Synthesis and Structural Characterization of Cyclopentadienyliron− and Cyclopentadienylmolybdenum−Gallium Compounds

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Reaction of K[CpFe(CO)$_2$] with a large excess of GaCl$_3$ yields [{CpFe(CO)$_2$}Ga(Cl·GaCl$_3$)(μ-Cl)]$_2$ (**1**), while reactions with 1 and 0.5 equiv yield [{CpFe(CO)$_2$}GaCl$_2$]$_n$ (**2**) and [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$, respectively. The molecular structure of compound **1** can be considered to be a GaCl$_3$ complex of dimeric **2**, in which the two GaCl$_3$ moieties coordinate via a near linear chloride bridge. [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$ is polymeric in the solid state, involving an infinite Ga−Cl···Ga−Cl backbone with pendent [CpFe(CO)$_2$] units; however, the solubility of [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$ in CH$_2$Cl$_2$ and toluene suggests that its polymeric structure is cleaved in solution. Compound **2** reacts with MeCN yielding [CpFe(CO)$_2$]GaCl$_2$(MeCN) (**3**). Reduction of [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$ with potassium in Et$_2$O yields the previously reported [CpFe(CO)$_2$]$_3$Ga and gallium metal. Reaction of K[CpFe(CO)$_2$] with GaI$_3$ yields [CpFe(CO)$_2$]GaI$_2$ (**4**), which upon hydrolysis gives the unusual galloxane, [CpFe(CO)$_2$]$_6$Ga$_6$(μ_3-O)$_4$(μ-OH)$_2$I$_2$ (**5**). Reaction of CpMo(CO)$_3$H with Ga(^{t}Bu)$_3$ yields [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$ (**6**), which forms a Lewis acid−base complex with MeCN: [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$(MeCN) (**7**). The structure of compound **6** shows evidence of unusual intra- and intermolecular carbonyl···gallium interactions. The aluminum analogue of compound **6**, [CpMo(CO)$_3$]Al(^{t}Bu)$_2$ (**8**), has been prepared, as has the sterically hindered aryloxide derivative, [CpMo(CO)$_3$]Al(BHT)$_2$ (**9**). The structures of compounds **1**, **5**·Et$_2$O, **6**, and [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$ have been determined by X-ray crystallography.

Introduction

Compounds containing bonds between transition metals and a main group metal have become known in recent years as “inorganometallic”.[2] However, compounds involving a direct covalent bond between a transition metal and a group 13 metal were first reported in the late 1960s.[3] Since this time, a large number of compounds have been prepared.[4−10] Kaesz and co-workers demonstrated that volatile derivatives may be used as MOCVD precursors to alloy thin films.[11] The work of Robinson and co-workers has centered interest on the types of bonding between transition metals and low-valent group 13 elements.[12]

Herein we report details on some of our own studies on transition metal−gallium compounds.

Results and Discussion

Cyclopentadienyliron Compounds. The reaction of K[CpFe(CO)$_2$] with GaCl$_3$ yields [{CpFe(CO)$_2$}Ga(Cl·GaCl$_3$)(μ-Cl)]$_2$ (**1**), [{CpFe(CO)$_2$}GaCl$_2$]$_n$ (**2**), and [{CpFe(CO)$_2$}$_2$Ga(μ-Cl)]$_\infty$, depending on the ratio of reactants (Scheme 1). Thus, reaction of K[CpFe(CO)$_2$] with a large excess of GaCl$_3$ in toluene allows for the isolation of

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(1) (a) Department of Chemistry, Rice University. (b) Department of Chemistry, University of Houston.

(2) *Inorganometallic Chemistry*; Fehlner, T. P., Ed. Plenum: New York, 1992.

(3) See for example: (a) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem*. **1966**, *5*, 1586. (b) Onaka, S.; Iwamoto, T.; Sasaki, Y. *Bull. Chem. Soc. Jpn*. **1968**, 1033. (c) Patmore, D. J.; Graham, W. A. G. *Inorg. Nucl. Chem. Lett*. **1968**, *4*, 201. (d) Robinson, W. R.; Schussler, D. P. *Inorg. Chem*. **1973**, *12*, 848.

(4) (a) Haupt, H.-J.; Neumann, F. *J. Organomet. Chem*. **1974**, *74*, 185. (b) Preut, H.; Haupt, H.-J. *Chem. Ber*. **1974**, *107*, 2860. (c) Haupt, H.-J.; Flörke, U.; Preut, H. *Acta Crystallogr., Sect. C* **1986**, *42*, 665. (d) Flörke, U.; Balsaa, P.; Haupt, H.-J. *Acta Crystallogr., Sect. C* **1986**, *42*, 275. (e) Haupt, H.-J.Neumann, F.; Schwab, B. *Z. Anorg. Allg. Chem*. **1982**, *485*, 234.

(5) (a) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem*. **1990**, *31*, 91. (b) Norman, N. C.; Webster, *Z. Naturforsch., B* **1989**, *44*, 91. (c) Clarkson, L. M.; Clegg, W.; Norman, N. C.; Tuker, A. J.; Webster, P. M. *Inorg. Chem*. **1988**, *27*, 2653. (d) Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Norman, N. C.; Marder, T. B. *J. Chem. Soc., Dalton Trans*. **1991**, 2229. (e) Clarkson, L. M.; McCrudden, K.; Norman, N. C.; Farrugia, L. J. *Polyhedron* **1990**, *28*, 503. (f) Campbell, R. M.; Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Pickett, N. L.; Norman, N. C. *Chem. Ber*. **1992**, *125*, 55.

(6) (a) Vanderhooft, J. C.; Ernst, R. D.; Cagle, F. W.; Neustadt, R. J.; Cymbaluk, T. H. *Inorg. Chem*. **1982**, *21*, 1876. (b) Cymbaluk, T. H.; Ernst, R. D. *Inorg. Chem*. **1980**, *19*, 2381.

(7) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans*. **1975**, 1945.

(8) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem*. **1977**, *129*, 2763.

(9) Green, M. L. H.; Mountford, P.; Smout, G. J.; Speel, S. R. *Polyhedron* **1990**, *9*, 2763.

(10) (a) Fischer, R. A.; Behm, J.; Priermeir, T.; Scherer, W. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 746. (b) Fischer, R. A.; Priermeir, T.; Scherer, W. *J. Organomet. Chem*. **1993**, *459*, 65. (c) Fischer, R. A.; Miehr, A.; Priermeir, T. *Chem. Ber*. **1995**, *128*, 831.

(11) See for example: (a) Chen, Y.-J.; Kaesz, H. D.; Kim, Y. K.; Müller, H.-J.; Williams, R. S.; Xue, Z. *Appl. Phys. Lett*. **1989**, *55*, 2760. (b) Fischer, R. A.; Kaesz, H. D.; Khan, S. I.; Müller, H.-J. *Inorg. Chem*. **1990**, *29*, 1601.

(12) Su, J.; Li, X.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511.

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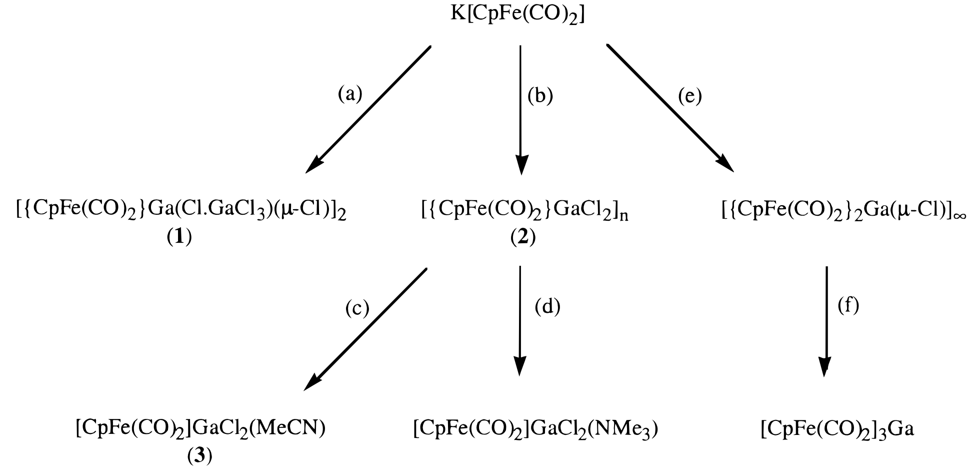
Scheme 1. Summary of Reactions of Iron−Gallium Compounds: (a) $GaCl_3$, excess, (b) 1 equiv of $GaCl_3$, (c) MeCN, (d) NMe_3, (e) 1/2 equiv of $GaCl_3$, (f) K in Et_2O



$[\{CpFe(CO)_2\}Ga(Cl{\cdot}GaCl_3)(\mu\text{-}Cl)]_2$ (**1**) in moderate yield (see Experimental Section). In contrast, $[\{CpFe(CO)_2\}GaCl_2]_n$ (**2**) and $[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]_\infty$ are prepared by the use of stoichiometric amounts (see Experimental Section).[13] The ^1H and ^{13}C NMR spectra for all three compounds show resonances for a single type of cyclopentadienyl group, and the IR spectrum indicates retention of the iron dicarbonyl moiety.

