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Syntheses and Structures of the Phenylbismuth/Transition-Metal Carbonyl Compounds [PPN][$Ph_2BiFe(CO)_4$], $(Ph_2Bi)_2Fe(CO)_4$, [$PhBiFe(CO)_4$]$_2$, and $Ph_2BiMn(CO)_5$

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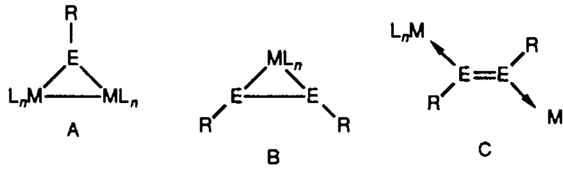
Treatment of $Na_2Fe(CO)_4$ with 1 equiv of Ph_2BiCl in tetrahydrofuran (THF) affords Na[$Ph_2BiFe(CO)_4$], characterized as the [PPN]$^+$ (PPN = bis(triphenylphosphine)nitrogen(1+)) salt ([PPN][I]); adding a second 1 equiv of Ph_2BiCl produces $(Ph_2Bi)_2Fe(CO)_4$ (II), which decomposes to [$PhBiFe(CO)_4$]$_2$ (III) in solution. III is also obtained in poor yield from the reaction of $PhBiBr_2$ and $Na_2Fe(CO)_4\cdot{}^3/_2$diox (diox = dioxane) in THF. The reduction of Ph_2BiCl with 2 equiv of sodium in liquid NH_3 followed by addition of $Fe(CO)_5$ yields II and III along with traces of Ph_4Bi_2. I, II, and III$\cdot CH_2Cl_2$ have been characterized by single-crystal X-ray diffraction. Crystals of [PPN][I] are monoclinic, *Cc* (No. 9), with a = 13.08 (1) Å, b = 15.832 (9) Å, c = 23.18 (1) Å, β = 99.53 (6)°, V = 4733 (6) Å^3, and Z = 4. Convergence was achieved with R = 5.8% and R_w = 6.0% for 2584 observed reflections. The iron atom has a trigonal-bipyramidal coordination geometry with the pyramidal Ph_2Bi group occupying an axial position. The Bi–Fe distance is 2.676 (4) Å. II crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 12.009 (3) Å, b = 13.074 (2) Å, c = 17.264 (2) Å, β = 96.78 (1)°, V = 2691.5 (8) Å^3, and Z = 4. The structure was refined to R = 5.0% and R_w = 5.8% for 3698 observed reflections. The octahedral $Fe(CO)_4$ group in II is bonded to two Ph_2Bi groups in cis positions. The average Bi–Fe distance in this compound is 2.828 (6) Å. III$\cdot CH_2Cl_2$ crystallizes in the monoclinic crystal system, space group $C2/c$ (No. 15) with a = 17.681 (6) Å, b = 7.069 (2) Å, c = 21.573 (10) Å, β = 101.19 (3)°, V = 2645 (2) Å^3, and Z = 4. The structure was refined to R = 4.2% and R_w = 4.9% for 1821 reflections with $I > 3\sigma(I)$. The structure consists of a Bi_2Fe_2 planar parallelogram situated about an inversion center with an average Bi–Fe distance of 2.786 (3) Å. Each bismuth atom is bonded to one phenyl group. The iron carbonyl groups exhibit cis-pseudooctahedral coordination environments. The reaction of Ph_2BiX (X = Cl, I) with Na[$Mn(CO)_5$] produces octahedral $Ph_2BiMn(CO)_5$ (IV), which crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 10.135 (4) Å, b = 13.484 (4) Å, c = 6.567 (4) Å, α = 99.11 (3)°, β = 92.53 (4)°, γ = 86.46 (2)°, V = 883.9 (6) Å^3, Z = 2, R = 4.4%, and R_w = 5.6% for 2036 observed reflections. The Bi–Mn distance is 2.842 (2) Å.

Introduction

Organobismuth compounds have been studied extensively, yet comparatively little is known about their transition-metal derivatives.[1] Several examples exist, however, in which an alkyl- or arylbismuth is coordinated to a group VIA transition-metal carbonyl. These compounds include $M(CO)_5BiR_3$, where M = Cr, Mo, or W and R = Me,[2] Et,[2,3] cyclohexyl,[2] Ph,[4] or Me_3C.[5] The compound *cis*-$Mo(CO)_4(BiEt_3)_2$ has also been reported.[3] Nickel carbonyl complexes $Ni(CO)_3BiEt_3$[3] and $(Me_3C)_3BiNi(CO)_3$,[5] are formed by treatment of nickel tetracarbonyl with the corresponding trialkylbismuthine. Several alkylbismuth/vanadium carbonyl compounds have also been synthesized and include [Et_4N][$V(CO)_5BiEt_3$], $CpV(CO)_3BiEt_3$, and $CpV(CO)_2(BiEt_3)_2$, where Cp = C_5H_5.[6] Although a $BiPh_3$ complex of iron was reported a number of years ago, this compound is dubious, and $Fe(CO)_4$ complexes of BiR_3 (R = Et, Pr, Bu) have only been recently prepared.[7] The triphenylphosphine-substituted compound $Co(BiPh_2)(CO)_3(PPh_3)$ is isolated from the reaction of $Co_2(CO)_8$ with tetraphenyldibismuthine in the presence of PPh_3.[8] Of these, only $M(CO)_5BiPh_3$ (M = Cr, Mo, W) and $Co(BiPh_2)(CO)_3(PPh_3)$ have been structurally characterized.[4,8]

Chart I



The treatment of $RECl_2$ (E = P, As, Sb; R = alkyl, aryl) with reactive transition-metal carbonyl compounds (ML_n) has been shown to form several basic structures (Chart I). Type A may exhibit planar or pyramidal geometries depending on whether there is delocalized bonding.[1] The reaction of $Na_2[Fe(CO)_4]$ and $(Me_3Si)_2CHSbCl_2$ forms {$Fe_2CO)_8[SbCH(SiMe_3)_2]$}, type A, plus {$Fe(CO)_4[SbCH(SiMe_3)_2]_2$}, type B.[9] Alternatively, the treatment of $Na_2[Fe(CO)_4]$ with $(Me_3Si)_2CHPCl_2$[10] or $(Me_3Si)_2NECl_2$ (E = P, As)[11] produces compounds of type C. Variations of these basic structural types are found when chromium,[12] molybdenum,[13] tungsten,[14] vanadium,[15] cobalt,[16] and manganese[17] carbonyl reactants are used. When $Na_2[Fe(CO)_4]$ is reacted with $RPCl_2$ (R = 2,4,6-$Me_3C_6H_2$), [$Fe_3(CO)_9(\mu$-$CO)(\mu$-$PR)$], which exhibits a tetrahedral core geometry, is formed.[18] Similarly, when $PhAsCl_2$ is treated with $Na_2[Fe(CO)_4]$, the trigonal-bipyramidal compound $Fe_3(CO)_9(\mu_3$-$AsPh)_2$ is generated.[19] The organobismuth complexes $Cp(CO)_2FeBiMe_2$ and $[Cp(CO)_2Fe]_2BiMe$,[20a] EtBi-

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$\{CpMo(CO)_3\}_2$, $PhBi\{ML_n\}_2$ (ML_n = $CpMo(CO)_3$, $Co(CO)_3PPh_3$),[20b] and $Ph_2BiRe(CO)_5$ have been reported.[21]

The dimeric bismuth–iron compound $[MeBiFe(CO)_4]_2$ has recently been synthesized and structurally characterized in our laboratories (eq 1). This complex is not stable in solution and

$$BiCl_3 + [Et_4N]_2[Fe_2(CO)_8] + MeI \rightarrow [MeBiFe(CO)_4]_2 \qquad (1)$$

undergoes decomposition to $Bi_2Fe_3(CO)_9$ upon standing at room temperature for several days.[22] Phenylbismuth compounds are known to be more stable than alkylbismuth compounds, yet the phenyl analogue of $[MeBiFe(CO)_4]_2$ was not produced under the same reaction conditions when PhBr was used as the phenylating agent. In this paper we describe the syntheses of X-ray analyses of $[PPN][Ph_2BiFe(CO)_4]$ (I), *cis*-$(Ph_2Bi)_2Fe(CO)_4$ (II), $[PhBiFe(CO_4]_2$ (III), and $Ph_2BiMn(CO)_5$ (IV).

