Synthesis and Solid-State Structure of $[HB(3,5\text{-}Me_2pz)_3]GaFe(CO)_4$: A Compound with a Short, Two-Electron Ga(I)→Fe Dative Bond[†]

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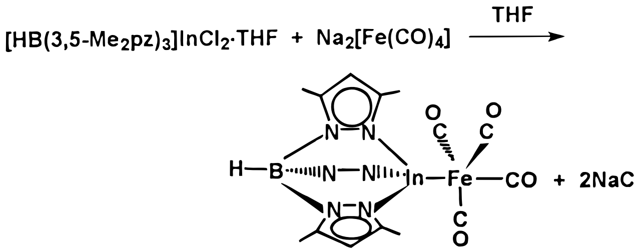
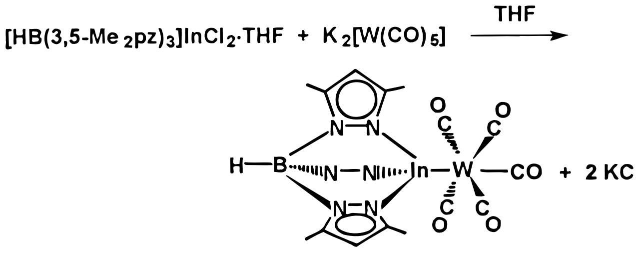
Summary: The complex $[HB(3,5\text{-}Me_2pz)_3]GaFe(CO)_4$ has been synthesized in the reaction of $[HB(3,5\text{-}Me_2pz)_3]GaMeCl$ and $Na_2Fe(CO)_4$·(dioxane). The short Ga−Fe bond distance of 2.315(3) Å is described as a normal two-electron dative bond (Ga→Fe).

Introduction

The chemistry of complexes that contain group 13 elements bonded to transition metals is of interest due to the potential of using these complexes as precursors to intermetallic films using OMCVD methods.[1] We have used our tris(pyrazolyl)borate complex $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ (pz = pyrazolyl ring) as a starting material to form unusually stable complexes containing In−Fe and In−W bonds:[2]





Both of these complexes contain short In−transition-metal bonds. For iron, the In−Fe distance of 2.463(2) Å is the shortest bond of this type yet reported.[3] The short In−Fe bond can be explained by two alternative bonding descriptions. Given that $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ forms from displacement of two Cl^- ligands from $[HB(3,5\text{-}Me_2pz)_3]InCl_2(THF)$ by $[Fe(CO)_4]^{2-}$, it can be considered as containing an In═Fe double bond. If this bonding description were correct, $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ would be the first example of a compound containing a group 13−transition-metal multiple bond. Alternatively, the bonding can be viewed as containing an indium(I) $[HB(3,5\text{-}Me_2pz)_3]In$ group acting as a Lewis base to the Lewis acid $Fe(CO)_4$ (In→Fe). We favored this dative bonding description in our earlier paper and supported this position by Fenske−Hall molecular orbital calculations.[2] The carbonyl stretching bands at 2011, 1919, and 1890 cm^{-1} certainly rule out describing the bonding as a contact ion pair, $\{[HB(3,5\text{-}Me_2pz)_3]In\}^{2+}[Fe(CO)_4]^{2-}$.[4]

There is considerable interest in compounds containing multiple bonds between transition metals and main-group metals.[5] Two recent reports are particularly important in this regard. Power has prepared $(\eta^5\text{-}C_5H_5)(CO)_2MoGe(C_6H_3\text{-}2,6\text{-}Mes_2)$ (Mes = $2,4,6\text{-}Me_3C_6H_2$), a complex that clearly contains a Mo≡Ge triple bond.[6] More relevant to our work is the report by Robinson of the synthesis of $(C_6H_3\text{-}2,6\text{-}Trip_2)GaFe(CO)_4$ (Trip = $2,4,6\text{-}Pr^i{}_3C_6H_2$):[7]

$$(C_6H_3\text{-}2,6\text{-}Trip_2)GaCl_2 + Na_2[Fe(CO)_4] \rightarrow (C_6H_3\text{-}2,6\text{-}Trip_2)GaFe(CO)_4 + 2NaCl$$

In the structure of $(C_6H_3\text{-}2,6\text{-}Trip_2)GaFe(CO)_4$, the

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[†] Dedicated to Prof. Warren Roper on the occasion of his 60th birthday.