Norman and co-workers[5f] have previously reported the synthesis of the monochloride via the ligand exchange reaction (eq 1). On the basis of the mass

$$2[CpFe(CO)_2]_3Ga + GaCl_3 \rightarrow 3[CpFe(CO)_2]_2GaCl \qquad (1)$$

spectrum they proposed a dimeric structure. The solubility of the monochloride in CH_2Cl_2 and toluene and the observation of a single cyclopentadienyl environment in the solution NMR spectra (see Experimental Section) are consistent with a molecular species. However, the solid-state structure of the compound $[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]_\infty$ has been determined to be polymeric by X-ray crystallography (see below). We have previously reported similar results for $[(Mes)InI_2]_\infty$ (Mes = 2,4,6-$Me_3C_6H_2$), which is a dimer in solution but a polymer in the solid state.[14] In contrast, compound **2** is essentially insoluble in noncoordinating solvents. This observation is suggestive of a polymeric structure which does not dissociate in solution. By analogy with $[(Mes)MCl_2]_\infty$ (M = Ga,[15] In[16]) we propose compound **2** to have a chloride-bridged structure, i.e., **I**.

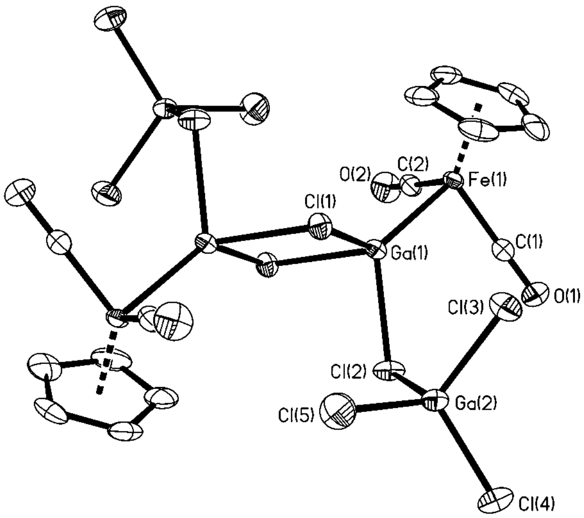
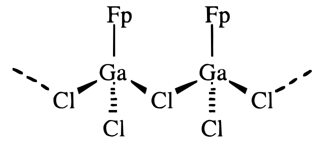


Figure 1. Molecular structure of $[\{CpFe(CO)_2\}Ga(Cl{\cdot}GaCl_3)(\mu\text{-}Cl)]_2$ (**1**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.



Fp = CpFe(CO)$_2$

(**I**)

The molecular structure of $[\{CpFe(CO)_2\}Ga(Cl{\cdot}GaCl_3)(\mu\text{-}Cl)]_2$ (**1**) is shown in Figure 1; selected bond lengths and angles are given in Table 1. The centrosymmetric structure of compound **1** consists of a Ga_2Cl_2 dimeric core, each of the gallium distorted tetrahedral coordination environments being completed by a chlorine and an iron from a $CpFe(CO)_2$ moiety. The chloride ligand is not terminal, but is capped with a $GaCl_3$ unit. The $CpFe(CO)_2$ moieties are mutually trans with respect to the Ga_2Cl_2 dimeric core. The Ga(1)−Cl(1) and Ga(1)−Cl(1′) distances [2.355(1) and 2.389(1) Å] are not unusually long for such Ga_2Cl_2 dimeric species,[17] despite the steric bulk of the $CpFe(CO)_2$ “ligand”. The exocyclic chloride bridge distances [2.382(1) and 2.311(2) Å] are comparable to those observed previously. As expected, the bridging Ga−Cl distances are longer than the terminal distances to Ga(2), 2.130(2)−2.149(2) Å. The

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[13] The indium analogues of compound **2** and $[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]_\infty$ have been previously reported, but without stuctural characterization; see: Hsieh, A. T. T.; Mays, M. J. *J. Organomet. Chem.* **1972**, *37*, 9.

[14] Leman, J. T.; Ziller, J. W.; Barron, A. R. *Organometallics* **1991**, *10*, 1766.

[15] Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1987**, *6*, 2088.

[16] Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 2214.

[17] (a) Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron* **1992**, *11*, 477. (b) Beachley, O. T., Jr.; Hallock, R. B.; Zhang, H. M.; Atwood, J. L. *Organometallics* **1985**, *4*, 1675. (c) Wallwork, S. C.; Worrall, I. J. *J. Chem. Soc.* **1965**, 1816.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in [{$CpFe(CO)_2$}$Ga(Cl{\cdot}GaCl_3)(\mu\text{-}Cl)]_2$ (1)

Ga(1)–Fe(1)	2.286(1)	Ga(1)–Cl(1)	2.355(1)
Ga(1)–Cl(2)	2.382(1)	Ga(1)–Cl(1′)	2.389(1)
Ga(2)–Cl(4)	2.130(2)	Ga(2)–Cl(5)	2.138(2)
Ga(2)–Cl(3)	2.149(2)	Ga(2)–Cl(2)	2.311(2)
Fe(1)–C(1)	1.766(5)	Fe(1)–C(2)	1.767(5)
Fe(1)–Cp$_{(av)}$	2.094(5)	C(1)–O(1)	1.146(6)
C(2)–O(2)	1.138(6)		

Fe(1)–Ga(1)–Cl(1)	123.52(4)	Fe(1)–Ga(1)–Cl(2)	125.11(4)
Cl(1)–Ga(1)–Cl(2)	96.93(5)	Fe(1)–Ga(1)–Cl(1′)	122.70(4)
Cl(1)–Ga(1)–Cl(1′)	87.55(5)	Cl(2)–Ga(1)–Cl(1′)	91.11(5)
Cl(4)–Ga(2)–Cl(5)	114.74(7)	Cl(4)–Ga(2)–Cl(3)	112.87(7)
Cl(5)–Ga(2)–Cl(3)	114.09(8)	Cl(4)–Ga(2)–Cl(2)	105.94(7)
Cl(5)–Ga(2)–Cl(2)	105.20(7)	Cl(3)–Ga(2)–Cl(2)	102.51(6)
Ga(1)–Cl(1)–Ga(1′)	92.45(5)	Ga(2)–Cl(2)–Ga(1)	108.46(5)
Ga(1)–Fe(1)–C(1)	89.4(1)	Ga(1)–Fe(1)–C(2)	92.2(2)
C(1)–Fe(1)–C(2)	94.1(2)	Fe(1)–C(1)–O(1)	178.9(5)
Fe(1)–C(2)–O(2)	178.2(4)		

latter are typical for a Lewis base complex of $GaCl_3$.[18] Thus, the overall structure is best considered as a Lewis acid complex of [{$CpFe(CO)_2$}$GaCl_2]_2$, rather than a cation–anion complex of two $[GaCl_4]^-$ anions coordinated to two cationic gallium centers. The exocyclic chloride bridge is near ideal tetrahedral [Ga(1)–Cl(2)–Ga(2) = 108.46(5)°] in a manner similar to that observed for $[(Mes)GaCl_2]_\infty$ [106.0(1)°].[15] The geometry about Ga(2) is typical for a Lewis base complex of $GaCl_3$; however, the geometry about Ga(1) is highly distorted from tetrahedral. The Cl(1)–Ga(1)–Cl(2) angle [96.93(5)°] is significantly smaller than the Fe(1)–Ga(1)–Cl(2) angle [123.52(4)°]. This distortion at Ga(1) is most likely due to the greater steric bulk of $CpFe(CO)_2$ compared to chloride. The Ga(1)–Fe(1) bond length [2.286(1) Å] is shorter than the range previously observed for other "$CpFe(CO)_2$" compounds [2.3618(3)–2.4565(4) Å].[5f,10b,c,19] This shortening is undoubtedly due to the greater Lewis acidity of the gallium chloride fragment; however, the bond lengths and angles for the $CpFe(CO)_2$ fragment are within the range previously reported for such species.[5f,10b,c,19] No close Ga···CO intra- or intermolecular interactions are present (see below).