Experimental Section

All reactions were performed under an inert atmosphere of nitrogen or argon. Solvents were dried and distilled under nitrogen by conventional methods. The compounds Ph_2BiCl,[23] Ph_2BiI,[24] $PhBiBr_2$,[25] $Na_2Fe(CO)_4$,[26] $Na_2Fe(CO)_4\cdot{}^3/_2diox$[27] (diox = dioxane), and [PPN]Cl[28] were synthesized by literature procedures. Ph_2BiCl and $PhBiBr_2$ were recrystallized from hot toluene and hot benzene, respectively. Infrared spectra were taken with a Perkin-Elmer 1600 Series FTIR instrument, and NMR spectra were obtained from a JEOL FX90Q spectrometer. Galbraith Analytical (Knoxville, TN) and Texas Analytical (Stafford, TX) Laboratories provided the elemental analyses.

Synthesis of I. Ph_2BiCl (0.460 g, 1.15 mmol) was added dropwise as a suspension in THF (15 mL) to a stirring solution (THF, 10 mL) of $Na_2Fe(CO)_4$ (0.246 g, 1.15 mmol). The brown solution that resulted was stirred for 0.5 h and filtered, followed by addition of [PPN]Cl (0.66 g). The solution was stirred for a short time and refiltered, leaving a gray solid. The THF was removed, and 40 mL toluene was added to the red oil; yellow crystals formed out of the solution standing at room temperature. Yield: 0.815 g (66%). IR (ν_{CO} in cm^{-1}, CH_2Cl_2): 2029 (vw), 2005 (w), 1982 (2), 1921 (w, sh), 1891 (m, sh), 1873 (s, br). ^1H NMR (ppm, CD_3CN): δ = 7.19 mm, 7.59 mm, 7.90 mm. Anal. Calcd: C, 58.39; H, 3.77. Found: C, 57.78; H, 3.65. I is soluble in THF, CH_2Cl_2, and acetone, slightly soluble in Et_2O and toluene, but insoluble in hexane.

Syntheses of II and III from $NaBiPh_2$ and $Fe(CO)_5$. Method 1. Diphenylbismuth chloride (500 mg, 1.25 mmol) was added to a 200-mL Schlenk flask equipped with a Dewar condensor and a bubbler. The resulting gray to brown residue was washed with hexane, producing a slightly yellow solution, which was discarded. The apparatus was cooled by a dry ice/acetone bath, and approximately 20 mL of NH_3 was condensed into the flask. Upon addition of freshly cut Na (0.06 g, 2.4 mmol) to the stirring reaction mixture, the solution gradually turned from green to red-brown. After the mixture was allowed to stir for several minutes, excess $Fe(CO)_5$ (0.5 mL, 3.72 mmol) was introduced via syringe and the solution slowly changed to dark green. The reaction was stirred for approximately 3 h, during which time the NH_3 and excess $Fe(CO)_5$ slowly boiled away. The resulting gray to brown residue was washed with hexane, producing a slightly yellow solution, which was discarded. Dichloromethane was then added producing an orange-red solution. This solution was filtered, and the solvent was removed under vacuum. The residue was then extracted with hexane several times, yielding a very air-sensitive orange-yellow solution that gave infrared CO stretches characteristic of II. Upon initial concentration of the hexane solution, crystals of Ph_4Bi_2 formed. Upon further cooling of the solution, crystals of II were obtained. IR (ν_{CO} in cm^{-1}, CH_2Cl_2): 2050 (s) 1990 (m), 1973 (2). IR (ν_{CO} in cm^{-1}, hexane): 2081 (w), 2051 (s), 1998 (m), 1992 (sh), 1976 (s). ^1H NMR (CD_2Cl_2); δ = 7.40 dd, 7.84 dd. Anal. Calcd C, 37.61; H, 2.25; Bi, 46.74; Fe, 6.24. Found: C, 37.44; H, 2.05; Bi, 46.90; Fe, 6.17. II is soluble in hexane, toluene, CH_2Cl_2, and most polar solvents. The residue remaining after the hexane extraction dissolved into CH_2Cl_2 and after filtration was concentrated and cooled, yielding black needlelike crystals of III. IR (ν_{CO} in cm^{-1}, CH_2Cl_2): 2040 (s), 1991 (s). ^1H NMR (CD_2Cl_2): δ = 7.37 mm, 7.76 mm. ^1H NMR (benzene-d_6): δ = 7.8 mm, 7.2 mm, 4.4 s (due to CH_2Cl_2). Anal. Calcd: C, 26.46; H, 2.20; Bi, 46.00; Fe, 12.30. Found: C, 26.28; H, 0.96; Bi, 44.54; Fe, 11.29; Cl, <0.15. A FABS mass spectrum was attempted but showed only decomposition products and no parent ion. III is soluble in CH_2Cl_2, tetrahydrofuran, acetone, benzene, and 1,2-dichloroethane, slightly soluble in diethyl ether and MeOH, and insoluble in hexane.

Synthesis of III from $PhBiBr_2$. Method 2. The synthesis of $[PhBiFe(CO)_4]_2$ was attempted by stirring $PhBiBr_2$ (300 mg, 0.672 mmol) and $Na_2Fe(CO)_4\cdot{}^3/_2diox$ (233 mg, 0.673 mmol) in 30 mL of THF. The solution was filtered after 1 h, leaving a black precipitate. The solvent was removed from the filtrate under vacuum, and the residue was then extracted with CH_2Cl_2. Upon layering of the reddish solution with hexane, a few black crystals were obtained in poor yield. An IR spectrum of the CH_2Cl_2 extract gave CO stretching frequencies indicative of III.

Synthesis of III from Ph_2BiCl and $Na_2[Fe(CO)_4]$. Method 3. THF (Ca. 30 mL) was added to $Na_2Fe(CO)_4\cdot{}^3/_2diox$ (0.200 g, 0.578 mmol) and Ph_2BiCl (0.460 g, 1.15 mmol) in a 100-mL Schlenk flask. The solution immediately turned green and then after about 30 s became reddish orange. The reaction solution was filtered after several hours, leaving a gray solid. The solvent was removed from the filtrate under vacuum. After extraction of the residue with CH_2Cl_2, followed by filtration, a reddish solution was obtained, which, upon concentration, yielded dark red to black crystals. Yield: 0.28 g, 50% (based on iron). IR (ν_{CO}, CH_2Cl_2): 2040 (s), 1991 (s) cm^{-1}.

Synthesis of II from Ph_2BiCl and $Na[Ph_2BiFe(CO)_4]$. A solution of $Na[Ph_2BiFe(CO)_4]$, produced as above from Ph_2BiCl (0.230 g, 0.575 mmol) and $Na_2Fe(CO)_4$ (0.123 g, 0.575 mmol), was stirred for 40 min. An IR spectrum taken at this point showed CO stretching frequencies indicative of $[Ph_2BiFe(CO)_4]^-$. A second 1 equiv of Ph_2BiCl (0.123 g, 0.575 mmol) was introduced as a solid to the reaction solution, and the mixture was stirred for 15 min. The product, identified by IR spectroscopy, was $(Ph_2Bi)_2Fe(CO)_4$. Yield: 0.15 g, 29%.

Synthesis of II from Ph_2BiCl and $Na[Fe(CO)_4]$. Approximately 20 mL of THF was added to an ice-cooled flask containing Ph_2BiCl (0.460 g, 1.15 mmol) and $Na_2Fe(CO)_4$ (0.125 g, 0.584 mmol). The reaction mixture changed from a yellow to an orange color and was allowed to stir for 40 min at 0 °C. After filtration the THF was removed in vacuo, leaving a red to brown oil. Extraction of the oil with 30 mL of hexane afforded a reddish solution whose infrared spectrum matched that of II and yielded red crystals upon cooling. Yield: 0.37 g, 72%.

NMR Analysis of the Decomposition Products Formed from Stirring II. II was dissolved in approximately 2 mL of CD_2Cl_2 (degassed). The IR spectrum at this time already indicated the presence of III along with II. The solution was freeze–pump–thawed degassed once and allowed to stir, producing a substantial amount of fine, black precipitate, presumably Bi^0. An IR spectrum taken after 6 days revealed that III was the predominant species in solution. The solvent was transferred, at this point, via vacuum line, to another flask, and a ^1H NMR spectrum was taken. A singlet at ca. 7.2 ppm was identified as benzene.

