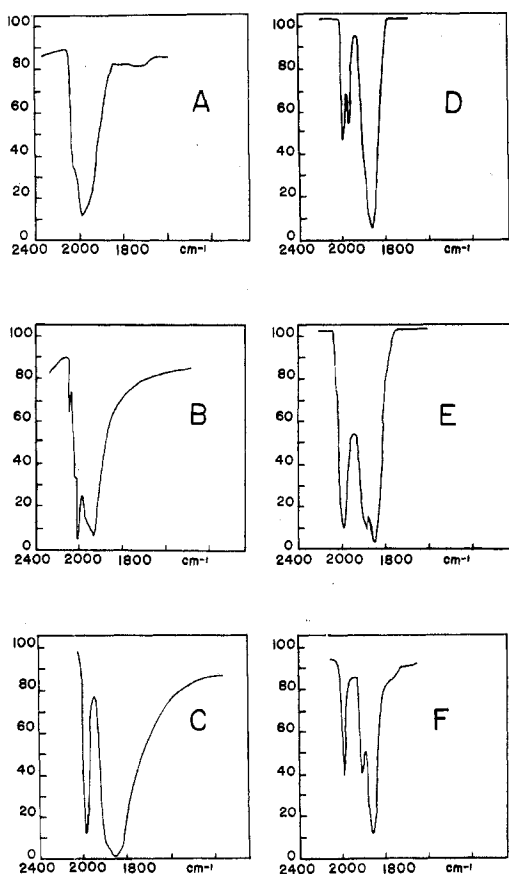


Figure 1. Nujol mull infrared spectra in the C-O stretching region for (A) $C_2H_5GaFe(CO)_4$, (B) $(THF)(C_2H_5)GaFe(CO)_4$, and (C) $(TMEDA)(C_2H_5)GaFe(CO)_4$ and CH_2Cl_2 solution infrared spectra for (D) $(bpy)(C_2H_5)GaFe(CO)_4$, (E) $(py)_2(C_2H_5)GaFe(CO)_4$, and (F) $(TMEDA)(C_2H_5)GaFe(CO)_4$.

is superior to other procedures as it is quick, the presence of benzophenone in solution retards the side reaction between $Fe(CO)_4^{2-}$ and $Fe(CO)_5$ (producing $Fe_2(CO)_8^{2-}$), no base molecules such as dioxane are present in the product which might be undesirable in certain instances,¹¹ and it does not involve metal dispersions whose potential excesses or insoluble impurities would be inseparable from product $Na_2Fe(CO)_4$.

From a reaction at $-78^\circ C$ of ethylgallium diiodide, $[(C_2H_5)GaI_2]_2$, with $Na_2Fe(CO)_4$ in tetrahydrofuran, the compound $[(THF)(C_2H_5)GaFe(CO)_4]_n$ can be readily isolated, which serves as a basis for the synthesis of other Lewis base adducts. Reaction with nitrogen donor ligands results in the incorporation of two donor atoms in $B_2(C_2H_5)GaFe(CO)_4$ species, where $B = py$ (pyridine) or $B_2 = bpy$, TMEDA (tetramethylethylenediamine). All products are very air sensitive and fairly soluble in typical organic solvents, except hydrocarbons.

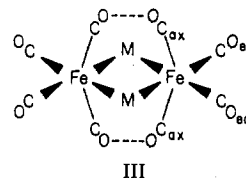
The infrared spectrum of the mono(tetrahydrofuran) complex in the C-O stretching region (see Figure 1) is similar in position and pattern to those of other associated species,^{1,2} indicating this molecule to be associated, as would be expected if the gallium atoms are to attain four-coordination. While sensitivity problems have not allowed solution molecular weight determination, a preliminary structural investigation has confirmed a dimeric structure.¹² It is noteworthy that the dimeric nature of $(B)RGaFe(CO)_4$ species was predicted on

Table I. Solution Infrared Spectral Data for $(C_2H_5)GaFe(CO)_4$ Base Adducts in CH_2Cl_2 ^a

base adduct	$\nu(C-O)$, cm^{-1}
THF	1986 br
bipyridine	1992 ms, 1967 ms, 1863 s, br
bis(pyridine)	1991 ms, 1906 sh, 1859 s, br
TMEDA	1985 ms, 1902 ms, 1856 s, br

^a v = very, s = strong, m = medium, br = broad, sh = shoulder.