The structure of a single polymeric chain of [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$ is shown in Figure 2; selected bond lengths and angles are given in Table 2. The solid-state structure of [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$ consists of an infinite Ga–Cl···Ga–Cl backbone with two pendent [$CpFe(CO)_2$] units per gallium. The chloride bridges are near linear [171.9(7)°] and symmetrical, resulting in the gallium centers being the teeth of a zigzag chain (see Figure 2). The $CpFe(CO)_2$ groups are positioned above and below the plane defined by the Ga–Cl···Ga–Cl chain and are oriented to provide C_2 symmetry about the gallium. The Ga(1)–Fe(1) bond distance [2.3654(7) Å] is similar to those in $[CpFe(CO)_2]_3Ga$[5f] and $[CpFe(CO)_2]GaCl_2(NMe_3)$.[10c] The crystal packing of the chains is shown in Figure 3.

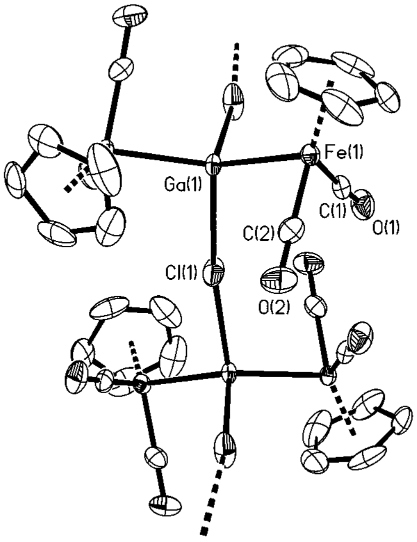

Figure 2. Structure of part of the polymeric chain of [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$. Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$

Ga(1)–Fe(1)	2.3654(7)	Ga–Cl(1)	2.5388(5)
Fe(1)–C(1)	1.766(4)	Fe(1)–C(2)	1.753(5)
Fe(1)–Cp$_{(av)}$	2.085(6)	C(1)–O(1)	1.144(5)
C(2)–O(2)	1.146(5)		

Fe(1)–Ga–Fe(1′)	135.58(4)	Fe(1)–Ga–Cl(1)	101.74(4)
Fe(1)–Ga–Cl(1′)	105.61(4)	Cl(1)–Ga–Cl(1′)	102.61(2)
Ga(1)–Fe–C(1)	85.7(1)	Ga(1)–Fe–C(2)	85.8(2)
C(1)–Fe–C(2)	95.7(2)	Ga(1)–Cl(1)–Ga(1′)	171.97(7)
Fe(1)–C(1)–O(1)	176.5(4)	Fe(1)–C(2)–O(2)	177.0(4)

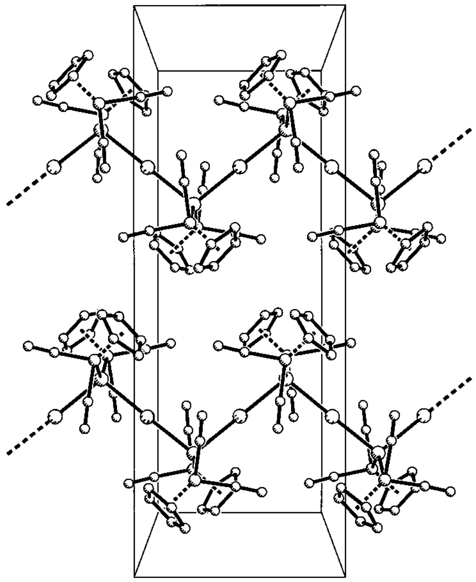

Figure 3. Crystal packing diagram of [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$.

Reaction of compound **2** with MeCN and NMe_3 results in the formation of $[CpFe(CO)_2]GaCl_2(MeCN)$ (**3**) and $[CpFe(CO)_2]GaCl_2(NMe_3)$,[10c] respectively. The mass spectrum of $[CpFe(CO)_2]GaCl_2(NMe_3)$[20] and compound **3** shows only $M^+ - L$.

Reduction of [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$ with potassium in Et_2O yields gallium metal and the previously reported $[CpFe(CO)_2]_3Ga$;[5f] see Scheme 1. Addition of pyridine to [{$CpFe(CO)_2$}$_2Ga(\mu\text{-}Cl)]_\infty$ indicates that it exists as a

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[18] (a) Beachley, O. T., Jr.; Pazik, J. C. *Organometallics* **1988**, *7*, 1516. (b) Lee, B.; Moise, F.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1992**, *26*, 187.

[19] He, X.; Bartlett, R. A.; Power, P. P. *Organometallics* **1994**, *13*, 548.

[20] Mass spectrum (EI, %): *m/z* 318 ($M^+ - NMe_3$, 25), 290 ($M^+ - NMe_3 - CO$, 45), 262 ($M^+ - NMe_3 - 2\ CO$, 100).

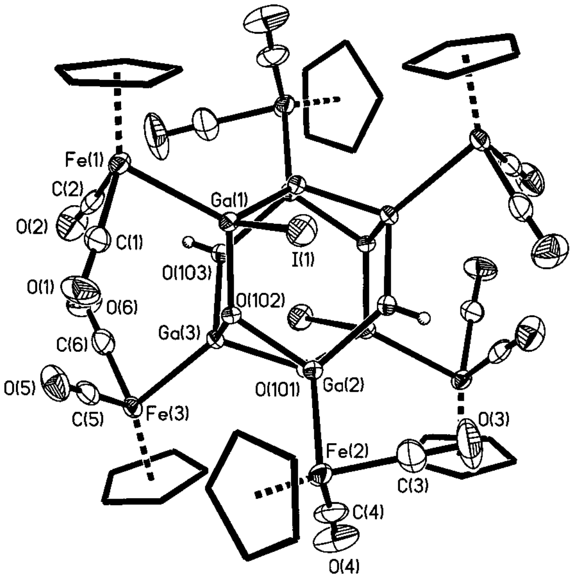

Figure 4. Molecular structure of $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2$ (**5**). Thermal ellipsoids are shown at the 30% level. For clarity, hydroxide hydrogen atoms are omitted and cyclopentadienyl ligands are shown as simple line representations.

single species, rather than an equilibrium with $[CpFe(CO)_2]_3Ga$; the latter is thus presumably formed through a disproportionation reaction, i.e., eqs 2 and 3. $[CpFe(CO)_2]_3Ga$ may also be prepared by the reaction of $[CpFe(CO)_2]K$ with Me_2GaCl (see Experimental Section).

$$[CpFe(CO)_2]_2GaCl \xrightarrow[-KCl]{+K} \text{“}[CpFe(CO)_2]_2Ga\text{”} \quad (2)$$

$$3\text{“}[CpFe(CO)_2]_2Ga\text{”} \rightarrow 2[CpFe(CO)_2]_3Ga + Ga^0 \quad (3)$$

Reaction of $[CpFe(CO)_2]K$ with GaI_3 yields the diiodide complex, $[CpFe(CO)_2]GaI_2$ (**4**) (see Experimental Section). The ^1H and ^{13}C NMR spectra of compound **4** show resonances for a single type of cyclopentadienyl group, and the IR spectrum indicates retention of the iron dicarbonyl moiety (see Experimental Section). Upon exposure to wet Et_2O, compound **4** decomposes to yield a small quantity of yellow crystals. On the basis of X-ray crystallography (see below) the hydrolysis product was determined to be $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2$ (**5**). The formation of compound **5** may be rationalized as being due to the hydrolysis of compound **4** (i.e., eq 4) with the subsequent addition of HI to the galloxane cage (eq 5).

$$6[CpFe(CO)_2]GaI_2 + 6H_2O \rightarrow [\{CpFe(CO)_2\}Ga(\mu_3\text{-}O)]_6 + 12HI \quad (4)$$

$$[\{CpFe(CO)_2\}Ga(\mu_3\text{-}O)]_6 + 2HI \rightarrow [CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2 \quad (5)$$

We have previously observed similar cage-opening reactions for the *tert*-butylalumoxanes.[21]

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2\cdot Et_2O$ (5)