Synthesis of IV from Ph_2BiI and $Na[Mn(CO)_5]$. $Mn_2(CO)_{10}$ (1.0 g, 2.6 mmol) was reduced in 20 mL of THF with 4 mL of sodium amalgam (from 0.6 g Na/116 g Hg). After the solution became light yellow, it was removed from the amalgam via syringe, filtered through Celite, and added to a slurry of 2.50 g of Ph_2BiI (5.10 mmol) in THF. The resulting brownish solution was stirred overnight. The THF was removed under vacuum, the product was extracted into 50 mL of, hexane and the solution was filtered. Upon cooling, orange crystals formed. Yield: 0.94 g, 33%. Mp: 75–78 °C. IR (ν_{CO}, hexane): 2085 (m), 2023 (w), 1995 (vs) cm^{-1}. The mass spectrum shows the parent ion at *m/e* 558 with consecutive loss of five carbonyl groups. Fragments are also seen for $MnBiPh_2$, $BiPh_2$, BiPh, MnBi, Mn, and Bi. The ^1H NMR spectrum shows complex multiplets between δ = 7.2 and 7.9 pmm in $CDCl_3$ for the Ph groups. IV is soluble in most common organic solvents.

Crystal Structure Determinations of I–IV. A summary of data collection parameters for compounds I–IV is found in Table I. All data were measured with a Rigaku AFC5S four-circle automated diffractometer (Rigaku CONTROL Automatic Data Collection Series, Molecular Structure Corp., The Woodlands, TX) using graphite-monochromated Mo Kα radiation (0.71069 Å). All crystals were mounted on glass fibers with Epoxy cement, and data were collected with $2\theta-\omega$ scans at 4°/min. In each case three standard reflections were monitored for decay and/or reorientation every 150 reflections throughout data collection. Corrections for anomalous dispersion and Lorentz/polarization effects were made for all of the compounds. The programs used in solving the structures were part of the Molecular Structure Corp. data reduction and refinement programs (TEXRAY Structure Analysis Package, versions 2.0 and 5.0). Full-matrix least-squares refinement minimized $\sum w(|F_o| -$

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Table I. Crystallographic Data for I–IV

	[PPN][I]	II	III·CH_2Cl_2	IV
empirical formula	$BiFeC_{52}H_{40}NO_4P_2$	$Bi_2FeC_{28}H_{20}O_4$	$Bi_2Fe_2Cl_2C_{21}H_{12}O_8$	$BiMnC_{17}H_{10}O_5$
fw	1069.67	894.27	958.91	558.18
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	*Cc* (No. 9)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, Å	13.08 (1)	12.009 (3)	17.681 (6)	10.135 (4)
b, Å	15.832 (9)	13.074 (2)	7.069 (2)	13.484 (4)
c, Å	23.18 (1)	17.264 (2)	21.573 (10)	6.567 (4)
α, deg	90	90	90	99.11 (3)
β, deg	99.53 (6)	96.78 (1)	101.19 (3)	92.53 (4)
γ, deg	90	90	90	86.46 (2)
V, Å^3	4733 (6)	2691.5 (8)	2645 (2)	883.9 (6)
Z	4	4	4	2
D_{calcd}, g/cm^3	1.50	2.21	2.49	2.10
μ, cm^{-1} (Mo Kα)	41.17	135.69	145.50	106.19
T(max)/*T*(min)	1.0/0.44	1.0/0.32	1.0/0.22	1.0/0.10
T, °C	23	23	−60	23
residuals, %: *R*; R_w	5.8; 6.0	5.0; 5.8	4.2; 4.9	4.4; 5.6

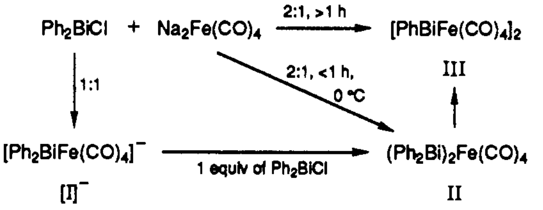
$|F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ (σ^2 = variance).[29]

Large yellow crystals of I were obtained by the procedure described above and were recrystallized from CH_2Cl_2/toluene prior to data collection. A yellow crystal (0.3 × 0.2 × 0.5 mm^3) was used for data collection, with the primitive unit cell determined from 25 random reflections collected between $7.4 \leq 2\theta \leq 12.4°$. The starting cell (monoclinic, *C*-centered) was determined by following Delaunay reduction and was confirmed by measuring Laue symmetry equivalent reflections. Data were collected for $+h,+k,\pm l$, ranging from *h*, 0 to 17, k, 0 to 21, and *l*, −30 to 30 with $2\theta_{max} = 55°$. Final cell parameters were determined from high angle data ($22.4 \leq 2\theta \leq 31.5°$). The acentric space group *Cc* (No. 9) was selected on the basis of the systematic absences and intensity statistics. The structure was solved by using the program MITHRIL[30] to locate the Bi atom and subsequent full matrix least-squares difference maps and Fourier syntheses to find the remaining non-hydrogen atoms; the hydrogens were included in calculated positions. To determine the correct enantiomorph, least-squares refinement was carried to convergence on both enantiomorphs without anomalous dispersion corrections applied. Anomalous dispersion and the Friedel pairs were then included and each enantiomorph rerefined. The resulting weighted *R* factors were compared [0.0807 (*S* = 2.72) and 0.0599 (*S* = 2.02), respectively], and the model with the lower value was chosen as the correct enantiomorph. When refined individually, the phenyl ring carbons located on Bi atom yielded distorted bond metricals; thus, the carbons were refined as rigid groups. The bismuth, iron, oxygen, and carbonyl carbon atoms of the anion and the N and P atoms of the cation were refined anisotropically; the remaining non-hydrogen atoms were refined with isotropic thermal parameters. The data were corrected for absorption (ψ scans) and decay (3.5%, average). The largest peak in the final difference map was 1.60 e/Å^3.

Crystals of II suitable for X-ray diffraction were obtained by cooling the hexane extract of the residue obtained from method 1. Data for II were successfully collected on a red cube-shaped crystal (0.4 × 0.4 × 0.4 mm^3). The primitive unit cell was determined from a least-squares fit of 25 random reflections between $6 \leq 2\theta \leq 12°$, with the final cell constants based on high-angle data ($33.7 \leq 2\theta \leq 43.0°$). Systematic absences and intensity statistics indicated that the space group was $P2_1/n$ (No. 14). The data were corrected for absorption (ψ scans) but not for decay (average decay <2%). The structure was solved by using the program MITHRIL, which located the heavy atoms. The remaining non-hydrogen atoms were found from Fourier syntheses after full-matrix least-squares refinements. The hydrogens on the phenyl groups were included in calculated positions. All nonhydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the final difference map was 1.54 e/Å^3.

Data for compound III·CH_2Cl_2, produced from the reaction of Ph_2BiCl and $Na_2Fe(CO)_4$, were collected as described above. Crystals were obtained from a cooled, concentrated CH_2Cl_2 solution, and a freshly grown dark red needlelike crystal (0.5 × 0.2 × 0.1 mm^3) was used for data collection. The presence of solvent molecules in the crystal lattice necessitated data collection at low temperature (−60 °C). The unit cell (monoclinic, *C*-centered) was determined from a least-squares fit of 25 random reflections ($7 \leq 2\theta < 16°$). Data were collected at 8°/min ($2\theta_{max}$ = 55°) for the quadrant $+h,+k,\pm l$ ranging from *h*, 0 to 23, *k*, 0 to 9, and *l*, −28 to 28. The final average loss in intensity of the standards was 6.3%. Systematic absences and intensity data indicated that the space group was centrosymmetric $C2/c$ (No. 15). The data were corrected for decay and absorption (ψ scans). The structure was solved by using the direct methods program SHELXS86,[31] which located the heavy atoms. Full-matrix least-squares and Fourier syntheses revealed the remaining non-hydrogen atoms. The hydrogens were included in calculated positions but were not refined. Significant peaks in later stages of refinement indicated the possible presence of a disordered solvent molecule. The existence of methylene chloride in the lattice was confirmed by ^1H NMR spectroscopy of the compound in benzene-d_6. All atoms of the metal complex, excluding the hydrogens, were refined anisotropically; the CH_2Cl_2 carbon was refined isotropically. Two residual peaks of 4.3 e/Å^3 remained in the final difference map, which were ghost peaks close to the Bi atom. The next largest peak was 1.2 e/Å^3.

