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Syntheses and Solid State Structures of $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ and $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ (pz = Pyrazolyl Ring). Intermetallic Complexes with Short Metal–Metal Bonds

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The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ (pz = pyrazolyl ring) with $Na_2Fe(CO)_4$ in THF yields $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$. The solid state structure shows that the geometry about the iron atom is a trigonal bipyramid with the indium located at an axial position. The In–Fe bond length of 2.463(2) Å is the shortest reported to date. Molecular orbital calculations indicate that little charge polarization exists in the iron–indium bond. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ with $Na_2W(CO)_5$ in THF yields $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$. This complex, with an In–W bond distance of 2.783(2) Å, is the first complex with an In–W bond to be structurally characterized. Crystal data: $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4\cdot 1.5C_6H_6$, monoclinic, $P2_1/n$, $a = 13.927(2)$, $b = 13.701(2)$, and $c = 17.957(3)$ Å, $\beta = 97.97(1)^\circ$, $V = 3393.3(9)$ Å^3, $Z = 4$, $T = 296$ K, $R = 6.84\%$; $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$, monoclinic, $C2/c$, $a = 13.609(4)$, $b = 19.478(9)$, and $c = 20.099(9)$ Å, $\beta = 107.63(4)^\circ$, $V = 5077(7)$ Å^3, $Z = 8$, $T = 296$ K, $R = 6.46\%$.

Introduction

Research on the synthesis and characterization of complexes containing transition metal to main group metal bonds is ongoing[1] and has accelerated recently due to the interest in using these complexes as precursors to intermetallic films using OMCVD methods.[2] The bulk of this research has centered on main group elements in group 14, an area recently reviewed by Lappert[3] and also van Koten.[4] A series of complexes of the type $L_nM'{-}MX_2$ (M′ = transition metal; M = Ge, Sn, Pb; X = alkyl, amide, alkoxide) has been prepared. Many of these complexes are oligomeric, depending on the metals and X groups. For example, $Cr(CO)_5(Sn[CH(SiMe_3)_2]_2)$ is monomeric[5] whereas $\{Me_2SnFe(CO)_4\}_2$ exists as a cyclic dimer.[6] Another aspect of this chemistry is that a Lewis base is often coordinated to the group 14 element, making it four-coordinate (e.g., $(CO)_5Cr[Sn(\text{di-}tert\text{-butyl})(\text{pyridine})]$).[6]

In complexes such as $Cr(CO)_5(Sn[CH(SiMe_3)_2]_2)$, the metal–metal bond can be viewed as a Lewis acid, Lewis base interaction of $Cr(CO)_5$ and the "carbene-like," tin(II) $Sn[CH(SiMe_3)_2]_2$ group.[5] Mössbauer studies indicate that the oxidation state of the tin is +2 in these complexes.[5b] Lappert has suggested that backbonding from the metal to a vacant orbital on tin contributes to the metal–metal bonding (a contention disputed by Veith[7]). The assertion that the tin can back-bond in these complexes is supported by the structure of $Fe(CO)_4[Sn(OC_6H_2\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}Me)_2]$ that shows a short Fe–Sn bond distance with the tin located in an equatorial position. The SnO_2 group is oriented such as to maximize back-bonding.[8]

A variety of complexes with bonds between group 13 metals and transition metals have also been prepared.[9] Three very recent papers have appeared in this area, which stress the importance of gallium– or indium–transition metal complexes as potential single-source precursors to bimetallic thin films. Cowley et al. have used a chelate ligand bonded to indium to stabilize complexes such as $[\{(2,6\text{-}Me_2NCH_2)_2C_6H_3\}In\{Co(CO)_4\}_2]$.[10] R. A. Fischer et al. have also used the stabilizing effects of a chelate ligand in complexes such as $[CpFe(CO)_2][In(CH_2CH_2CH_2NMe_2)_2]$.[11] Power et al. have used bulky alkyl ligands to prepare complexes of the types $Bu^tGa[Fe(Cp)(CO)_2]_2$ and $Bu^t_2Ga[Fe(Cp)$-

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$(CO)_2]$.[12] In contrast to the group 14 complexes discussed above, the group 13 transition metal bonds in these complexes are best described as electron pair bonds.