Ga(1)−I(1)	2.636(2)	Ga(1)−Fe(1)	2.359(2)
Ga(1)−O(101′)	1.907(5)	Ga(1)−O(102)	1.893(5)
Ga(2)−Fe(2)	2.344(2)	Ga(2)−O(101)	1.914(6)
Ga(2)−O(102)	1.915(5)	Ga(2)−O(103′)	1.918(5)
Ga(3)−Fe(3)	2.340(2)	Ga(3)−O(101)	1.923(5)
Ga(3)−O(102)	1.931(6)	Ga(3)−O(103)	1.923(5)
Fe(1)−C(1)	1.74(1)	Fe(1)−C(2)	1.74(1)
Fe(2)−C(3)	1.75(1)	Fe(2)−C(4)	1.73(2)
Fe(3)−C(5)	1.77(1)	Fe(3)−C(6)	1.73(1)
Fe(1)−$Cp_{(av)}$	2.10(1)	Fe(2)−$Cp_{(av)}$	2.15(4)
Fe(3)−$Cp_{(av)}$	2.07(1)	C(1)−O(1)	1.14(1)
C(2)−O(2)	1.15(1)	C(3)−O(3)	1.11(1)
C(4)−O(4)	1.17(1)	C(5)−O(5)	1.16(1)
C(6)−O(6)	1.17(1)		

I(1)−Ga(1)−Fe(1)	108.56(6)	I(1)−Ga(1)−O(101)	101.3(2)
I(1)−Ga(1)−O(102)	100.4(2)	Fe(1)−Ga(1)−O(101′)	122.2(2)
Fe(1)−Ga(1)−O(102)	120.8(2)	O(101′)−Ga(1)−O(102)	100.0(2)
Fe(2)−Ga(2)−O(101)	124.6(2)	Fe(2)−Ga(2)−O(102)	121.4(2)
Fe(2)−Ga(2)−O(103′)	117.4(2)	O(101)−Ga(2)−O(102)	85.0(2)
O(101)−Ga(2)−O(103′)	97.2(2)	O(102)−Ga(2)−O(103′)	104.7(2)
Fe(3)−Ga(3)−O(101)	121.0(2)	Fe(3)−Ga(3)−O(102)	125.3(2)
Fe(3)−Ga(3)−O(103)	118.3(2)	O(101)−Ga(3)−O(102)	84.3(2)
O(101)−Ga(3)−O(103)	104.4(2)	O(102)−Ga(3)−O(103)	96.6(2)
Ga(1′)−O(101)−Ga(2)	123.5(3)	Ga(1′)−O(101)−Ga(3)	121.7(3)
Ga(2)−O(101)−Ga(3)	93.3(2)	Ga(1)−O(102)−Ga(2)	122.0(3)
Ga(1)−O(102)−Ga(3)	123.6(3)	Ga(2)−O(102)−Ga(3)	92.9(2)
Ga(2′)−O(103)−Ga(3)	127.8(3)	C(1)−Fe(1)−C(2)	94.4(5)
C(3)−Fe(2)−C(4)	95.2(7)	C(5)−Fe(3)−C(6)	96.1(5)
Fe(1)−C(1)−C(1)	178(1)	Fe(1)−C(2)−C(2)	175.9(9)
Fe(1)−C(3)−C(3)	177(2)	Fe(1)−C(4)−C(4)	178(1)
Fe(1)−C(5)−C(5)	179.5(8)	Fe(1)−C(6)−C(6)	176(1)

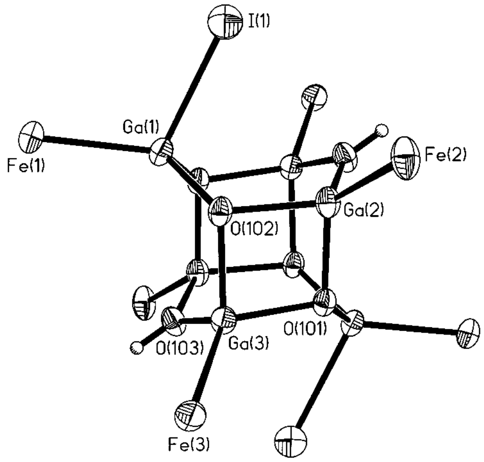

Figure 5. Structure of the core of $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2$ (**5**). Thermal ellipsoids are shown at the 30% level. Cyclopentadienyl and carbonyl ligands are omitted for clarity.

The molecular structure of $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2$ (**5**) is shown in Figure 4; selected bond lengths and angles are given in Table 3. The Ga_6O_6 core structure (Figure 5) consists of two fused boat conformation Ga_3O_3 rings and can be described as being derived from the opening of two opposing edges of a hexagonal prism (see Scheme 2). The geometries and bond distances around the Ga and O atoms are similar to those we have previously reported for other *tert*-butylgalloxane compounds,[22] while the Ga−Fe bond lengths are comparable to the compounds already discussed.[5f,10b,c,19] The Ga(1)−I(1) terminal distance is comparable to other inorganometallic gallium iodides.[23]

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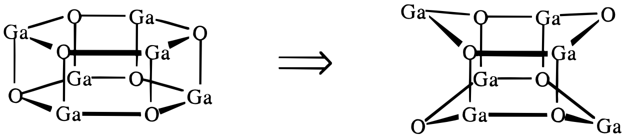
[21] (a) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465. (b) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 2213. (c) Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5514.

[22] Landry, C. C.; Harlan, C. J.; Bott, S. G.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1202.

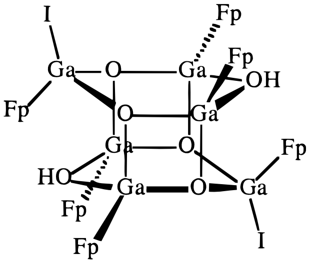
[23] Haupt, H.-J.; Balsaa, P.; Flörke, U. *Z. Anorg. Allg. Chem.* **1988**, *557*, 69.

Scheme 2. Structural Relationship between the Ga$_6$O$_6$ Cages in [CpFe(CO)$_2$]$_6$Ga$_6$(μ_3-O)$_4$(μ-OH)$_2$I$_2$ (5) and Its Proposed Galloxane Precursor, [{CpFe(CO)$_2$}Ga(μ_3-O)]$_6$[a]

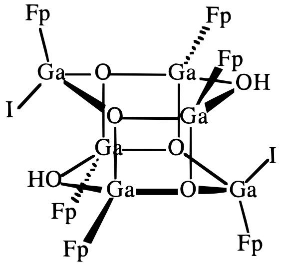


[a] "CpFe(CO)$_2$" groups are omitted for clarity.

One unusual feature of the structure, however, is the anti position of the iodides (**II**). This suggests that the addition of HI is a stepwise reaction, rather than concerted, since the latter would result in the iodides and hydroxides being adjacent, i.e., a syn disposition of the iodides (**III**). Initial protonation of an oxide would result in the formation of a hydroxide and a three-coordinate gallium; this would then be followed by coordination of the iodide through exo attack (see Scheme 3).



(**II**)



(**III**)

Cyclopentadienylmolybdenum Compounds. Reaction of CpMo(CO)$_3$H with Ga(^{t}Bu)$_3$ yields [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$ (**6**). Although the mass spectrum of compound **6** does not show the presence of a parent ion (the highest mass peak is M$^+$ − ^{t}Bu), it is consistent with a monomeric structure. The molecular structure of compound **6** as determined by X-ray crystallography is essentially monomeric; see below. The strongest bands in the carbonyl region of the IR spectrum (1961, 1916, 1865 cm^{-1}) are similar to those reported for [CpW(CO)$_3$]GaMe$_2$ (1964, 1905, 1889 cm^{-1}).[8] Single environments are observed in solution by ^{1}H and ^{13}C NMR spectroscopy for the cyclopentadienyl and *tert*-butyl ligands, and a single carbonyl resonance is observed in the ^{13}C NMR (see Experimental Section). As an indication of the presence of a coordinately unsaturated gallium in solution, compound **6** readily forms a Lewis acid−base complex upon recrystallization with acetonitrile, [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$(MeCN) (**7**) (see Experimental Section).

The molecular structure of [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$ (**6**) is shown in Figure 6; selected bond lengths and angles are given in Table 4. The overall structure is similar to that reported for [CpW(CO)$_3$]GaMe$_2$,[8] with the gallium alkyl groups oriented in the Ga−Mo−Cp plane. The Ga(1)−Mo(1) distance in **6** is comparable to the Ga−W distance in [CpW(CO)$_3$]GaMe$_2$. However, the geometry about both Mo(1) and Ga(1) is not as straightforward as it first appears.