Scheme I



Crystals of IV were obtained by cooling a concentrated hexane solution, and data were treated as above. The unit cell was determined from a least-squares fit of 25 reflections ($3.8 \leq 2\theta \leq 7.1°$). Data were collected for $+h,\pm k,\pm l$ from h, 0 to 13, *k*, −18 to 18, and *l*, −9 to 9, for $2\theta_{max}$ = 55°. The data were corrected for absorption but not for decay. The structure was solved by using the program MITHRIL to locate the Bi and Mn atoms with subsequent difference Fourier maps yielding the positions of the remainig non-hydrogen atoms. The hydrogen atoms on the phenyl rings were included in calculated positions but were not refined. The largest peak in the final difference map was 1.56 e/Å^3.

Results

Syntheses. The reaction of $Fe(CO)_5$ with $NaBiPh_2$, produced from the reduction of Ph_2BiCl with Na in liquid NH_3, yields two main products, II and III, along with a small amount of Ph_4Bi_2. Compound III can be synthesized in good yield from the reaction of Ph_2BiCl and $Na_2Fe(CO)_4$ (Scheme I) and in small amounts by the addition of $Na_2Fe(CO)_4\cdot{}^3/_2$diox to $PhBiBr_2$. Compound II can also be synthesized from Ph_2BiCl and $Na_2Fe(CO)_4$ if the reaction time is shortened with respect to that used to produce III. When a 1:1 ratio of Ph_2BiCl and $Na_2Fe(CO)_4$ is used, the product is I, which, when produced in situ and allowed to react with an additional equivalent of Ph_2BiCl, affords II. Moreover, solutions of II slowly convert to III, suggesting that II is an intermediate in the production of III.

Yellow rectangular prisms of I form oily solutions in THF, acetone, and CH_2Cl_2 but are easily recrystallized upon layering the oil with toluene. The complex is only moderately air-sensitive.

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(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–101 and 149–150.

(30) Gilmore, G. J. *J. App. Crystallogr.* **1984**, *17*, 42.

(31) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189.

Table II. Selected Positional Parameters and B(eq) Values for [PPN][I]

atom	x	y	z	B(eq),[a] Å^2
Bi(1)	0.1287	0.79492 (5)	0.1389	5.44 (4)
Fe(1)	0.2594 (2)	0.8914 (2)	0.0903 (1)	4.4 (1)
O(1)	0.404 (2)	0.757 (1)	0.1389 (8)	10 (1)
O(2)	0.241 (1)	1.030 (1)	0.171 (1)	8 (1)
O(3)	0.101 (2)	0.885 (1)	−0.014 (1)	8 (1)
O(4)	0.404 (2)	0.977 (2)	0.029 (1)	11 (2)
C(1)	0.346 (2)	0.807 (2)	0.120 (1)	6 (1)
C(2)	0.245 (2)	0.975 (2)	0.139 (1)	6 (1)
C(3)	0.162 (2)	0.884 (2)	0.025 (1)	6 (1)
C(4)	0.345 (2)	0.941 (2)	0.054 (1)	7 (2)
C(11)	−0.014 (1)	0.877 (1)	0.136 (1)	9.1 (4)
C(12)	−0.098 (2)	0.833 (1)	0.151 (1)	9.1 (4)
C(13)	−0.191 (2)	0.876 (1)	0.153 (1)	9.1 (4)
C(14)	−0.200 (1)	0.961 (1)	0.140 (1)	9.1 (4)
C(15)	−0.116 (2)	1.005 (1)	0.125 (1)	9.1 (4)
C(16)	−0.023 (1)	0.963 (1)	0.122 (1)	9.1 (4)
C(21)	0.187 (1)	0.816 (1)	0.2376 (5)	5.7 (2)
C(22)	0.285 (1)	0.848 (1)	0.2612 (6)	5.7 (2)
C(23)	0.3152 (9)	0.8523 (9)	0.3218 (7)	5.7 (2)
C(24)	0.248 (1)	0.825 (1)	0.3587 (5)	5.7 (2)
C(25)	0.151 (1)	0.793 (1)	0.3351 (6)	5.7 (2)
C(26)	0.1203 (9)	0.7887 (9)	0.2746 (7)	5.7 (2)

[a] $B(\mathrm{eq}) = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table III. Selected Positional Parameters and B(eq) Values for II

atom	x	y	z	B(eq),[a] Å^2
Bi(1)	0.70150 (5)	0.19921 (4)	0.20085 (3)	2.44 (2)
Bi(2)	0.47629 (4)	0.11649 (4)	0.34328 (3)	1.65 (2)
Fe(1)	0.4828 (2)	0.1149 (1)	0.1803 (1)	1.73 (7)
O(1)	0.488 (1)	0.1162 (9)	0.0119 (6)	4.2 (6)
O(2)	0.6052 (9)	−0.0797 (8)	0.2090 (7)	3.7 (5)
O(3)	0.420 (1)	0.3299 (9)	0.1931 (8)	5.6 (7)
O(4)	0.256 (1)	0.0332 (9)	0.1669 (7)	4.3 (6)
C(1)	0.490 (1)	0.116 (1)	0.0789 (9)	2.7 (7)
C(2)	0.599 (1)	−0.002 (1)	0.2005 (8)	2.0 (6)
C(3)	0.447 (1)	0.245 (1)	0.1885 (9)	3.0 (7)
C(4)	0.346 (1)	0.065 (1)	0.1731 (8)	2.5 (6)
C(1A1)	0.800 (1)	0.076 (1)	0.1505 (8)	2.4 (6)
C(1A2)	0.896 (1)	0.040 (1)	0.1899 (8)	3.2 (7)
C(1A3)	0.966 (1)	−0.028 (1)	0.155 (1)	3.9 (8)
C(1A4)	0.939 (2)	−0.057 (1)	0.078 (1)	5 (1)
C(1A5)	0.845 (2)	−0.024 (2)	0.035 (1)	5 (1)
C(1A6)	0.775 (1)	0.045 (1)	0.070 (1)	3.9 (8)
C(1B1)	0.756 (1)	0.156 (1)	0.3241 (8)	2.6 (8)
C(1B2)	0.781 (1)	0.056 (2)	0.353 (1)	4.0 (8)
C(1B3)	0.806 (2)	0.037 (2)	0.431 (1)	5 (1)
C(1B4)	0.802 (2)	0.118 (2)	0.483 (1)	6 (1)
C(1B5)	0.776 (2)	0.215 (2)	0.459 (1)	5 (1)
C(1B6)	0.753 (1)	0.233 (1)	0.379 (1)	5 (1)
C(2A1)	0.470 (1)	−0.051 (1)	0.3657 (7)	1.5 (5)
C(2A2)	0.539 (1)	−0.090 (1)	0.4269 (8)	2.8 (7)
C(2A3)	0.541 (2)	−0.196 (1)	0.4435 (9)	4.3 (9)
C(2A4)	0.473 (2)	−0.261 (1)	0.400 (1)	4 (1)
C(2A5)	0.402 (2)	−0.225 (1)	0.340 (1)	4.4 (9)
C(2A6)	0.401 (1)	0.123 (1)	0.322 (1)	3.0 (7)
C(2B1)	0.293 (1)	0.151 (1)	0.3500 (8)	2.1 (6)
C(2B2)	0.211 (1)	0.076 (1)	0.355 (1)	3.0 (7)
C(2B3)	0.104 (1)	0.102 (1)	0.371 (1)	3.2 (7)
C(2B4)	0.078 (1)	0.203 (2)	0.382 (1)	4.2 (9)
C(2B5)	0.158 (1)	0.277 (1)	0.377 (1)	4.3 (9)
C(2B6)	0.265 (1)	0.254 (1)	0.3637 (9)	2.7 (7)