An interesting example of a complex that can be viewed as a gallium(I) Lewis base adduct of $Fe(CO)_4$ is (bipy)EtGaFe$(CO)_4$ (shown to be monomeric in solution).[13] The analogous complex with only one Lewis base coordinated to gallium is dimeric, $[(THF)(C_2H_3)GaFe(CO)_4]_2$, as characterized by X-ray crystallography.[14] The complexes $[\{(CO)_5Cr\}_2InBr]^{2-}$ [15] and $\{(CO)_5Cr\}InBr(THF)$,[16] both of which have been characterized in the solid state by X-ray crystallography, can be viewed as containing indium(I) acting as a Lewis base to the transition metal.

We and others have recently prepared a variety of complexes of gallium(III) and indium(III) containing one or two poly(pyrazolyl)borate ligands.[17] These bulky ligands form a variety of stable, monomeric complexes. As part of these studies, we have found that $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ (pz = pyrazolyl ring) is a particularly good starting material for reactions with other ligands containing either a -1 or -2 charge.[17h] We felt that this system could be used for the preparation of monomeric complexes with post transition metal−transition metal bonds. Reported here are the reactions of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ with the dianionic metal carbonyl complexes $[Fe(CO)_4]^{2-}$ and $[W(CO)_5]^{2-}$. Both products of these reactions, $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ and $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$, have been characterized in the solid state by X-ray crystallography and contain short In−M bonds. Also described are theoretical studies aimed at characterizing the In−M bonding in these complexes.

Experimental Section

General Procedure. All solvents were dried, degassed, and distilled prior to use. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$,[17h] $Na_2Fe(CO)_4$,[18a] and $Na_2W(CO)_5$[18b] were prepared according to published methods. Elemental analyses were performed by Robertson Laboratory, Inc.

([Hydrotris(3,5-dimethylpyrazolyl)borato]indium)tetracarbonyliron ($[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$, 1). $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ (0.55 g, 1.0 mmol) and $Na_2Fe(CO)_4$ (0.21 g, 1.0 mmol) were charged into a flask. THF (30 mL) was added via syringe and the mixture stirred overnight. The solvent was removed under vacuum and the product extracted with benzene (30 mL). The solution was filtered and the solvent removed under vacuum to yield a brown solid. This solid was recrystallized in toluene at −20 °C to yield yellow crystals (0.55 g, 0.95 mmol, 95%); dec = 159−165 °C. ^1H NMR (C_6D_6): δ 5.19 (3; s; 4-H pz); 2.36, 1.94 (9, 9; s, s; 3,5-Me pz). ^{13}C NMR (C_6D_6): δ 217.2 (CO); 151.9, 146.1 (3,5-C pz); 106.8 (4-C pz); 12.24, 12.17 (3,5-Me pz). IR (cm^{-1}, Nujol mull): 2552 (m) (ν BH); 2011 (s), 1919 (vs, b), 1890 (s), 1864 (sh) (ν CO). Mass spectrum (*m/z*): 580 (M^+); 552 ($M^+ - CO$); 496 ($M^+ - 3\ CO$); 468 ($M^+ - 4\ CO$). Anal. Calcd for $C_{19}H_{22}N_6BFeInO_4$: C, 39.35; H, 3.83; N, 14.49. Found: C, 39.41; H, 3.73; N, 14.63.

Table 1. Crystallographic Data for $\{[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4\}\cdot 1.5C_6H_6$ (1) and $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ (2)

	1	2
formula	$C_{28}H_{31}BFeInN_6O_4$	$C_{20}H_{22}BInN_6O_5W$
formula wght	697.1	735.9
space group	$P2_1/n$	$C2/c$
a, Å	13.927(2)	13.309(4)
b, Å	13.701(2)	19.478(9)
c, Å	17.957(3)	20.099(9)
β, deg	97.97(1)	107.63(4)
V, Å^3	3393.3(9)	5077(7)
Z	4	8
T, °C	296	296
λ, Å (Mo Kα)	0.71073	0.71073
ϱ(calcd), g Å^{-3}	1.364	1.925
μ, cm^{-1}	11.45	54.77
max 2θ, deg	45	45
rflns collected	5369	3451
indepndt rflns	5211	3340
obsrvd rflns	2694 ($4\sigma F_o$)	1697 ($5\sigma F_o$)
$R(F)$, $R(wF)$[a]	6.84, 8.20	6.46, 7.73

[a] $R(F) = \sum\Delta/\sum(F_o)$; $R(wF) = \sum[\Delta w^{1/2}]/[F_o w^{1/2}]$; $\Delta = |F_o - F_c|$; $w^{-1} = \sigma^2(F_o) + gF_o^2$.