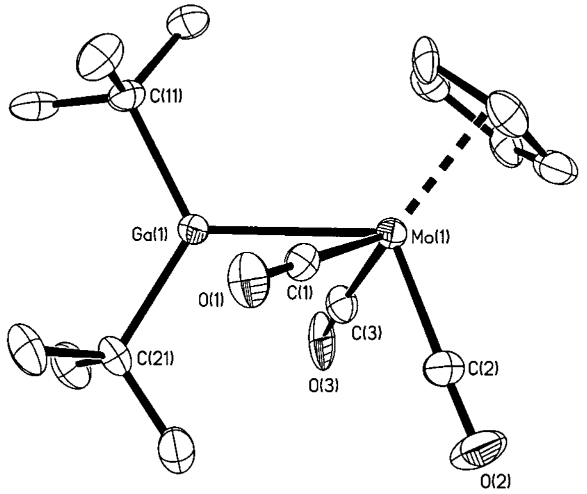
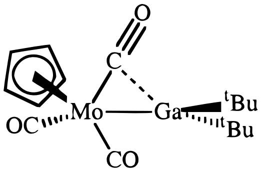


Figure 6. Molecular structure of [CpMo(CO)$_3$]Ga(^{t}Bu)$_2$ (**6**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity. The close intramolecular Ga⋯C$_{\text{(carbonyl)}}$ interaction is shown as a dashed line.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in [CpMo(CO)$_3$]Ga(^{t}Bu)$_3$ (6)

Ga(1)−Mo(1)	2.7376(5)	Ga(1)−C(11)	2.026(4)
Ga(1)−C(21)	2.021(4)	Mo(1)−C(1)	1.959(4)
Mo(1)−C(2)	1.962(4)	Mo(1)−C(3)	1.974(4)
Mo(1)−Cp$_{\text{(av)}}$	2.348(4)	C(1)−O(1)	1.158(5)
C(2)−O(2)	1.146(5)	C(3)−O(3)	1.155(3)
Mo(1)−Ga(1)−C(11)	117.7(1)	Mo(1)−Ga−C(21)	119.7(1)
C(11)−Ga(1)−C(21)	121.2(2)	Ga(1)−Mo(1)−C(1)	61.24(8)
Ga(1)−Mo(1)−C(2)	113.2(1)	Ga(1)−Mo(1)−C(3)	64.4(1)
C(1)−Mo(1)−C(2)	79.5(2)	C(1)−Mo(1)−C(3)	108.6(2)
C(2)−Mo(1)−C(3)	83.0(1)	Mo(1)−C(1)−O(1)	175.7(2)
Mo(1)−C(2)−O(2)	177.4(3)	Mo(1)−C(3)−O(3)	174.8(4)

Viewing along the Ga(1)−Mo(1) vector there is a distinct asymmetry to the Ga(^{t}Bu)$_2$ moiety, also in the orientation of the carbonyl ligands with respect to the gallium. Furthermore, one of the carbonyl carbon atoms [C(1)] is positioned significantly closer to Ga(1) than expected [Ga(1)⋯C(1) = 2.484 Å]. In fact, this distance is shorter than those observed for the Ga⋯C$_{\text{(aromatic)}}$ π-type interactions in (^{t}Bu)$_2$Ga(OCPh$_3$) [2.894(6) Å][24] and GaPh$_3$ (3.42 Å).[25] Values for the van der Waals radius of Ga(III) are not available, but previous workers[25] have assumed a value between 1.7 and 2.0 Å. If these values are combined with that of the carbonyl group (ca. 1.7 Å),[26] then a Ga⋯C distance of 3.4−3.7 Å is expected. Thus, on the basis of the orientation of the carbonyl and the closeness of the Ga(1)⋯C(1) interaction we propose the presence of a weak bridging carbonyl interaction (**IV**).[27]



(**IV**)

It is reasonable to propose the presence of a possible interaction involving donation of electron density from

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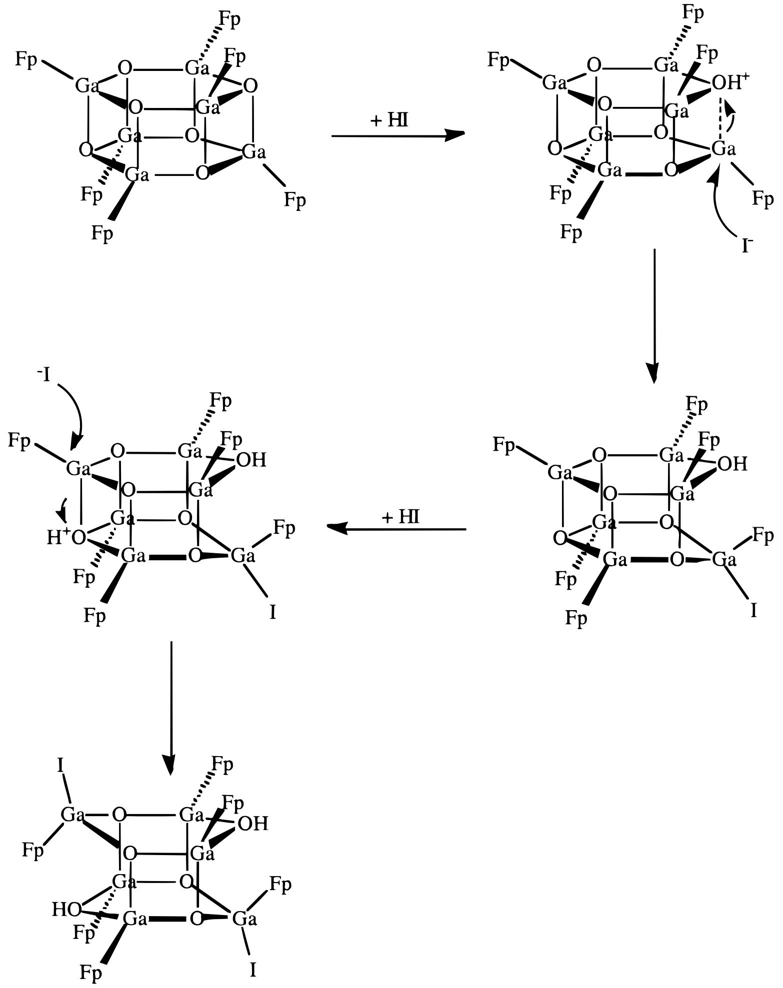
[24] Cleaver W. M.; Barron, A. R. *Organometallics* **1993**, *12*, 1001.

[25] Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3362.

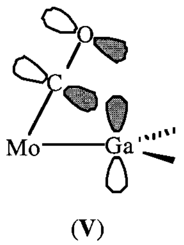
[26] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

[27] For an extensive review of π-CO and asymmetric bridging carbonyl interactions see: Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

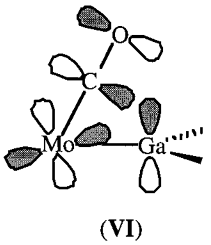
Scheme 3. Proposed Pathway for the *exo* Addition of HI in the Formation of $[CpFe(CO)_2]_6Ga_6(\mu_3\text{-}O)_4(\mu\text{-}OH)_2I_2$ (5)



the π-system of the carbonyl into the vacant p-orbital of the gallium (**V**). In line with the proposed interactions of the π-CO ligands in $Cp_2Mo_2(CO)_4$, an alternative interaction may involve a combination of the vacant p-orbital of the gallium with a filled Mo d-orbital back-donation to the carbonyl π*-orbital (**VI**).[28]



(V)



(VI)

If there exists a bonding interaction between the carbonyl and the gallium, then some distortion of the $MoGaC_2$ plane and/or bending at C(1) is expected. Indeed the gallium atom lies ca. 0.16 Å above the MoC_2 plane, but away from C(1)! Furthermore, while the carbonyl ligand [C(1)–O(1)] appears to bend away from the gallium, a similar distortion from linearity is observed for C(3)–O(3). Thus, if any intramolecular Ga···$C_{(carbonyl)}$ interaction does exist, it is very weak. A