[a] $B(\mathrm{eq}) = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table IV. Positional Parameters and B(eq) Values for III·CH_2Cl_2

atom	x	y	z	B(eq),[a] Å^2
Bi(1)	0.27389 (2)	0.49924 (8)	0.51330 (2)	1.85 (2)
Fe(1)	0.1329 (1)	0.3229 (3)	0.4707 (1)	1.94 (7)
O(11)	0.1304 (5)	0.237 (1)	0.6045 (5)	3.6 (5)
O(12)	0.1842 (6)	0.370 (10	0.3496 (5)	3.4 (5)
O(13)	0.0546 (5)	0.692 (2)	0.4616 (6)	4.4 (5)
O(14)	−0.0071 (6)	0.096 (2)	0.4212 (5)	4.0 (5)
C(1)	0.2687 (7)	0.587 (2)	0.6128 (7)	2.4 (5)
C(2)	0.3344 (8)	0.587 (2)	0.6586 (7)	2.9 (6)
C(3)	0.3352 (8)	0.664 (2)	0.7173 (8)	3.6 (7)
C(4)	0.272 (1)	0.751 (2)	0.7314 (8)	4.0 (8)
C(5)	0.2050 (8)	0.752 (2)	0.6849 (8)	3.4 (7)
C(6)	0.2038 (7)	0.667 (2)	0.6270 (7)	2.8 (6)
C(11)	0.1323 (7)	0.272 (2)	0.5524 (8)	2.5 (6)
C(12)	0.1653 (7)	0.348 (2)	0.3971 (7)	2.3 (5)
C(13)	0.0861 (7)	0.550 (2)	0.4650 (7)	2.5 (6)
C(14)	0.0479 (7)	0.182 (2)	0.4403 (7)	2.5 (6)

[a] $B(\mathrm{eq}) = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table V. Selected Positional Parameters and B(eq) Values for IV

atom	x	y	z	B(eq),[a] Å^2
Bi(1)	0.15537 (5)	0.66560 (3)	0.24856 (7)	2.92 (2)
Mn(1)	−0.0344 (2)	0.8158 (1)	0.1473 (3)	2.77 (7)
O(11)	−0.151 (1)	0.7877 (7)	0.541 (1)	4.4 (5)
O(12)	0.118 (1)	0.8086 (8)	−0.230 (1)	4.8 (5)
O(13)	0.140 (1)	0.9654 (8)	0.392 (2)	5.6 (5)
O(14)	−0.202 (1)	0.6572 (8)	−0.075 (2)	5.7 (6)
O(15)	−0.228 (1)	0.9750 (9)	0.048 (2)	6.9 (6)
C(11)	−0.106 (1)	0.7984 (9)	0.390 (2)	3.1 (5)
C(12)	0.062 (1)	0.810 (1)	−0.086 (2)	3.5 (6)
C(13)	0.076 (2)	0.907 (1)	0.299 (2)	4.4 (7)
C(14)	−0.134 (2)	0.715 (1)	0.010 (2)	3.8 (6)
C(15)	−0.154 (1)	0.915 (1)	0.089 (2)	3.8 (6)
C(1A)	0.218 (1)	0.5842 (8)	−0.064 (2)	3.1 (5)
C(1B)	0.128 (1)	0.535 (1)	−0.202 (2)	3.8 (6)
C(1C)	0.168 (2)	0.469 (1)	−0.373 (2)	4.0 (6)
C(1D)	0.298 (2)	0.452 (1)	−0.409 (2)	5.1 (8)
C(1E)	0.388 (2)	0.501 (1)	−0.276 (3)	5.3 (8)
C(1F)	0.349 (2)	0.567 (1)	−0.104 (2)	4.7 (7)
C(2A)	0.333 (2)	0.7574 (9)	0.302 (2)	3.8 (6)
C(2B)	0.385 (2)	0.809 (1)	0.162 (2)	4.8 (7)
C(2C)	0.488 (2)	0.869 (1)	0.210 (3)	5.4 (8)
C(2D)	0.549 (2)	0.874 (1)	0.403 (4)	7 (1)
C(2E)	0.506 (2)	0.821 (2)	0.542 (3)	6 (1)
C(2F)	0.399 (2)	0.763 (1)	0.493 (2)	5.0 (7)

[a] $B(\mathrm{eq}) = 8\pi^2/3(U_{11}aa^{*2} + U_{22}bb^{*2} + U_{33}cc^{*2} + 2U_{12}aba^*b^* \cos\gamma + 2U_{13}aca^*c^* \cos\beta + 2U_{23}bcb^*c^* \cos\alpha)$.

Table VI. Selected Bond Metricals for [PPN][I]

	Distances (Å)		
Bi(1)–Fe(1)	2.676 (4)	Bi(1)–C(11)	2.27 (2)
Bi(1)–C(21)	2.32 (1)	Fe(1)–C(1)	1.81 (3)
Fe(1)–(2)	1.77 (3)	Fe(1)–C(3)	1.81 (3)
Fe(1)–C(4)	1.70 (3)	O(1)–C(1)	1.13 (3)
O(2)–C(2)	1.15 (3)	O(3)–C(3)	1.10 (3)
O(4)–C(4)	1.19 (4)		
	Angles (deg)		
Fe(1)–Bi(1)–C(11)	104.0 (6)	Fe(1)–Bi(1)–C(21)	101.6 (4)
C(11)–Bi(1)–C(21)	94.9 (7)	Bi(1)–Fe(1)–C(1)	79.5 (9)
Bi(1)–Fe(1)–C(2)	90.8 (9)	Bi(1)–Fe(1)–C(3)	84.7 (9)
Bi(1)–Fe(1)–C(4)	172 (1)	C(1)–Fe(1)–C(2)	115 (1)
C(1)–Fe(1)–C(3)	126 (1)	C(1)–Fe(1)–C(4)	97 (1)
C(2)–Fe(1)–C(3)	116 (1)	C(2)–Fe(1)–C(4)	97 (1)
C(3)–Fe(1)–C(4)	92 (1)	Fe–C–Co, range	175 (2)–179 (3)

The ^{1}H NMR spectrum of I is comprised of phenyl proton signals. Compound II crystallizes as red cube-shaped crystals, which are difficult to obtain as the compound tends to oil upon concentration. It is very air-sensitive in solution. On the other hand, III is stable in solution over long periods and crystallizes as dark red to black plate- or needlelike crystals that form with solvent in the lattice when recrystallized from CH_2Cl_2. IV is produced from a 1:1 reaction of Ph_2BiX (X = Cl, I) and Na[Mn(CO)$_5$] in THF solution. The compound is soluble in hexane and most other common organic solvents.

Structure of I. An ORTEP[32] diagram of the anion of I is shown in Figure 1. Selected positional parameters and bond distances

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(32) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN.

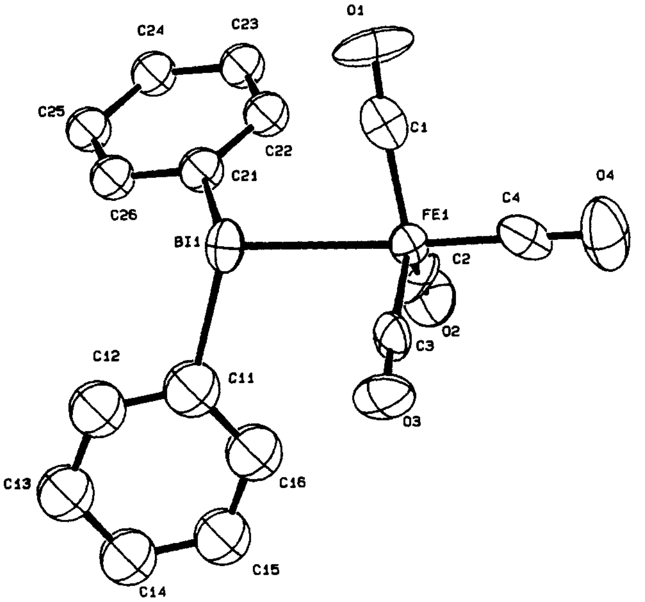


Figure 1. ORTEP view of I, showing atom labeling with 30% probability ellipsoids.

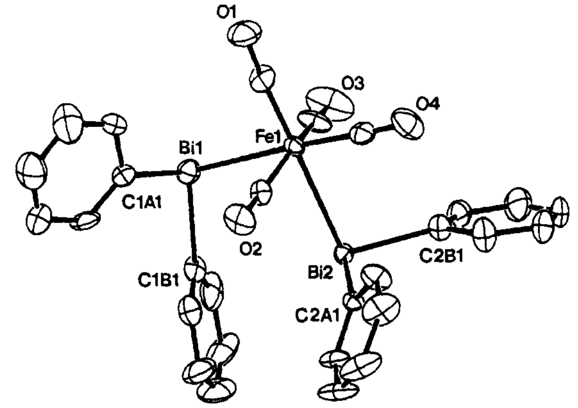


Figure 2. ORTEP view of II, showing atom labeling. Carbonyl carbons are labeled according to the oxygen to which they are attached. Phenyl group carbons are labeled consecutively around each ring.