([Hydrotris(3,5-dimethylpyrazolyl)borato]indium)pentacarbonyltungsten ($[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$, 2). $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ (0.55 g, 1.0 mmol) was charged into a flask. THF (30 mL) was added via syringe. A solution of $Na_2W(CO)_5$ in THF was then added via cannula and the resultant yellow solution stirred overnight. The solvent was removed under vacuum and the product extracted with benzene (25 mL). The solution was filtered and the solvent removed under vacuum to yield a yellow solid. This solid was recrystallized in toluene at −20 °C to yield yellow crystals (0.24 g, 0.33 mmol, 33%); dec = 205−509 °C. ^1H NMR ($CDCl_3$): δ 5.82 (3; s; 4-H pz); 2.32, 2.00 (9, 9; s, s; 3,5-Me pz). ^{13}C NMR ($CDCl_3$): δ 202.1, 201.3 (CO; $J_{W-C} = 121.5$ Hz); 150.9, 146.0 (3,5-C pz); 106.8 (4-C pz); 13.9, 13.0 (3,5-Me pz). IR (cm^{-1}, Nujol mull): 2553 (m) (ν BH); 2048 (m), 2041 (sh), 1961 (sh), 1928 (vs), 1903 (vs), 1880 (s) (ν CO). Mass spectrum (*m/z*): 736 (M^+); 680 ($M^+ - 2\ CO$); 652 ($M^+ - 3\ CO$); 596 ($M^+ - 5\ CO$). Anal. Calcd for $C_{20}H_{22}N_6BInO_5W$: C, 32.64; H, 3.02; N, 11.42. Found: C, 32.31; H, 3.07; N, 11.09.

X-ray Crystallographic Structure Determinations. Crystallographic quality crystals were grown from benzene at 0 °C for **1** and from toluene at −20 °C for **2**. Crystallographic data are collected in Table 1. Both samples were affixed in thin-walled capillaries with epoxy cement. Data were collected on a Siemens P4 diffractometer. Photographic characterization revealed $2/m$ Laue symmetry for both. For **1** systematic absences in the data uniquely defined the space group, while in **2** the absences agreed with either Cc or $C2/c$. The centrosymmetric alternative was suggested by the E statistics and later confirmed by the refinement behavior. Semiempirical corrections for absorption were applied to both data sets. Heavy-atom methods were used to locate both metal atoms in both structures. For **1** all non-hydrogen atoms were anisotropically refined, whereas for **2** data limitations prevented anisotropic refinement of the carbon atoms. In the crystal lattice for **1**, 1.5 molecules of benzene, the recrystallization