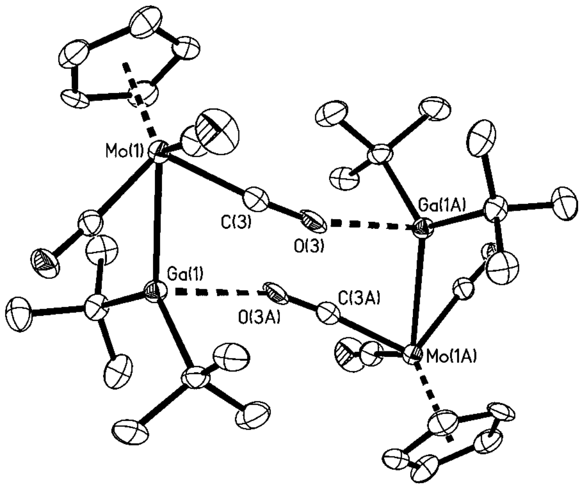


Figure 7. Crystal packing diagram of $[CpMo(CO)_3]Ga(^tBu)_2$ (**6**) showing the intermolecular Ga···$O_{(carbonyl)}$ interactions.

consideration of the crystal packing diagram of $[CpMo(CO)_3]Ga(^tBu)_2$ (**6**) suggests that the distortion of the $MoGaC_2$ plane is actually due to an intermolecular Ga···$O_{(carbonyl)}$ interaction (see Figure 7). Similar σ-CO complexes have been previously reported for the group 13 metals, especially aluminum.[29] However, the Ga(1)···O(3) distance (3.28 Å) is significantly longer than those observed for simple Lewis acid–base complexes between

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[28] Morris-Sherwood, B. J.; Powell, C. B.; Hall, M. B. Unpublished results; see ref 27.

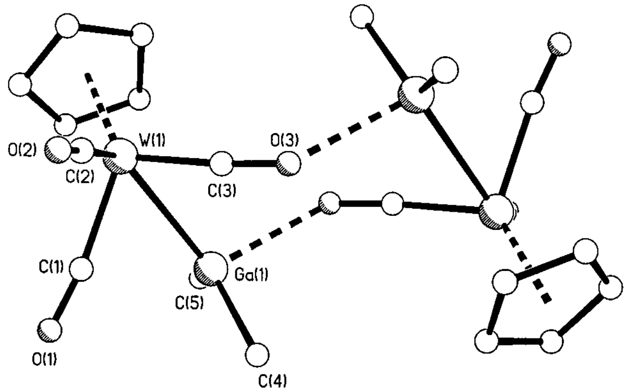

Figure 8. Crystal packing diagram of $[CpW(CO)_3]GaMe_2$ showing the intermolecular carbonyl···Ga interactions. Data were obtained from ref 8.

metal carbonyls and group 13 metals, e.g., $[\{CpW(CO)_3\}AlMe_2]_2$ [1.79(1) Å],[30] $[CpFe(CO)_2Ga(^tBu)_2][Cp_2Fe_2(CO)_4]$ [2.334(9) Å],[19] and $[CpW(CO)_3]_3Al(THF)_3$ [1.827(9) Å].[31] However, we propose that the solid-state structure of compound **6** is consistent with the presence of both intra- and intermolecular carbonyl···gallium interactions as a consequence of the electron-deficient nature of the gallium.

Although no intra- or intermolecular carbonyl···gallium interactions were described at the time of publication, an analysis of the structure of $[CpW(CO)_3]GaMe_2$ reported by Oliver and co-workers[8] suggests the presence of similar interactions. As with compound **6,** the gallium in $[CpW(CO)_3]GaMe_2$ is 0.16 Å out of the WC_2 plane. In addition, one of the carbonyl groups is positioned with a short C(1)···Ga(1) interaction (2.49 Å). Finally, a space-filling diagram of $[CpW(CO)_3]GaMe_2$ indicates the presence of intermolecular $Ga\cdots O_{(carbonyl)}$ interactions (2.46 Å) (see Figure 8). It should be noted, however, that neither type of interaction appears present in $[CpFe(CO)_2]Ga(^tBu)_2$.[19]

The aluminum analogue of compound **6**, $[CpMo(CO)_3]Al(^tBu)_2$ (**8**), has been prepared by the reaction of $CpMo(CO)_3H$ with $Al(^tBu)_3$. On the basis of NMR and IR spectroscopic characterization, compound **8** is isostructural to compound **6**. The reaction of $CpMo(CO)_3H$ with $(BHT)_2AlH(Et_2O)$ yields the sterically hindered aryloxide derivative, $[CpMo(CO)_3]Al(BHT)_2$ (**9**) (see Experimental Section).

Experimental Section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000−400 cm^{-1}) were obtained using a Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250 and Avance 200 spectrometers. Chemical shifts are reported relative to internal solvent resonances. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Unfortunately, the extreme air sensitivity of several compounds resulted in highly variable analysis results. The syntheses of $[CpFe(CO)_2]K$,[32] $CpMo(CO)_3H$,[33] $Ga(^tBu)_3$,[34] $Al(^tBu)_3$,[35] and $(BHT)_2AlH(Et_2O)$[36] were performed according to literature methods. Solvents were distilled and degassed prior to use.

$[\{CpFe(CO)_2\}Ga(Cl{\cdot}GaCl_3)(\mu\text{-}Cl)]_2$ (1). To a suspension of the solvent-free $K[CpFe(CO)_2]$ (2 g, 9.26 mmol) in toluene (20 mL) at −78 °C was added a solution of $GaCl_3$ (4.00 g, 22.66 mmol) in toluene (20 mL). After warming to room temperature and stirring for 1 h, the mixture was filtered. The filtrate was concentrated to ca. 10 mL and cooled to −29 °C, from which yellow crystals grew overnight. The pale yellow residue remaining after the filtration was extracted with toluene (50 mL), concentrated (to ca. 10 mL) and cooled to −29 °C, from which further yellow crystals grew overnight. Total yield: 35%. Mp: 127 °C. Anal. (calcd, %): C 16.96 (17.03), H 1.30 (1.02). Mass spectrum (EI, %): *m/z* 318 $[CpFe(CO)_2GaCl_2$, 30], 290 $[CpFe(CO)GaCl_2$, 40], 262 ($CpFeGaCl_2$, 100). IR (cm^{-1}): 2072 (w), 2006 (s), 1953 (s), 1923 (sh), 859 (m), 630 (m), 583 (s). ^1H NMR (C_6D_6): δ 4.09 (s, C_5H_5). ^{13}C NMR (C_6D_6): δ 83.28 (C_5H_5).

$[\{CpFe(CO)_2\}GaCl_2]_n$ (2). To a suspension of the solvent-free $K[CpFe(CO)_2]$ (2.00 g, 9.26 mmol) in toluene (20 mL) at −78 °C was added a solution of $GaCl_3$ (1.64 g, 9.26 mmol) in toluene (20 mL). After warming up to room temperature and stirring for 1 h, the mixture was filtered and the resulting pale yellow solid dried in a vacuum. Yield: ca. 75%. Mp: 159−161 °C. Mass spectrum (EI, %): *m/z* 318 (M^+, 25), 290 ($M^+ - CO$, 35), 262 ($M^+ - 2\ CO$, 100). IR (cm^{-1}): 1997 (s), 1940 (s), 871 (w), 833 (w), 721 (w), 643 (m), 596 (s). ^1H NMR (CD_3CN): δ 4.81 (s, C_5H_5). ^{13}C NMR (CD_3CN): δ 83.83 (C_5H_5).[37]

$[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]_\infty$. To a suspension of the solvent-free $K[CpFe(CO)_2]$ (2.00 g, 9.26 mmol) in toluene (20 mL) at −78 °C was added a solution of $GaCl_3$ (0.817 g, 4.63 mmol) in toluene (10 mL). After warming to room temperature and stirring for 1 h, the mixture was filtered. The filtrate was concentrated (ca. 10 mL) and cooled to −29 °C, from which brown crystals grew overnight. The brown residue remaining after filtration was placed in the Soxhlet extractor and extracted with CH_2Cl_2 (50 mL) for 5 h. The extract was concentrated (to ca. 10 mL) and cooled to −29 °C, from which brown crystals grew overnight. Total yield: 56%. Mp: 165−167 °C. Anal. (calcd, %): C 36.19 (36.63), H 2.03 (2.20). Mass spectrum (EI, %): *m/z* 458 (M^+, 8), 430 ($M^+ - CO$, 80), 402 ($M^+ - 2\ CO$, 100), 346 ($M^+ - 4\ CO$, 8). IR (cm^{-1}): 1994 (s), 1982 (s), 1971 (s), 1937 (s), 1922 (sh), 1896 (sh), 857 (w), 832 (m), 669 (m), 638 (m), 583 (s). ^1H NMR (C_6D_6): δ 4.20 (s, C_5H_5). ^{13}C NMR (C_6D_6): δ 83.00 (C_5H_5), 214.65 (CO).[38]

$[CpFe(CO)_2]GaCl_2(MeCN)$ (3). To a suspension of the solvent-free $K[CpFe(CO)_2]$ (2.00 g, 9.26 mmol) in toluene (20 mL) at −78 °C was added a solution of $GaCl_3$ (1.64 g, 9.26 mmol) in toluene (20 mL). After warming to room temperature

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[29] (a) Kotz, J. C.; Turnipseed, C. D. *J. Chem. Soc, Dalton Trans.* **1970**, 41. (b) Burlitch, J. M.; Peterson, R. B. *J. Organomet. Chem.* **1970**, *24*, C65. (c) Burlitch, J. M.; Leonowicz, M. E.; Peterson, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097. (d) Chatt, J.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 38. (e) Chatt, J.; Crabtree, R. H.; Jeffrey, E. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1167. (f) Aresta, M. *Gazz. Chim. Ital.* **1972**, *102*, 781. (g) Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Chem. Commun.* **1972**, 650. (h) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086.