Table VII. Selected Bond Metricals for II

Distances (Å)			
Bi(1)–C(1B1)	2.22 (2)	Bi(1)–C(1A1)	2.23 (1)
Bi(1)–Fe(1)	2.832 (2)	Bi(2)–C(2A1)	2.23 (1)
Bi(2)–C(2B1)	2.26 (1)	Bi(2)–Fe(1)	2.823 (2)
Fe(1)–C(1)	1.76 (2)	Fe(1)–C(2)	1.80 (1)
Fe(1)–C(3)	1.77 (2)	Fe(1)–C(4)	1.76 (2)
O(1)–C(1)	1.15 (2)	O(2)–C(2)	1.16 (2)
O(3)–C(3)	1.16 (2)	O(4)–C(4)	1.16 (2)
Angles (deg)			
C(1B1)–Bi(1)–Fe(1)	100.6 (3)	C(1A1)–Bi(1)–Fe(1)	101.4 (4)
C(4)–Fe(1)–C(1)	95.0 (7)	C(4)–Fe(1)–C(3)	97.8 (7)
C(4)–Fe(1)–C(2)	98.4 (6)	C(4)–Fe(1)–Bi(2)	86.5 (5)
C(4)–Fe(1)–Bi(1)	176.8 (5)	C(1)–Fe(1)–C(3)	96.4 (7)
C(1)–Fe(1)–C(2)	96.7 (6)	C(1)–Fe(1)–Bi(2)	178.5 (5)
C(1)–Fe(1)–Bi(1)	88.1 (5)	C(3)–Fe(1)–C(2)	158.2 (7)
C(3)–Fe(1)–Bi(2)	83.0 (5)	C(3)–Fe(1)–Bi(1)	80.9 (5)
C(2)–Fe(1)–Bi(2)	83.5 (4)	C(2)–Fe(1)–Bi(1)	82.1 (4)
Bi(2)–Fe(1)–Bi(1)	90.39 (6)	Fe–C–Co, range	176 (1)–179 (1)

Table VIII. Selected Bond Metricals for III·CH_2Cl_2

Distances (Å)			
Bi(1)–Fe(1)	2.779 (2)	Bi(1)–Fe(1A)	2.793 (2)
Bi(1)–C(1)	2.25 (1)	Fe(1)–C(11)	1.80 (2)
Fe(1)–C(12)	1.80 (1)	Fe(1)–C(13)	1.80 (1)
Fe(1)–C(14)	1.82 (1)	O(11)–C(11)	1.16 (2)
O(12)–C(12)	1.15 (2)	O(13)–C(13)	1.15 (2)
O(14)–C(14)	1.15 (2)	C(1)–C(2)	1.37 (2)
C(1)–C(6)	1.37 (2)	C(2)–C(3)	1.37 (2)
C(3)–C(4)	1.37 (2)	C(4)–C(5)	1.39 (2)
C(5)–C(6)	1.38 (2)		
Angles (deg)			
Fe(1)–Bi(1)–Fe(1A)	98.33 (5)	C(11)–Fe(1)–C(13)	98.9 (6)
Fe(1)–Bi(1)–C(1)	103.8 (3)	Bi(1)–Fe(1)–Bi(1A)	81.67 (5)
Bi(1)–Fe(1)–C(12)	80.1 (4)	Bi(1)–Fe(1)–C(14)	172.6 (4)
Bi(1)–Fe(1)–C(11)	86.6 (4)	Bi(1)–Fe(1)–C(13)	89.7 (4)
Bi(1)–Fe(1A)–C(12A)	84.8 (4)	Bi(1)–Fe(1A)–C(14A)	91.4 (4)
Bi(1)–Fe(1A)–C(11A)	80.3 (4)	Bi(1)–Fe(1A)–C(13A)	171.3 (4)
C(12)–Fe(1)–C(14)	96.9 (6)	C(12)–Fe(1)–C(11)	161.4 (5)
C(12)–Fe(1)–C(13)	94.1 (6)	C(14)–Fe(1)–C(11)	94.7 (6)
C(14)–Fe(1)–C(13)	97.3 (6)	Fe–C–Co, range	177 (1)–179 (1)

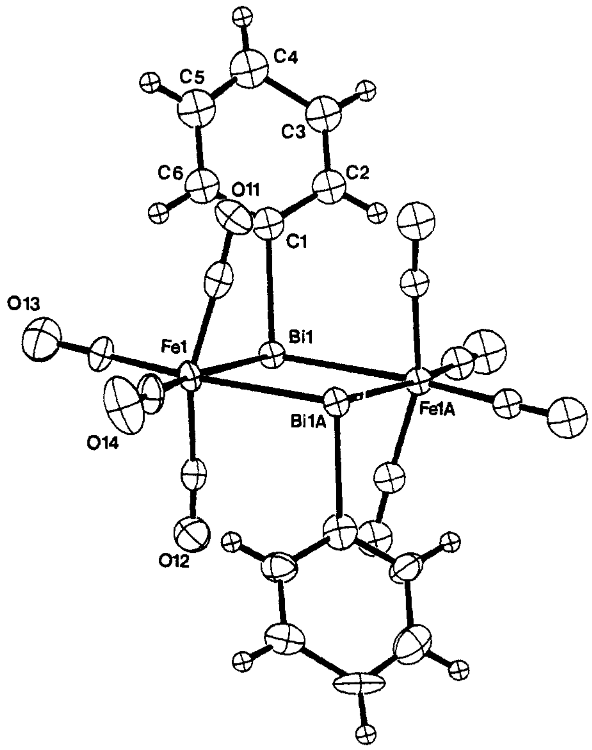


Figure 3. ORTEP diagram of III, showing atom labeling. Carbonyl carbons are labeled according to the oxygen to which they are bonded.

and angles are found in Tables II and VI, respectively. The compound crystallizes with one $[PPN]^+$ per $[Ph_2BiFe(CO)_4]^-$ anion. The iron atom is bonded in a trigonal-bipyramidal fashion to four carbonyl groups and Ph_2Bi, with the Ph_2Bi group occupying an axial position. The bismuth atom exhibits a pyramidal coordination geometry, with a stereochemistry active lone pair of electrons.

Structure of II. The ORTEP diagram with atom-labeling scheme for II is shown in Figure 2. Selected positional parameters and bond distances and angles are found in Tables III and VII, respectively. In the molecule the two Ph_2Bi ligands are coordinated to a pseudooctahedral $Fe(CO)_4$ group in cis positions. The bismuth atoms are pyramidally coordinated with a stereochemically active lone pair of electrons occupying the fourth site.

Structure of III. The molecular structure with atom-labeling scheme for III is shown in Figure 3. This compound exhibits a central planar Bi_2Fe_2 parallelogram situated about an inversion center. The $Fe(CO)_4$ groups have a pseudooctahedral geometry with the μ-PhBi groups occupying cis positions. Each bismuth is three-coordinate and has an apparent lone pair of electrons. The phenyl groups are oriented trans to each other across the Bi_2Fe_2 parallelogram. The carbonyl ligands on the $Fe(CO)_4$ groups are bent toward the bismuth atom, as is seen in many main-group/transition-metal carbonyl compounds. The carbon atom and one chlorine atom of a lattice CH_2Cl_2 molecule lie on a crystallographic 2-fold axis. The second chlorine lies off the axis and is thus required to be disordered statistically between two crystallographically equivalent sites. The thermal parameters of the chlorine atoms suggest that the solvent may be present at less

Table IX. Selected Intramolecular Bond Metricals for IV

Distances (Å)			
Bi(1)-Mn(1)	2.842 (2)	Bi(1)-C(1A)	2.27 (1)
Bi(1)-C(2A)	2.23 (1)	Mn(1)-C(11)	1.83 (1)
Mn(1)-C(12)	1.84 (1)	Mn(1)-C(13)	1.86 (1)
Mn(1)-C(14)	1.84 (1)	Mn(1)-C(15)	1.82 (1)
O(11)-C(11)	1.14 (1)	O(12)-C(12)	1.12 (1)
O(13)-C(13)	1.13 (2)	O(14)-C(14)	1.14 (2)
O(15)-C(15)	1.13 (2)		