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4 \cdot 1.5C_6H_6$

	x	*y*	*z*	*U*(eq)[a]
In(1)	5561.6(6)	−283.8(7)	2545.3(5)	61.3(3)*
Fe(1)	7051.7(1)	−322.4(17)	3460.9(10)	76.8(7)*
N(1)	4079(7)	55(7)	2742(5)	64(2)*
N(2)	3355(7)	11(7)	2128(5)	61(2)*
N(3)	5218(7)	569(7)	1508(5)	70(2)*
N(4)	4331(6)	407(7)	1077(5)	62(2)*
N(5)	4900(6)	−1514(7)	1860(5)	65(2)*
N(6)	4033(6)	−1350(7)	1423(5)	56(2)*
B(1)	3606(10)	−312(12)	1347(7)	70(2)*
O(16)	6043(8)	−1830(9)	4196(6)	128(2)*
O(17)	6676(9)	1725(9)	3725(7)	140(2)*
O(18)	8768(10)	−438(12)	4544(9)	202(2)*
O(19)	8034(9)	−824(11)	2160(7)	162(2)*
C(1)	4247(10)	468(12)	4072(8)	115(2)*
C(2)	3665(9)	341(10)	3324(7)	73(2)*
C(3)	2703(9)	464(9)	3099(7)	76(2)*
C(4)	2515(8)	254(10)	2362(7)	70(2)*
C(5)	1574(8)	252(10)	1849(8)	93(2)*
C(6)	6653(9)	1593(10)	1486(8)	97(2)*
C(7)	5675(9)	1229(10)	1156(7)	76(2)*
C(8)	5121(9)	1487(11)	496(7)	83(2)*
C(9)	4275(9)	957(10)	451(6)	72(2)*
C(10)	3423(9)	954(11)	−119(7)	95(2)*
C(11)	6012(9)	−2927(11)	2220(9)	110(2)*
C(12)	5105(9)	−2474(10)	1792(7)	74(2)*
C(13)	4373(9)	−2909(10)	1326(7)	73(2)*
C(14)	3718(8)	−2180(10)	1099(7)	67(2)*
C(15)	2786(9)	−2270(10)	604(7)	95(2)*
C(16)	6436(10)	−1229(11)	3914(7)	87(2)*
C(17)	6811(10)	884(13)	3622(8)	94(2)*
C(18)	8125(10)	−383(13)	4117(9)	123(2)*
C(19)	7661(10)	−611(12)	2663(9)	103(2)*
C(101)	10682(21)	−1574(18)	3313(15)	265(3)
C(102)	11508(16)	−1552(16)	3972(13)	190(3)
C(103)	12417(18)	−1747(17)	4167(16)	234(3)
C(104)	13072(18)	−2104(16)	3619(13)	218(3)
C(105)	12079(15)	−2193(15)	2996(13)	180(3)
C(106)	10974(19)	−2100(19)	2750(17)	262(3)
C(111)	644(17)	137(18)	−590(16)	218(3)
C(112)	214(15)	1013(18)	−258(12)	186(3)
C(113)	−379(14)	620(16)	285(12)	163(3)

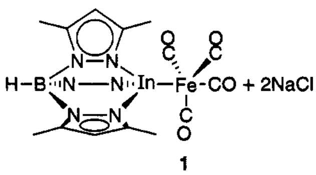
[a] Starred values: equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

solvent, occur per Fe/In molecule. All computations used the SHELXTL (4.2) program library (G. Sheldrick, Siemens Corp., Madison, WI). Tables 2 and 3 contain the atomic coordinates and isotropic thermal parameters for **1** and **2**.

Results and Discussion

$[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2 \cdot THF$ with $Na_2Fe(CO)_4$ in THF yields $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ (eq 1). The compound is soluble in aromatic and chlorinated hydrocarbons but only sparingly soluble in saturated hydrocarbons. Complex **1** is very stable and solutions of it can be handled in air without noticeable decomposition.

$$[HB(3,5\text{-}Me_2pz)_3]InCl_2 \bullet THF + Na_2[Fe(CO)_4] \xrightarrow{THF}$$



+ 2NaCl (1)

1

The structure of the molecule has been determined by X-ray crystallography. Figure 1 shows an ORTEP drawing and Table 4 important bond distances and angles. The geometry about the iron atom is a trigonal bipyramid with the indium located at an axial position. The C–Fe–C bond angles from the axial carbonyl group range from 94.1(7) to 95.7(7)° and those in the equatorial plane range from 117.9(7) to 121.4(7)°. The In–Fe–C angles to these equatorial carbonyl groups ranged from 84.6(4) to 85.8(4)°. While this arrangement is very close to a regular trigonal bipyramid, the equatorial CO ligands are tilted toward the bulky $[HB(3,5\text{-}Me_2pz)_3]In$ group to a greater extent than normally observed in other axial substituted $Fe(CO)_4L$ (L = PPh_3, PPh_2H, C_5H_5N, $C_4H_4N_2$, C_3Ph_2S) complexes.[19]

The indium atom has pseudo tetrahedral geometry. The N–In–N angles are restrained to 84.7(4) to 85.7-