[30] Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499.

[31] Peterson, R. B.; Stezowski, J. J.; Wan, C.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3532.

[32] Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.

[33] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 313.

[34] Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.

[35] (a) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37. (b) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708. (c) Lehmkuhl, H.; Olbrysch, O. *Liebigs Ann. Chem.* **1973**, 715.

[36] (a) Healy, M. D.; Gravelle, P. W.; Mason, M. R.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441. (b) Healy M. D.; Barron, A. R. *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 921.

[37] On the basis of the NMR spectra of $[CpFe(CO)_2]GaCl_2(MeCN)$ (**3**), it is likely that the ^1H and ^{13}C NMR spectra of compound **2** are actually of the CD_3CN complex. Unfortunately, compound **2** is insoluble in noncoordinating solvents.

[38] The product was spectroscopically identical to that previously reported; see ref 5f.

Table 5. Summary of X-ray Diffraction Data

	[{CpFe(CO)$_2$}Ga(Cl·GaCl$_3$)(μ−Cl)]$_2$ (**1**)	[{CpFe(CO)$_2$}$_2$-Ga(μ-Cl)]$_\infty$
empir. formula	$C_{14}H_{10}Cl_{10}Fe_2Ga_4O_4$	$C_{14}H_{10}Cl_1Fe_2GaO_4$
M_w	987.30	459.09
cryst size, mm	0.12 × 0.13 × 0.21	0.11 × 0.21 × 0.25
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	*Ibca*
a, Å	9.325(2)	21.286(4)
b, Å	11.062(2)	18.429(4)
c, Å	7.828(2)	7.894(2)
α, deg	92.88(3)	
β, deg	94.35(3)	
γ, deg	113.65(3)	
V, Å^3	734.7(3)	3097(1)
Z	1	8
D(calcd), g/cm^3	2.232	1.969
μ, mm^{-1}	5.51	3.76
temp, K	298	298
2θ range, deg	4.0−55.0	4.4−55.0
no. collected	3590	1779
no. ind	3380	1777
no. obsd	2976 ($\|F_o\| > 4.0\sigma\|F_o\|$)	1296 ($\|F_o\| > 4.0\sigma\|F_o\|$)
R	0.041	0.047
R_w	0.110	0.120
largest diff peak, e Å^{-3}	1.10	0.73

	[CpFe(CO)$_2$]$_6$Ga$_6$(μ_3-O)$_4$(μ-OH)$_2$I$_2$·Et$_2$O (**5**)	[CpMo(CO)$_3$]-Ga(^{t}Bu)$_2$ (**6**)
empir. formula	$C_{46}H_{42}Fe_6Ga_6I_2O_{19}$	$C_{16}H_{23}GaMoO_3$
M_w	1906.02	429.02
cryst size, mm	0.10 × 0.22 × 0.25	006 × 0.21 × 0.33
cryst system	monoclinic	triclinic
space group	$P2_1/m$	$P\bar{1}$
a, Å	12.644(3)	8.4600(8)
b, Å	19.633(4)	10.4259(9)
c, Å	12.125(2)	12.2099(8)
α, deg		66.063(6)
β, deg	90.00(3)	89.424(6)
γ, deg		66.258(8)
V, Å^3	3019(1)	885.8(1)
Z	2	2
D(calcd), g/cm^3	2.103	1.608
μ, mm^{-1}	5.13	22.13
temp, K	298	298
2θ range, deg	4.0−45.0	3.0−50.0
no. collected	5470	3114
no. ind	3938	3114
no. obsd	2643 ($\|F_o\| > 4.0\sigma\|F_o\|$)	2771 ($\|F_o\| > 6.0\sigma\|F_o\|$)
R	0.0413	0.0246
R_w	0.106	0.0283
largest diff peak, e Å^{-3}	0.70	0.72

and stirring for 1 h, the mixture was filtrated. The pale yellow residue remaining after the filtration was extracted with MeCN (30 mL). The extract was concentrated (ca. 5 mL) and cooled to −29 °C, from which yellow precipitate formed over a period of several days. The product was filtered and washed with CH_2Cl_2 (10 mL). Yield: 27%. Mp: 149−151 °C. Mass spectrum (EI, %): *m/z* 318 (M$^+$ − MeCN, 25), 290 (M$^+$ − MeCN − CO, 45), 262 (M$^+$ − MeCN − 2CO, 100). IR (cm^{-1}): 2005 (s), 1991 (s), 1955 (s), 1941 (s), 1930 (s), 1012 (w), 871 (w), 844 (m), 723 (w), 644 (m), 595 (s). ^{1}H NMR (CD_3CN): δ 1.96 (3H, s, CH_3), 4.81 (5H, s, C_5H_5). ^{13}C NMR (CD_3CN): δ 83.76 (C_5H_5).

Ga[FeCp(CO)$_2$]$_3$. Method 1. To a suspension of the solvent-free K[CpFe(CO)$_2$] (0.797 g, 3.69 mmol) in toluene (10 mL) was added a solution of Me_2GaCl (0.50 g, 3.69 mmol) in toluene (15 mL) at −78 °C. After warming to room temperature and stirring for 1 h, all volatile materials were removed under vacuum. The resulting dark oil was washed with hexane (10 mL), producing brown solid. Extraction with toluene (30 mL) followed by filtration afforded a dark yellow-brown solution. The filtrate was concentrated (ca. 5 mL) and cooled to −29 °C, from which dark brown crystals grew overnight. Yield: 40%.

Method 2. A solution of [{CpFe(CO)$_2$}$_2$GaFe(μ-Cl)]$_\infty$ (0.2 g, 0.44 mmol) in Et_2O (5 mL) was stirred with K (0.026 g, 0.66 mmol) for 12 h. The volatiles were removed under vacuum. Extraction with toluene (10 mL) followed by filtration afforded a dark red-brown solution. The filtrate was concentrated (ca. 3 mL) and cooled to −29 °C, from which dark brown crystals grew overnight. Yield: 45%. Mp: 196 °C. Mass spectrum (EI, %): *m/z* 572 (M$^+$ − CO, 2), 544 (M$^+$ − 2 CO, 5), 516 (M$^+$ − 3 CO, 7), 488 (M$^+$ − 4 CO, 6), 460 (M$^+$ − 5CO, 15), 432 (M$^+$ − 6 CO, 50), 423 (M$^+$ − FeCp(CO)$_2$, 100), 367 (M$^+$ − FeCp(CO)$_2$ − 2CO, 60). IR (cm^{-1}): 1985 (s), 1979 (s), 1951 (s), 1915 (s), 1896 (s), 1261 (w), 1070 (w), 1058 (w), 1014 (m), 999 (w), 924 (w), 866 (m), 851 (m), 830 (m), 647 (s), 585 (s). ^{1}H NMR (C_6D_6): δ 4.40 (s, C_5H_5). ^{13}C NMR (C_6D_6): δ 83.40 (C_5H$_5$), 217.04 (CO).[38]

[CpFe(CO)$_2$]GaI$_2$ (4). Toluene (20 mL) was added to the solid mixture of K[CpFe(CO)$_2$] (0.50 g, 2.31 mmol) and GaI_3 (1.044 g, 2.31 mmol). After stirring for 2 h, a yellow solid was formed which was isolated by filtration and drying in a vacuum. Yield: ca. 80%. Mp: 180−181 °C (dec). Anal. (calcd, %): C 16.21 (16.80), H 1.10 (1.01). Mass spectrum (EI, %): *m/z* 500 (M$^+$, 15), 472 (M$^+$ − CO, 100), 444 (M$^+$ − 2CO, 60), 373 (M$^+$ − I, 40). IR (cm^{-1}): 2002 (sh), 1984 (s), 1930 (sh), 1917 (s), 1260 (w), 1011 (w), 841 (w), 637 (m), 591 (s). ^{1}H NMR (CD_3-CN): δ 4.78 (s, C_5H_5). ^{13}C NMR (CD_3CN): δ 86.31 (C_5H$_5$).