Angles (deg)			
C(2A)-Bi(1)-C(1A)	94.5 (5)	C(14)-Mn(1)-Bi(1)	88.7 (4)
C(2A)-Bi(1)-Mn(1)	99.2 (4)	C(12)-Mn(1)-C(13)	92.0 (6)
C(1A)-Bi(1)-Mn(1)	103.3 (3)	C(12)-Mn(1)-Bi(1)	84.2 (4)
C(15)-Mn(1)-C(11)	96.4 (6)	C(13)-Mn(1)-Bi(1)	85.7 (5)
C(15)-Mn(1)-C(14)	93.1 (6)	C(15)-Mn(1)-C(12)	96.3 (6)
C(15)-Mn(1)-C(13)	92.5 (6)	C(15)-Mn(1)-Bi(1)	178.1 (4)
C(11)-Mn(1)-C(14)	89.5 (6)	C(11)-Mn(1)-C(12)	167.2 (6)
C(11)-Mn(1)-C(13)	88.3 (6)	C(11)-Mn(1)-Bi(1)	83.0 (4)
C(14)-Mn(1)-C(12)	89.0 (6)	C(14)-Mn(1)-C(13)	174.2 (6)
Mn-C-O, range	176 (1)-179 (1)		

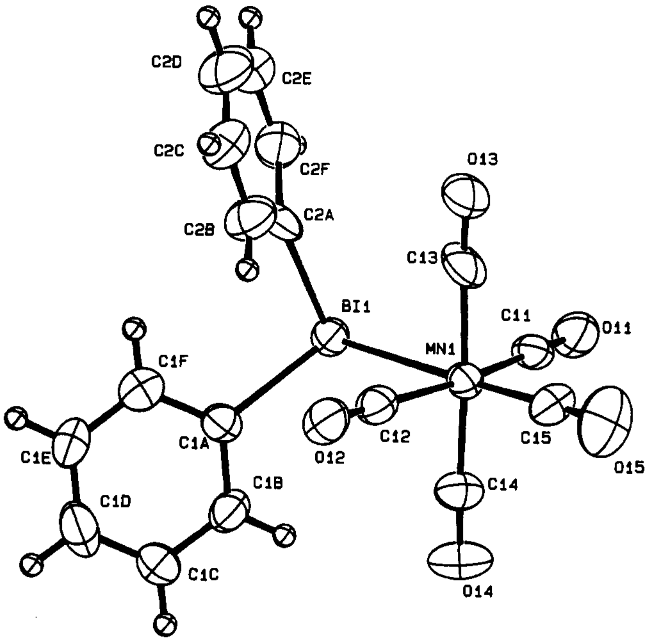


Figure 4. ORTEP diagram of IV, showing atom labeling.

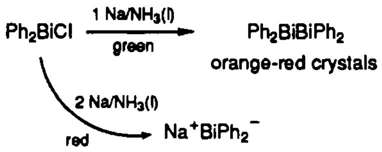
than full occupancy, but owing to the disorder the occupancy was not refined. Selected atomic coordinates and bond distances and angles can be found in Tables IV and VIII, respectively.

Structure of IV. Selected positional parameters and bond distances and angles for IV are given in Tables V and IX, respectively. An ORTEP diagram of IV is shown in Figure 4. The structure consists of a diphenylbismuth moiety bonded to a $Mn(CO)_5$ group. The manganese atom coordination geometry is approximately octahedral. The bismuth atom is three-coordinate, with pyramidally arranged substituents.

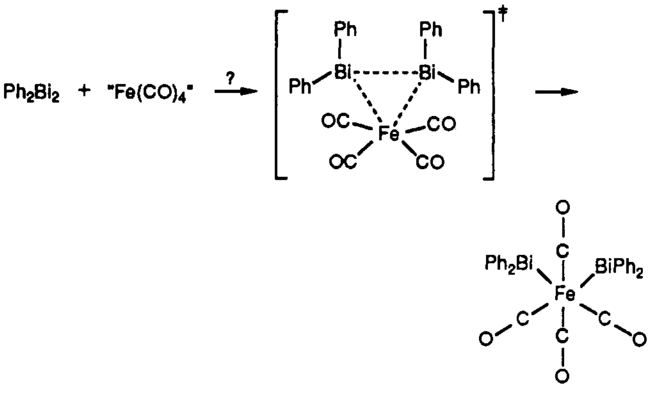
Discussion

The reduction of Ph_2BiX (X = CL, Br, I) with 1 equivalent of sodium in liquid ammonia is known to produce a green solution from which Ph_4Bi_2 is isolated.[33,34] On the other hand, addition of 2 equiv of Na to the reaction is believed to form $Na^+[BiPh_2]^-$ as a red solution (Scheme II).[34] Sodium biphenylbismuthide is unstable at room temperature;[33,35] thus, for our reactions the bismuthide ion was produced in situ and treated with $Fe(CO)_5$.

Scheme II



Scheme III



II

This reaction produces both II and III along with small amounts of Ph_4Bi_2. Following addition of $Fe(CO)_5$ the solution changes to a green color, possibly indicating that a redox reaction is occurring in which the bismuthide undergoes oxidation back to the diphenylbismuth radical or Bi_2Ph_4. Formation of II could occur via an insertion of a reactive $Fe(CO)_4$ fragment into a Bi–Bi bond of Ph_4Bi_2, similar to the generation of $(Ph_2Bi)_2CH_2$ from diazomethane and Ph_4Bi_2,[36] since $Fe(CO)_4$ and CH_2 are isolobal (Scheme III).[37]

Ph_4Bi_2 is also known to react with $Co_2(CO)_8$ to produce $Co(CO)_4(BiPh_2)$.[8] The involvement of Ph_4Bi_2 as a byproduct of these reactions was not immediately recognized, since it evidently crystallizes in at least two crystal modifications (monoclinic, space group $P2_1/n$ (No. 14) with a = 11.531 (2) Å, b = 5.801 (3) Å, c = 16.691 (4) Å, β = 104.87 (2)°; tetragonal, space group $I4_1/a$ (No. 88) with a = 28.07 (1) Å, c = 10.839 (2) Å) other than those reported in the literature.[33] Details of these structures will be reported elsewhere.

Bismuth carbon bonds are relatively weak, and their cleavage is not an unusual occurrence during the course of a reaction.[1] For example, the reaction of $Na[Fe(CO)_2Cp]$ and Me_2BiBr forms $Cp(CO)_2FeBiMe_2$ in 51% yield along with $[Cp(CO)_2Fe]_2BiMe$ in 10% yield.[20] Thus, it is not surprising that II might serve as an intermediate in the generation of III by loss of a phenyl ring and a $BiPh_2$ group. This is not completely certain, however, as organobismuth halides are known to undergo redistribution reactions very readily and these products could result from $[CpFe(CO)_2]^-$ reaction with $MeBiBr_2$ formed in situ. Since Br^- is generated during the course of the reaction, this may be even more likely. The production of III from $Na_2[Fe(CO)_4]$ and Ph_2BiCl occurs only when a 1:2 Fe:Bi mole ratio is used, suggesting that III must pass through the intermediate II. When a 1:1 ratio of Fe to Bi is used, $[Ph_2BiFe(CO)_4]^-$ is obtained, analogous to the compounds formed when chlorodiphenylphosphine and chlorodiphenylarsine are treated with $Na_2[Fe(CO)_4]$ (eq 2).[38] Although these phosphide and arsenide complexes are potentially

$$Na_2[Fe(CO)_4] + Ph_2ECl \rightarrow NaCl + Na^+Fe(CO)_4EPh_2^- \quad (2)$$

$$Na^+Fe(CO)_4EPh_2^- + Ph_2ECl \rightarrow NaCl + Fe(CO)_4E_2Ph_4 \quad (3)$$

$$E = P, As$$

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Table X. Comparison of Bi–Fe Distances

compd	$d_{\mathrm{Bi-Fe}}$(av), Å	ref
$[\mathrm{Et_4N}][\mathrm{BiFe_3(CO)_{10}}]$	2.650 (2)	46
$[\mathrm{Et_4N}]_3[\mathrm{Bi\{Fe(CO)_4\}_4}]$	2.750 (2)	47
$[\mathrm{Et_4N}]_2[\mathrm{Bi_2Fe_4(CO)_{13}}]$	2.650 (40)	48
$[\mathrm{Et_4N}][\mathrm{BiFe_3Cr(CO)_{17}}]$	2.708 (50)	22
$\mathrm{Bi_2Fe_3(CO)_9}$	2.628 (14)	39
$[\mathrm{Et_4N}]_2[\mathrm{Bi_4Fe_4(CO)_{13}}]$	2.725 (33)	49

nucleophilic at both the iron and main-group element, attack occurs at the phosphorus or arsenic atom when an additional 1 equiv of $\mathrm{Ph_2ECl}$ is introduced (eq 3). Our results suggest that in the bismuth analogue, $[\mathrm{I}]^-$, the nucleophilicity resides at the iron atom, not at the bismuth atom, since II is the product generated upon addition of a further 1 equiv of $\mathrm{Ph_2BiCl}$. Attempts in our laboratories to synthesize the previously reported $\mathrm{Fe(CO)_4(BiPh_3)_2}$,[7] whose existence is dubious, led only to the isolation of small amounts of $\mathrm{Bi_2Fe_3(CO)_9}$.[39]