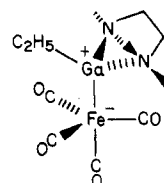
the basis of factors uncovered in the structural determination of $[(bpy)ZnFe(CO)_4]_2$.⁷ The factors turned out to involve a given system's ability to adapt to or relieve $O_{ax}-O_{ax}$ repulsions which are induced by ionic resonance hybrids involving a $Fe(CO)_4^{\delta-}$ species with metal atoms capping tetrahedral faces, as shown in III for the dimeric case. For cases when M is



III

large and electropositive, e.g., $M = Cd$, the system apparently cannot relieve the $O_{ax}-O_{ax}$ interactions sufficiently (mostly by contracting the $M-Fe-M$ angle) without inducing severe $M-M$ repulsions, so that a trimeric structure is instead formed. The dimeric nature of $[(bpy)ZnFe(CO)_4]_2$ indicated that $B(R)GaFe(CO)_4$ species should also be dimeric as gallium is less electropositive and hence should cause less axial carbonyl bending than observed in $[(bpy)ZnFe(CO)_4]_2$ through stabilization of the $Fe(CO)_4^{\delta-}$ resonance hybrids. In partial support of this, it can be noted that the C-O stretching modes in the zinc compound are found at substantially lower frequency than those for $[(THF)(C_2H_5)GaFe(CO)_4]_2$.⁷

Infrared spectra of the $B_2(C_2H_5)GaFe(CO)_4$ species show a notable shift to lower frequency as compared to the mono-(tetrahydrofuran) adduct. This type of shift is indicative of metal-metal bond cleavage which in this case results in monomeric $B_2RGa^+Fe^-(CO)_4$ species, with greater electronic population of the C-O π^* orbitals.^{1b-j,2} In agreement with this, the solution infrared band patterns for these species in the C-O stretching region (Figure 1 and Table I) are in excellent accord with a trigonal-bipyramidal iron coordination geometry ($2A_1 + E$ modes),¹³ and are found at frequencies between those reported for the known, isoelectronic $(py)(CH_3)_2GeFe(CO)_4$ (2021 s, 2040 m, sh, 1908 vs cm^{-1})^{2d} and $(py)_3ZnFe(CO)_4$ (1954 ms, 1857 ms, 1823 s cm^{-1})^{1j} monomers. The monomeric nature of these species is further demonstrated by an osmometric molecular weight determination for the 2,2'-bipyridyl adduct (see the Experimental Section). For the analogous TMEDA adduct, the proton NMR spectrum (see the Experimental Section) displays two separate *N*-methyl resonances, which is consistent with a monomeric structure such as IV (methyl groups omitted for clarity). Thus, in all adducts



IV

(11) In addition, the preparation of $Na_2Fe(CO)_4 \cdot 3/2$ dioxane becomes difficult at high altitudes where the boiling point of dioxane drops below the melting point of sodium.

(12) J. C. Vanderhooff, T. H. Cymbaluk, and R. D. Ernst, experiments in progress.

(13) (a) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975; (b) L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, **12**, 53 (1969); (c) G. Bor, *Inorg. Chim. Acta*, **1**, 81 (1967); (d) A. Reckziegel and M. Bigorgne, *J. Organomet. Chem.*, **3**, 341 (1965); (e) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973);

reported herein, four-coordinate gallium is present with either five- or six-coordinate iron.

It can be noted that for the usual nitrogen base systems, where monomeric species are formed, gallium tends to behave more like zinc (which favors $B_3ZnFe(CO)_4$ monomers)^{1j} than germanium (which favors $R_2GeFe(CO)_4$ dimers).^{2b,d} This is also the first case where the strength of the Lewis base has determined whether the complex was associated or not (chelation has been shown to be important in this regard also).^{1h-j} From this observation, it would appear rather crudely that the favorability of iron in forming a second bond to another gallium atom is intermediate between the favorability of oxygen and nitrogen atom donors bonding to gallium. It is thus possible that, in other systems where nitrogen donor ligands favor monomeric complexes (notably the $B_nZnFe(CO)_4$ series), oxygen donor ligands might well favor oligomeric complexes (e.g., $B_2ZnFe(CO)_4$).

The reaction of ethylgallium diiodide with $Na_2Fe(CO)_4$ in toluene yielded a product which was nearly inseparable from some dark impurity. Less than 0.1 g of purified product could be isolated (see the Experimental Section), and as a result, only its infrared spectrum could be used for characterization. Nevertheless, this spectrum seems to unambiguously identify the material as $[(C_2H_5)GaFe(CO)_4]_n$. As this compound contains one less electron-donating base than $[(THF)(C_2H_5)GaFe(CO)_4]_2$, there should be less bending of the axial carbonyls, and hence the compound is expected to be dimeric. The lower electronic population of the CO π^* orbitals is readily seen by a comparison of the infrared spectrum of this compound with that of the THF adduct. Essentially identical patterns are observed, with the C-O stretching modes of the

base-free compound coming at slightly higher frequency. In addition, bands attributable to Fe-C modes follow the expected pattern,¹⁴ with the base-free complex absorbing at 610 cm^{-1} while the THF adduct absorbs at 613 cm^{-1} .