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C−Ga−Fe−C (axial CO) fragment is nearly linear, and the Ga−Fe bond distance is very short[8] at 2.2248(7) Å. The Ga−Fe interaction was described as a triple bond, a contention challenged by others.[9]

Reported here are the synthesis and solid-state structure of [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$. This complex has a short Ga−Fe bond distance, although it is 0.09 Å longer than that reported in (C$_6$H$_3$-2,6-Trip$_2$)GaFe(CO)$_4$.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Proton NMR chemical shifts are reported in ppm versus TMS. Na$_2$Fe(CO)$_4$·(dioxane) was purchased from Aldrich, and [HB(3,5-Me$_2$pz)$_3$]GaClMe was prepared according to literature procedures.[10] Elemental analyses were performed by National Chemical Consulting, Inc.

Synthesis of HB[(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$. HB[(3,5-Me$_2$pz)$_3$]GaMeCl (0.12 g, 0.29 mmol) and Na$_2$Fe(CO)$_4$·(dioxane) (1:1.5) (0.10 g, 0.29 mmol) were placed in a flask, and 20.0 mL of dry, freshly distilled THF was added. The reaction mixture began golden brown and became magenta after stirring overnight. The THF was removed under vacuum to yield a golden brown solid. The solid was extracted with benzene, and the benzene was removed under vacuum to yield 0.052 g (33%) of a pale brown solid, mp 260 °C dec. ^{1}H NMR (CDCl$_3$) (300 MHz): δ 5.85 (s, 1); 2.60, (s, 3); 2.39 (s, 3). IR spectrum (Nujol, ν(CO), cm^{-1}): 2008, 1926, 1878. The mass spectrum shows clusters at *m/e* 534 (M$^+$), 506 (M$^+$ − CO), 450 (M$^+$ − 3 CO), and 422 (M$^+$ − 4 CO). Anal. Calcd for C$_{19}$H$_{22}$BFeGaN$_6$O$_4$: C, 42.73; H, 4.15; N, 15.71. Found: C, 43.01; H, 3.92; N, 15.65. Crystals suitable for X-ray crystallography were obtained by recrystallization from a toluene/hexane mixture at −30 °C. These crystals contain 1.5 equiv of toluene (NMR).

X-ray Structural Determination of HB[(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$·1.5(toluene). A crystal was affixed in a thin-walled capillary with epoxy cement. Data were collected on a Siemens P4 diffractometer, and details are shown in Table 1. All samples studied diffracted weakly and broadly due to the presence of disordered solvent molecules. Systematic absences in the diffraction data allowed a unique space-group assignment. The data were empirically corrected for absorption, and the structure was solved by direct methods. To conserve data, only atoms with $Z \geq 7$ were anisotropically refined. The asymmetric unit consists of one iron complex and one and a half molecules of toluene; one occupies a general site and was refined with a rigid hexagonal core, and the other is located on an inversion center and the methyl group was not located. All computation used the SHELXTL (5.2) program library (G. Sheldrick, Siemens Corp., Madison, WI).

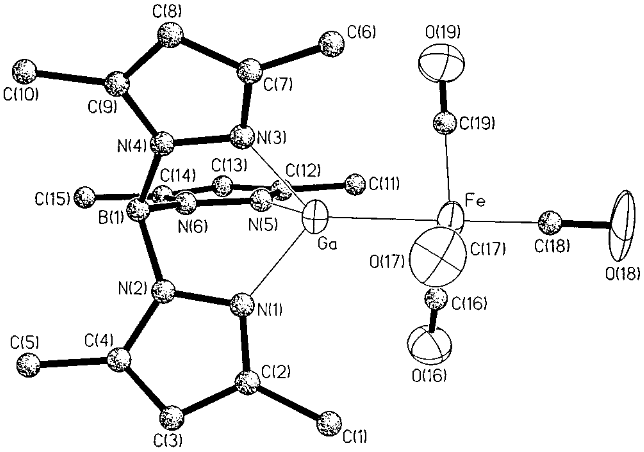


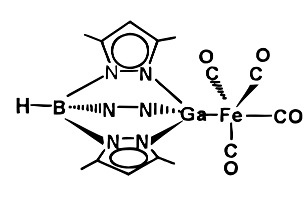
Figure 1. ORTEP diagram of [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$.

Table 1. Crystallographic Data for the Structural Analysis of [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$·1.5(toluene)

formula	C$_{29.5}$H$_{34}$BFeGaN$_6$O$_4$
fw	673.0
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	13.904(3)
b, Å	13.410(2)
c, Å	17.850(4)
β, deg	99.53(2)
V, Å^3	3282.3(11)
Z	4
cryst color	colorless plate
D(calc), g cm^{-3}	1.362
μ(Mo Kα), mm^{-1}	1.305
2θ range, deg	4.0−42.0
temp, K	296
no. of rflns collected	3621
no. of indep rflns	3482
radiation	Mo Kα (λ = 0.710 73 Å)
$R(F)$, $R_w(F)$	6.92, 8.78