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$

	x	*y*	*z*	*U*(eq)[a]
W(1)	2466.9(11)	4433.7(7)	2397.3(6)	47.5(5)*
In(1)	3553.7(15)	3820.8(10)	3656.0(9)	37.9(7)*
B(1)	4838(22)	3004(14)	5074(14)	29(8)*
N(1)	3077(15)	3530(10)	4597(10)	34(7)*
N(2)	3797(15)	3192(11)	5137(10)	36(7)*
N(3)	5024(17)	4087(11)	4457(11)	43(7)*
N(4)	5438(16)	3611(10)	5003(10)	36(7)*
N(5)	4169(16)	2706(10)	3798(11)	39(7)*
N(6)	4747(16)	2506(11)	4460(10)	40(7)*
O(16)	3791(20)	5799(12)	2568(12)	96(8)*
O(17)	3925(27)	3638(14)	1717(16)	143(9)*
O(18)	1025(21)	3167(15)	2137(14)	120(9)*
O(19)	1047(18)	5258(14)	3108(12)	100(8)*
O(20)	1187(22)	5040(12)	942(11)	104(8)*
C(1)	2252(21)	3670(14)	4786(13)	43(7)
C(2)	2465(21)	3409(15)	5472(13)	48(7)
C(3)	3363(18)	3139(12)	5682(12)	30(6)
C(4)	1338(22)	4043(15)	4347(15)	61(8)
C(5)	3983(21)	2835(16)	6375(14)	61(8)
C(6)	5737(23)	4583(15)	4516(14)	53(7)
C(7)	6631(22)	4444(16)	5094(14)	55(7)
C(8)	6388(24)	3824(16)	5391(16)	57(7)
C(9)	5540(22)	5137(15)	4013(14)	56(7)
C(10)	7029(25)	3511(18)	6013(17)	80(9)
C(11)	4203(19)	2197(13)	3390(12)	34(6)
C(12)	4886(22)	1695(16)	3760(15)	57(8)
C(13)	5168(21)	1886(15)	4416(14)	47(7)
C(14)	3544(24)	2257(18)	2624(15)	74(9)
C(15)	5915(26)	1567(18)	5029(16)	78(9)
C(16)	3368(24)	5295(17)	2546(16)	58(8)
C(17)	3367(22)	3997(15)	1971(15)	52(7)
C(18)	1551(23)	3641(15)	2253(14)	48(7)
C(19)	1554(25)	4955(17)	2855(15)	62(8)
C(20)	1647(25)	4833(17)	1471(17)	64(8)

[a] Starred values: equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

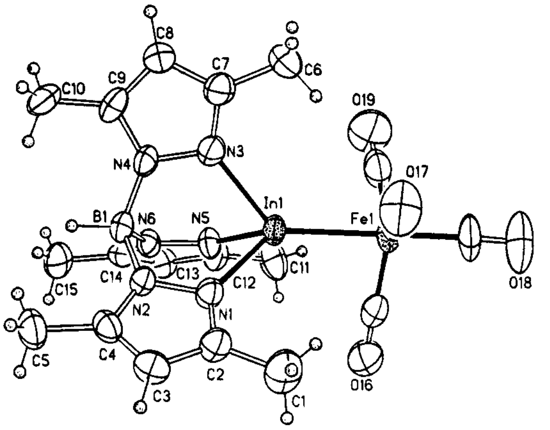


Figure 1. ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4 \cdot 1.5C_6H_6$ (**1**).

Table 4. Selected Bond Distances and Bond Angles for $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4\cdot 1.5C_6H_6$ (1) and $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ (2)