The present study demonstrates that stable $B_nRGaFe(CO)_4$ species may readily be prepared, in which the gallium atom tends to behave more like zinc in the fairly ionic $B_nZnFe(CO)_4$ complexes ($n = 0-3$) than like germanium in the considerably more covalent $B_nR_2GeFe(CO)_4$ complexes ($n = 0, 1$). Preliminary studies have also shown that analogous indium compounds may also be prepared and that their properties are intermediate between those of isoelectronic cadmium and tin species. These and related studies and their implications will be reported upon completion in the near future.¹⁵

Acknowledgment. R.D.E. wishes to express his gratitude for partial support of this research through grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from a Pennwalt Corp. Grant of Research Corp., and from the University of Utah Research Committee.

Registry No. $Na_2Fe(CO)_4$, 14878-31-0; $Fe(CO)_5$, 13463-40-6; $[(C_2H_5)GaI_2]_2$, 57286-39-2; $(THF)(C_2H_5)GaFe(CO)_4$, 73513-07-2; $(TMEDA)(C_2H_5)GaFe(CO)_4$, 73513-06-1; $(bpy)(C_2H_5)GaFe(CO)_4$, 73513-05-0; $(py)_2(C_2H_5)GaFe(CO)_4$, 73513-04-9; $(C_2H_5)GaFe(CO)_4$, 73513-03-8.

(14) For comparison,¹⁰ the Ga-C stretching mode for $[(C_2H_5)GaI_2]_2$ comes at 546 cm^{-1} . The bands at 610 and 613 cm^{-1} are therefore consistently assigned to Fe-C stretching modes and compare well with those of other related compounds.^{1h-j}

(15) J. Vanderhooft, D. R. Wilson, T. H. Cymbaluk, and R. D. Ernst, experiments in progress.

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Small Metallacarboranes with Metal-Metal Bonds. Crystal and Molecular Structures of $2,3-(CH_3)_2-1,2,4,5-(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$ and $2,3-(CH_3)_2-1,2,4,5-(\eta^5-C_5H_5)_2CoFe(H)C_2B_3H_3$

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Received February 20, 1980

The structures of the title compounds were determined by single-crystal X-ray diffraction and in both cases were found to contain 7-vertex pentagonal-bipyramidal $M_2C_2B_3$ cages ($M = Fe$ or Co) with cobalt in an equatorial vertex and cobalt or iron in an apical vertex. In both cases, the framework carbon atoms occupy adjacent positions in the equator. Both structures are in agreement with those proposed earlier from NMR data, except that the presumed face-bridging proton in the iron-cobalt cluster was not directly observed. The parent $1,2,4,5-(\eta^5-C_5H_5)_2Co_2C_2B_3H_4$ isomer is an isolable intermediate in the previously studied thermal rearrangement of the triple-decked complex $1,7,2,3-(\eta^5-C_5H_5)_2Co_2C_2B_3H_5$ to the $1,7,2,4$ isomer via the $1,2,3,5$ and $1,2,4,5$ species. The present structures provide the first structural confirmation of equatorial metal atoms in pentagonal-bipyramidal metallaboron cages and are the smallest metallacarboranes containing metal-metal bonds to be crystallographically established. Crystal data for $2,3-(CH_3)_2-1,2,4,5-(\eta^5-C_5H_5)_2Co_2C_2B_3H_3$: mol wt 338, space group $P2_1/c$, $Z = 4$; $a = 9.240$ (3), $b = 12.314$ (7), $c = 13.933$ (4) Å; $\beta = 108.94$ (4)°; $V = 1499$ Å³; $R = 0.057$ for 1230 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $2,3-(CH_3)_2-1,2,4,5-(\eta^5-C_5H_5)_2CoFe(H)C_2B_3H_3$: mol wt 338, space group $P2_1/c$, $Z = 8$ (two molecules per asymmetric unit); $a = 9.385$ (3), $b = 22.431$ (7), $c = 14.133$ (4) Å; $\beta = 90.86$ (4)°; $V = 2975$ Å³; $R = 0.056$ for 3548 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Metallacarboranes in which metal atoms occupy adjacent vertices in the polyhedral framework are of interest for several reasons. The understanding of metal-metal interactions in such systems presents a challenging theoretical and experimental problem, which is, of course, related to the general question of bonding in metal clusters. In metallacarboranes and metallaboranes having two or more metal atoms, the relationship between metal-metal interactions and thermodynamic stability is often complex;¹ thus, in certain systems

such as the 9-vertex $Co_2C_2B_5$ and 7-vertex $Co_2C_2B_3$ closo cages, studies in this laboratory have found reversible thermally induced metal atom migrations between adjacent and non-adjacent vertices.^{1c,e} Moreover, electrochemical studies of

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