Results and Discussion

[HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$ cannot be prepared as shown above for the indium analogue because [HB(3,5-Me$_2$pz)$_3$]GaCl$_2$ is unknown. Reaction of GaCl$_3$ with 1 equiv of K[HB(3,5-Me$_2$pz)$_3$] yields {[HB(3,5-Me$_2$pz)$_3$]$_2$Ga}-[GaCl$_4$] rather than the desired dichloride complex.[10] The formation of these ionic compounds can be prevented by replacing one of the chloride ligands with a methyl group before the introduction of the tris(pyrazolyl)borate ligand, leading to the synthesis of [HB(3,5-Me$_2$pz)$_3$]GaMeCl.[10] Reaction of this complex with Na$_2$Fe(CO)$_4$·(dioxane) yields [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$:



The compound is soluble in aromatic and halogenated solvents but only sparingly soluble in saturated hydrocarbons. It is air stable as a solid and only slowly decomposes in air in solution.

The structure of the molecule has been determined by X-ray crystallography. Figure 1 shows an ORTEP diagram and Table 2 important bond distances and angles. The geometry about the iron atom is a trigonal bipyramid with the gallium located at an axial position. The C−Fe−C bond angles from the axial carbonyl group

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[8] (a) Ga−Fe single bonds in a number of compounds average 2.43 A.[8b,c] An exception is (η^5-C$_5$H$_5$)Fe(CO)$_2$Ga(Cl)$_2$[NMe$_3$] where the short Ga−Fe bond length of 2.3618(3) was attributed to the high group electronegativity for the GaCl$_2$ fragment.[8d] (b) He, X.; Bartlett, R. A.; Power, P. P. *Organometallics* **1994**, *13*, 548. (c) Campbell, R. M.; Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Pickett, N. L.; Norman, N. C. *Chem. Ber.*, **1992**, *124*, 55. (d) Fischer, R. A.; Miehr, A.; Priermeier, T. *Chem. Ber.*, **1995**, *128*, 831.

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Table 2. Selected Bond Distances and Bond Angles for [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$·1.5(toluene)

	Bond Distances (Å)		
Ga−Fe	2.315(3)	Fe−C(16)	1.812(26)
Ga−N(1)	1.969(14)	Fe−C(17)	1.775(31)
Ga−N(3)	1.998(14)	Fe−C(18)	1.679(22)
Ga−N(5)	2.005(15)	Fe−C(19)	1.781(27)
	Bond Angles (deg)		
N(1)−Ga-Fe	125.2 (4)	Ga−Fe−C(18)	177.6(9)
N(3)−Ga-Fe	125.7 (4)	Ga−Fe−C(19)	84.9(8)
N(5)−Ga-Fe	124.1(4)	C(16)−Fe-C(17)	118.8(12)
N(1)−Ga-N(3)	90.8(6)	C(16)−Fe-C(18)	95.5(11)
N(1)−Ga-N(5)	90.3(6)	C(16)−Fe-C(19)	120.1(11)
N(3)−Ga-N(5)	89.9 (6)	C(17)−Fe-C(18)	96.2(12)
Ga−Fe−C(16)	83.3(7)	C(17)−Fe-C(19)	118.6(12)
Ga−Fe−C(17)	86.2(8)	C(18)−Fe-C(19)	94.0(12)

range from 94.0(12) to 96.2(12)°, and those in the equatorial plane range from 118.6(12) to 120.1(11)°. The Ga−Fe−C angles to these equatorial carbonyl groups range from 83.3(7) to 86.2(8)°. While this arrangement is very close to a regular trigonal bipyramid, the equatorial CO ligands are tilted toward the bulky [HB(3,5-Me$_2$pz)$_3$]Ga group to a greater extent than normally observed in other axially substituted Fe(CO)$_4$L (L = PPh$_3$, PPh$_2$H, C$_5$H$_5$N, C$_4$H$_4$N$_2$, C$_3$Ph$_2$S) complexes.[11] The arrangement is very similar to that observed in [HB(3,5-Me$_2$pz)$_3$]InFe(CO)$_4$, with which it is isomorphous.[2] The GaFe(CO)$_4$ part of the structure is also very similar to that in (η^5-C$_5$Me$_5$)GaFe(CO)$_4$, just recently reported by Jutzi.[12]

The gallium atom has pseudotetrahedral geometry. The N−Ga−N angles are restrained to 89.9(6)−90.8(6)° by the chelate rings. The Ga−N bond distances are normal and average 1.99 Å.[10] The metal halves of the molecule are oriented such that the pyrazolyl rings are staggered relative to the equatorial CO ligands on iron.