	1	2
	Bond Distances (Å)	
In−M	2.463(2)	2.783(2)
In−N(1)	2.192(9)	2.251(23)
In−N(3)	2.195(10)	2.217(19)
In−N(5)	2.211(10)	2.314(20)
M−C(16)	1.770(15)	2.045(33)
M−C(17)	1.719(18)	1.895(34)
M−C(18)	1.772(14)	1.950(30)
M−C(19)	1.807(17)	2.028(36)
M−C(20)		2.015(30)
	Bond Angles (deg)	
N(1)−In−M	128.5(2)	131.5(5)
N(3)−In−M	130.0(3)	132.4(6)
N(5)−In−M	127.1(2)	126.0(5)
N(1)−In−N(3)	85.7(4)	82.8(8)
N(1)−In−N(5)	85.5(3)	81.1(8)
N(3)−In−N(5)	84.7(4)	85.2(7)
In−M−C(16)	84.6(4)	95.1(8)
In−M−C(17)	85.8(4)	88.9(8)
In−M−C(18)	178.6(6)	86.3(8)
In−M−C(19)	85.5(4)	91.8(8)
In−M−C(20)		177.2(10)
C(16)−M−C(17)	118.7(7)	89.6(14)
C(16)−M−C(18)	94.5(7)	177.3(13)
C(16)−M−C(19)	121.4(7)	86.9(14)
C(16)−M−C(20)		87.6(12)
C(17)−M−C(18)	95.7(7)	92.8(13)
C(17)−M−C(19)	117.9(7)	176.5(13)
C(17)−M−C(20)		90.5(13)
C(18)−M−C(19)	94.1(7)	90.7(13)
C(18)−M−C(20)		91.1(12)
C(19)−M−C(20)		89.0(13)

(4)° by the chelate rings. The In−N bond distances average 2.20 Å, slightly shorter than those observed for this ligand in the structures of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$[17h] (average 2.248 Å) and $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot NCCH_3$ (average 2.250 Å).[17a] The two 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 the shortest In−Fe bond distance, 2.463(2) Å, reported to date. For comparison, the Fe−In bond distances in $\{InCl[Fe(CO)_2Cp]_2\}_2$ are 2.553(1) and 2.558(1) Å,[20] in $\{InCl(PMe_2Ph)[Fe(CO)_2Cp]_2\}_2$ 2.582(1) and 2.569(2) Å,[20] in $[CpFe(CO)_2][\overline{In(CH_2CH_2CH_2NMe_2)_2}]$ 2.6393(8) Å (a case where multiple In−Fe bonding was suggested),[11] in $[In\{Fe(CO_4)\}_3]^{3-}$ 2.633(1) Å,[21] and those in $[Et_4N][(2,2'\text{-bipyridine})InFe_2(CO)_8$ 2.545(3) and 2.552(3) Å.[22] These comparative bond distances are all for normal electron pair bonds. Given that the sum of the covalent radii of the two metals is 2.71 Å,[20] the bond distance observed in complex **1** is very short.

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. Alternatively, by analogy to the transition metal complexes of tin(II), $(bipy)EtGaFe(CO)_4$, and $\{(CO)_5Cr\}\text{-}InBr(THF)$ discussed in the Introduction, the bonding in **1** 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). A bonding description of this latter type is favored for the related complex $[\eta^2\text{-}HB(3,5\text{-}Me_2pz)_3]PFe(CO)_4$.[23] The bonding situation in **1** is different from $R_2Sn{-}M$ derivatives because a 5p orbital is available in the latter case for π-back-bonding. While certainly one would not want to invoke the use of the empty 5d orbitals on indium in such bonding, the antibonding orbitals arising from the In−N bonding interactions are certainly available for this type of interaction. This bonding is analogous to that recently advanced by Orpen and others for back-bonding in $M{-}PR_3$ complexes.[24]

In order to probe the bonding we have carried out Fenske−Hall molecular orbital calculations[25] on this molecule. The analysis shows that there is little charge polarization existing between the iron and indium atoms, with the iron atom being slightly more negative (−0.14 vs −0.08). The iron−indium bond is formed by a pd hybrid orbital on iron, using the $4p_z$ (11.6%) and $3d_{z^2}$ (25.0%) orbitals, and an sp hybrid orbital (10.9% s, 16.8% p) on the indium. There is no apparent back-bonding taking place from iron d orbitals interacting with σ^* orbitals on the indium fragment. The bond is therefore classified as a normal two-electron σ interaction, best described as a dative bond between indium(I) and iron(0).

$[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ shows strong carbonyl stretching bands at 2011, 1919, and 1890 cm^{-1}. For comparison other axial substituted $Fe(CO)_4L$ (L = $P(C_6H_5)_3$, $P(OCH_3)_3$, $P(n\text{-}C_4H_9)_3$, PCH_3H_2, $C_6H_5PH_2$, pyridine, pyrazine, etc.)[19c,27] complexes show three bands that average about 2050, 1980, and 1945 cm^{-1}, higher than those observed with **1**. Thus, using the Lewis acid−base description of the bonding, the $[HB(3,5\text{-}Me_2pz)_3]In$ group acts as a strong Lewis base/weak π-acceptor ligand in this complex.