[CpFe(CO)$_2$]$_6$Ga$_6$(μ_3-O)$_4$(μ-OH)$_2$I$_2$ (5). Attempted reduction of an Et_2O solution of [CpFe(CO)$_2$]GaI$_2$ with potassium metal resulted in precipitation of [CpFe(CO)$_2$]$_3$Ga. All soluble materials were extracted with toluene and stored for several days, whereupon a few crystals were deposited. Only the hydrolysis product was structurally characterized.

[CpMo(CO)$_3$]Ga(^{t}Bu)$_2$ (6). A solution of Ga(^{t}Bu)$_3$ (0.96 g, 3.98 mmol) in toluene (20 mL) was treated with freshly sublimed CpMo(CO)$_3$H (0.98 g, 3.98 mmol). Upon reflux for 3 h the solution became yellow and gas evolution was observed. The reaction mixture was cooled to −29 °C, from which large yellow crystals grew overnight. Yield: 60%. Mp. 116 °C. Anal. (calcd, %): C 44.90 (44.79), H 5.24 (5.40). Mass spectrum (EI, %): *m/z* 373 (M$^+$ − ^{t}Bu, 72), 345 (M$^+$ − ^{t}Bu − CO, 16), 316 (M$^+$ − 2 ^{t}Bu, 8), 260 [CpMo(CO)Ga$^+$, 43], 232 (CpMoGa$^+$, 100). IR (cm^{-1}): 2040 (w), 1971 (sh), 1961 (s), 1916 (m), 1865 (s), 1261 (m), 1162 (w), 1158 (w), 1010 (m), 940 (w), 834 (w), 810 (s), 803 (sh), 589 (m), 515 (m), 480 (m). ^{1}H NMR: (C_6D_6) δ 4.79 (5H, s, C_5H_5), 1.29 [18H, s, Ga−C(CH_3)$_3$]. ^{13}C NMR: (C_6D_6) δ 228.56 (CO), 90.67 (C_5H$_5$), 37.98 [Ga-C(CH$_3$)$_3$], 30.84 [Ga−C(CH$_3$)$_3$]. UV (nm) 310, 380.

[CpMo(CO)$_3$]Ga(^{t}Bu)$_2$(MeCN) (7). (^{t}Bu)$_2$GaMoCp(CO)$_3$ (1.0 g, 2.33 mmol) was recrystallized from MeCN (5 mL). Yield: 65%. Mp: 100−104 °C. Mass spectrum (EI, %): *m/z* 471 (M$^+$, 1), 414 (M$^+$ - ^{t}Bu, 1), 386 (M$^+$ - ^{t}Bu − CO, 1), 373 (M$^+$ - ^{t}Bu − MeCN, 60), 345 (M$^+$ - ^{t}Bu − CO − MeCN, 35), 289 [CpMoGa(^{t}Bu)$^+$, 100]. ^{1}H NMR: (C_6D_6) δ 4.91 [5H, s, C_5H_5], 1.39 [18H, s, Ga−C(CH_3)$_3$], 0.56 [3H, s, CH_3CN]. ^{13}C NMR: (C_6D_6) 90.00 (C_5H$_5$), 31.94 [C(CH$_3$)$_3$].

[CpMo(CO)$_3$]Al(^{t}Bu)$_2$ (8). A solution of Al(^{t}Bu)$_3$ (0.64 g, 3.23 mmol) in pentane (20 mL) was treated with freshly sublimed CpMo(CO)$_3$H (0.80 g, 3.25 mmol). Upon reflux for 3 h, the solution became yellow and gas evolution was observed. The reaction mixture was cooled to −29 °C, from which crystals grew in 5 days. Yield: 21%. Mp: 141−143 °C (dec). Anal. (calcd, %): C 50.01 (49.75), H 5.89 (6.00). Mass spectrum (EI, %): *m/z* 323 (M$^+$ − Cp, 100), 295 (M$^+$ − Cp − CO, 8), 267 (M$^+$ − Cp − 2CO, 8), 247 (^{t}BuAlMoCp$^+$, 33). IR (cm^{-1}): 2434 (w), 2027 (m), 1969 (s), 1941 (s), 1916 (sh), 1172 (w), 1000 (m), 935 (m), 901 (w), 812 (m), 797 (s), 667 (m), 610 (s), 584 (m), 546 (w), 505 (m), 471 (m). ^{1}H NMR: (C_6D_6) δ 5.10 (5H, s, C_5H_5), 1.26 [18H, s, Al(C(CH_3)$_3$]. ^{13}C NMR: (C_6D_6) δ 92.91 (C_5H$_5$), 2952, [Al−C(CH$_3$)$_3$], 23.06 [C(CH$_3$)$_3$].

[CpMo(CO)$_3$]Al(BHT)$_2$ (9). A solution of (BHT)$_2$AlH(Et$_2$O) (2.18 g, 4.04 mmol) in toluene (40 mL) was treated with freshly sublimed CpMo(CO)$_3$H (1.00 g, 4.07 mmol). The resulting yellow reaction mixture was stirred for 1 h. Gas evolution had subsided after 10 min. All volatile materials were then removed under vaccum. The residual yellow solid compound was recrystallized from MeCN. Yield: 60%. Mp: 179 °C (dec). Mass spectrum (EI, %): *m*/*z* 684 ($M^+ - CO$, 1), 628 ($M^+ - 3$ CO, 8), 465 [$M^+ - CpMo(CO)_3$, 3], 219 (BHT^+, 60), 163 ($CpMo^+$, 40). IR (cm^{-1}): 2330 (m), 2295 (w), 2249 (w), 2026 (s), 1942 (vs), 1853 (s), 1844 (sh), 1559 (s), 1263 (s), 1156 (w), 1126 (m), 1025 (m), 1010 (w), 966 (m), 936 (m), 924 (m), 909 (s), 889 (sh), 859 (m), 810 (m), 793 (m), 771 (m), 717 (m), 654 (m), 602 (m), 571 (w), 486 (s). ^{1}H NMR: (C_6D_6) δ 7.20 (4H, s, C_6H_2, BHT), 5.18 (5H, s, C_5H_5), 2.26 (6H, s, CH_3, BHT), 1.59 [36H, s, $C(CH_3)_3$, BHT]. ^{13}C NMR: (C_6D_6) δ 231.91 (*C*O), 152.49 (O*C*, BHT), 139.07 (*o*-C, BHT), 128.25 (*p*-C, BHT), 126.89 (*m*-*C*H), 90.81 (C_5H_5), 35.51 [$C(CH_3)_3$, BHT], 32.16 [$C(CH_3)_3$, BHT], 21.71 (CH_3, BHT).

Crystallographic Studies. Crystals of compounds **1**, $[\{CpFe(CO)_2\}_2Ga(\mu\text{-}Cl)]_\infty$, **5**, and **6** were sealed in a glass capillaries under argon. Crystal and data collection and solution details are given in Table 4. Standard procedures in our laboratory have been described previously.[39] Data were collected on either an Enraf-Nonius CAD-4 or Rigaku four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects and absorption. The structures were solved by using Patterson methods and difference Fourier synthesis and refined using full-matrix least squares.[40] An area of electron density was observed for compound **5** about a center of inversion. This was modeled successfully as a disordered molecule of Et_2O. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions and allowed to ride on the attached carbon atoms [$d(C-H) = 0.95$ Å]. A weight scheme of $w^{-1} = 0.04(|F_o|)^2 + \sigma(|F_o|)^2$ was applied to the data for compound **6**. A summary of cell parameters, data collection, and structure solution is given in Table 5. Scattering factors were taken from ref 41.

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Supporting Information Available: Full listings of bond length and angles, anisotropic thermal parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(40) MolEN−Enraf-Nonius. *MolEN*, An Interactive Structure Solution Procedure; Enraf-Nonius: Delft, Netherlands, 1990.

(41) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. IV, pp 99, 149.