The most interesting feature of the structure is the observation of a short Ga−Fe bond distance of 2.315(3) Å. For comparison, the single-bond Ga−Fe distances in a number of compounds, such as (η^5-C$_5$H$_5$)(CO)$_2$Fe−Ga(*t*-Bu)$_2$, average 2.43 Å.[8] Two complexes with comparable Ga−Fe bond distances have very recently been reported. A slightly shorter bond distance of 2.2731(4) Å is observed in (η^5-C$_5$Me$_5$)GaFe(CO)$_4$,[12] and a slightly longer bond distance of 2.338(2) Å is reported for (CO)$_4$FeGa[(Cl)(tmeda)] (tmeda = tetramethylethylenediamine).[13]

Interestingly, the Ga−Fe bond distance in [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$ is 0.12 Å shorter than the single-bond average and only 0.09 Å longer than the distance in (C$_6$H$_3$-2,6-Trip$_2$)GaFe(CO)$_4$. A longer bond distance is expected for [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$, given that the gallium atom is four-coordinate whereas it is only two-coordinate in (C$_6$H$_3$-2,6-Trip$_2$)GaFe(CO)$_4$. The same argument holds for (CO)$_4$FeGa[(Cl)(tmeda)], where the gallium atom is also four-coordinate. While ionic radii values for two- and four-coordinate Ga(I) do not appear to be available, for comparison the ionic radius of Cu(I), a close neighbor of Ga(I) on the periodic table, is 0.14 Å longer in four- versus two-coordination.[14] The coordination number for gallium in (η^5-C$_5$Me$_5$)GaFe(CO)$_4$ is not as clearly defined (ranging somewhere between 2 and 4), but the Ga−Fe bond distance is only 0.05 Å longer than that in (C$_6$H$_3$-2,6-Trip$_2$)GaFe(CO)$_4$.

As in our indium paper, *we favor describing the Ga−Fe bond in [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$ as a normal two-electron, dative bond*. The gallium(I) in the [HB(3,5-Me$_2$pz)$_3$]Ga group acts as a Lewis base to the Lewis acid Fe(CO)$_4$ (Ga→Fe). A bonding description of this type is favored for the related complexes [η^2-HB(3,5-Me$_2$pz)$_3$]PFe(CO)$_4$,[15] (η^5-C$_5$Me$_5$)AlFe(CO)$_4$,[16] (η^5-C$_5$Me$_5$)GaFe(CO)$_4$,[12] (C$_6$H$_3$-2,6-Mes$_2$)GeMo(η^5-C$_5$H$_5$)(CO)$_2$,[6] and the whole series of complexes of the general formula (CO)$_n$M−EXL$_2$ (M = Cr, Mo, W, Fe; n = 4, 5; X = Cl, Me; E = Al, Ga; L = Lewis base).[13] It is also the description favored by recent density function calculations on C$_6$H$_5$GaFe(CO)$_4$.[9a]

These arguments are supported by the carbonyl stretching bands observed at 2008, 1926, and 1878 cm^{-1} for [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$, very similar to those for [HB(3,5-Me$_2$pz)$_3$]InFe(CO)$_4$ (2011, 1919, and 1890 cm^{-1}). For comparison, other axial-substituted Fe(CO)$_4$L (L = P(C$_6$H$_5$)$_3$, P(OCH$_3$)$_3$, P(*n*-C$_4$H$_9$)$_3$, C$_6$H$_5$PH$_2$, pyridine, pyrazine, etc.)[4a,11c,17] complexes show three bands that average 2050, 1980, and 1945 cm^{-1}, higher than those observed with [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$. Thus, using the Lewis acid−base description of the bonding, the [HB(3,5-Me$_2$pz)$_3$]Ga group acts as a very strong Lewis base/weak π-acceptor ligand in this complex. The Lewis base strength of the Ga[(R)(tmeda)] (R = Me, Et) groups in (CO)$_4$FeGa[(R)(tmeda)] complexes is even stronger, given the carbonyl stretching bands observed at 1992, 1905, and 1863 cm^{-1}.[13]

The carbonyl stretching bands for (η^5-C$_5$Me$_5$)GaFe(CO)$_4$ are observed at 2037, 1966, and 1942 cm^{-1}, much higher than for [HB(3,5-Me$_2$pz)$_3$]GaFe(CO)$_4$. The (η^5-C$_5$Me$_5$)Ga group appears to be acting as a weaker Lewis base than the [HB(3,5-Me$_2$pz)$_3$]Ga group. This result is expected, given that the [HB(3,5-Me$_2$pz)$_3$] ligand has been shown to be more electron donating than the (η^5-C$_5$Me$_5$) ligand.[18]

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Supporting Information Available: Tables of complete data collection information, atomic coordinates, bond distances, angles, anisotropic thermal parameters, and positional parameters of H atoms (9 pages). Ordering information is given on any current masthead page.

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