$[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ with $Na_2W(CO)_5$ in THF yields $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ (eq 2). Complex **2** is also very stable, and solutions of it can be handled in air without noticeable decomposition. It shows strong carbonyl stretching bands at 2048, 1928, 1903, and 1880 cm^{-1}, slightly lower than typical $LW(CO)_5$ complexes. For example, $W(CO)_5(CNCH_3)$ has bands at 2069 and 1956 cm^{-1},[28] and the "carbene" complex $W(CO)_5\text{-}[C(C_6H_5)_2]$ at 2070, 1971, and 1963 cm^{-1}.[29]

This complex has also been characterized in the solid state by X-ray crystallography (Figure 2). The geometry

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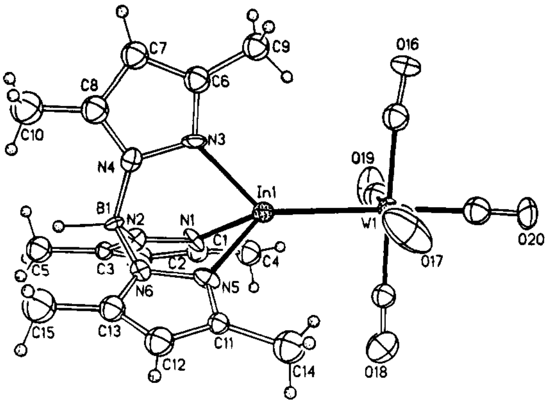
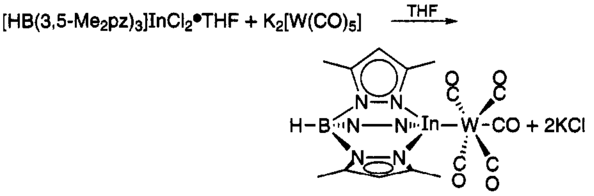


Figure 2. ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ (**2**).



(2)

2

about the tungsten atom is octahedral. The C–W–C angles from the carbonyl ligand *trans* to the indium atom range from 87.6(12) to 91.1(12)° and the adjacent *cis* C–W–C angles from 86.9(14) to 92.8(13)°. The In–W–C angles to the *cis* carbonyl ligands range from 86.3(8) to 95.1(8)°. The largest angle of this type is to C(16) which is the carbon atom of the only carbonyl ligand that is in close contact with a methyl group from a pyrazolyl ring.

As in the iron structure, the indium atom has pseudo tetrahedral geometry, but the N–In–N angles and bond distances are not as regular. The average In–N bond distance of 2.26 Å is 0.06 Å longer than in the iron structure, an increase that arises mainly from the In–N(5) bond length of 2.314(20) Å. These distortions in the In–W–C bond angles and the In–N bond distances are clearly caused by the inability of the four equatorial CO ligands in **2** to be arranged in a staggered configuration with respect to the three pyrazolyl rings, an arrangement readily available to the three equatorial CO ligands in **1**.

The In–W bond distance is 2.783(2) Å. $[HB(3,5\text{-}Me_2pz)_3]InW(CO)_5$ is the first complex with an In–W bond to be structurally characterized. Given that the sum of the covalent radii[30] is 3.05 Å, the In–W bond distance in this complex is short. Analogous to **1** as discussed above, the bonding in **2** is best viewed as an indium(I) group acting as a Lewis base to $W(CO)_5(In \rightarrow W)$.

Conclusion

Two new complexes, $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$ and $[HB(3,5\text{-}Me_2pz)_3]InFe(CO)_4$, have been prepared from the reaction of the transition metal carbonyl dianion and $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$. In both complexes, the M–M bonding is best described as a dative bond arising from donation of a lone pair of electrons on indium to the metal carbonyl group. We anticipate the future preparation of additional complexes of this type with other transition metal systems and group 13 elements.

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Supplementary Material Available: Tables of complete data collection information, bond distances, angles, anisotropic thermal parameters, and positional parameters of H atoms (14 pages). Ordering information is given on any current masthead page.

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