The generation of "inidenes" RE (E = P, As, Sb, Bi; R = alkyl, aryl) from an $\mathrm{REX_2}$ precursors (X = halide) is thought to occur in the presence of ML_n species, producing intermediate mononuclear complexes $\mathrm{L}_n\mathrm{M{=}ER}$.[40] Alternatively, the formation of III could be envisioned as a coupling of such intermediates and may be especially pertinent in the production of III from $\mathrm{PhBiBr_2}$ and $[\mathrm{Fe(CO)_4}]^{2-}$. Additionally, the production of III by stirring a solution of II also affords $\mathrm{C_6H_6}$, as shown by ^{1}H NMR analysis of the decomposition products formed, and could indicate an inidene intermediate (eq 4).

$$\mathrm{(Ph_2Bi)_2Fe(CO)_4} \rightarrow \mathrm{[PhBiFe(CO)_4]_2} + \mathrm{C_6H_6} + \mathrm{Bi^0} \quad (4)$$

In I the equatorial CO groups on the iron are all tilted toward the Bi atom with Bi–Fe–C angles ranging from 79.5 (9) to 90.8 (9)°. The Bi–Fe length of 2.676 (4) Å in I is similar to those found for other Bi–Fe bond distances listed in Table X. The similarity of the angular values about bismuth in I when compared to other organobismuth compounds is shown in Table XI.

The iron atom in II exhibits a cis-pseudooctahedral environment with the axial CO groups bent toward the $\mathrm{Ph_2Bi}$ groups. The Bi–Fe distances in II of 2.832 (2) and 2.823 (2) Å are at the long end of the range of values seen in other Bi–Fe compounds (Table X). This increased length may be due to steric interactions of the phenyl rings with the carbonyl groups, which is supported by the shorter values noted for the less crowded I. The Bi–C distances have an average value of 2.24 (2) Å and compare well to those found in $\mathrm{Ph_4Bi_2}$ (2.28 (2) and 2.26 (2) Å) and in $[\mathrm{MeBiFe(CO)_4}]_2$ (2.28 (1) Å). The angles around the bismuth atoms fall within the range observed for other organobismuth compounds (Table XI).

III is isostructural and isoelectronic to the known $[\mathrm{MeBiFe(CO)_4}]_2$ and consists of a $\mathrm{Bi_2Fe_2}$ ring in which the irons are pseudooctahedral with the bismuth atoms in cis positions. A phenyl group completes the pyramidal geometry about each bismuth atom. The Bi–Fe distances of 2.784 (3) and 2.788 (3) Å are comparable to those found in $[\mathrm{MeBiFe(CO)_4}]_2$ (2.786 (1) Å, average) and in other clusters (see Table X). The Bi–C distances compare well to those given above. The Bi⋯Bi (3.640 Å) and the Fe⋯Fe separations (4.219 Å) are long and considered nonbonding. For comparison, the Bi⋯Bi distance in elemental bismuth is 3.071 (1) Å[41] and the Bi–Bi bond distance in $\mathrm{Ph_4Bi_2}$ is 2.990 (2) Å. The Bi–C distance of 2.31 (3) Å is very similar to the Bi–C lengths in $\mathrm{Ph_4Bi_2}$ of 2.28 (2) and 2.26 (2) Å and in $[\mathrm{MeBiFe(CO)_4}]_2$ of 2.28 (1) Å. The dihedral angle (94.56°) between the least-squares plane containing the axial carbonyls and the irons and the $\mathrm{Bi_2Fe_2}$ ring plane shows little evidence for any steric interaction of the phenyl groups with the carbonyl ligands.

Table XI. Comparison of Bismuth Angles (deg) for Compounds for Representative Organobismuth Compounds

compd	∠C–Bi–C	∠C–Bi–M	∠M–Bi–M	ref
$\mathrm{Ph_2BiMn(CO)_5}$	94.5	99.2, 103.3		*a*
$\mathrm{Bi[Mn(CO)_5]_3}$			106.9 (1), 107.5 (1), 110.3 (1)	42
[PPN][I]	94.9 (6)	101.6, 103.9		*a*
$\mathrm{(Ph_2Bi)_2Fe(CO)_4}$	94.7, 97.6	100.6, 101.4		*a*
$[\mathrm{PhBiFe(CO)_4}]_2$		103.8 (3)	98.33 (5)	*a*
$[\mathrm{MeBiFe(CO)_4}]_2$		100.7, 104.1	98.5	22
$\mathrm{BiMe_3}$	96.7 ± 1.0			43
$\mathrm{BiPh_3}$	92 (1), 94 (1), 96 (1)			44
$\mathrm{Bi(Me_3C_6H_2)_3}$	95.2 (4), 105.5 (5), 107.4 (5)			45
$\mathrm{Ph_2BiCo(CO)_3(PPh_3)}$	95.7 (8)	100.9, 98.5		50

[a] This work.

Synthesis of compound IV was attempted as a potential precursor to BiMn, a known alloy with interesting magnetic properties. It is formed via a straightforward metathetical reaction (eq 5). A similar type reaction occurs when $\mathrm{BiCl_3}$ is treated with

$$\mathrm{Ph_2BiX} + \mathrm{Na[Mn(CO)_5]} \rightarrow \mathrm{Ph_2BiMn(CO)_5} + \mathrm{NaX} \quad (5)$$

$$\mathrm{X = Cl,\ I}$$

3 equiv of $\mathrm{Na[Mn(CO)_5]}$, producing $\mathrm{Bi[Mn(CO)_5]_3}$.[42] The analogous rhenium complex, $\mathrm{Ph_2BiRe(CO)_5}$, has been prepared from $\mathrm{Ph_2BiCl}$ and $\mathrm{Na[Re(CO)_5]}$ but has been characterized solely on the basis of carbon and hydrogen analysis.[21]

Compound IV exhibits an approximate octahedral coordination geometry around the manganese atom, similar to $\mathrm{Bi[Mn(CO)_5]_3}$. The Bi–Mn distance of 2.842 (2) Å in IV is shorter than the Bi–Mn bond lengths in the more sterically crowded $\mathrm{Bi[Mn(CO)_5]_3}$ (2.884 (1)–2.916 (1) Å) but longer than in $\{[\mathrm{CpMn(CO)_2}]_2\mathrm{BiCl}\}_2$ (2.467 (6)–2.471 (5) Å), where multiple-bond character has been attributed to the Mn–Bi bonds.[17] The bond parameters for the $\mathrm{Ph_2Bi}$ group in IV are nearly the same as those found in the isoelectronic I.

The geometries produced from the reactions of alkyl- or phenylbismuth reagents have thus far proven unlike those previously seen in analogous reactions with the lighter elements. In each bismuth/transition-metal compound we note that the bismuth is three-coordinate. The increased size of the bismuth element, as well as the "inertness" of the s-orbital lone pair, most likely play major roles in determining the structure formed.

A comparison of angles around tricoordinate, singly bonded bismuth atoms for several compounds is shown in Table XI. An electron diffraction study of $\mathrm{BiMe_3}$ has shown that the ∠C–Bi–C is 96.7 ± 1.0°.[43] The ∠C–Bi–C angles for $\mathrm{BiPh_3}$ average 94 (2)°,[44] whereas the C–Bi–C angles for the more sterically hindered trimesitylbismuth compound are significantly larger.[45] Thus, it appears that bonding to the bismuth atom is primarily p in character, with little sp^3 hybridization and with deviations from 90° resulting from steric interactions. This idea is clearly seen when the bismuth–manganese compounds IV and $\mathrm{Bi[Mn(CO)_5]_3}$

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are compared. In IV the angles around bismuth range from 94.5 to 103.3°, but in Bi[Mn(CO)$_5$]$_3$, with the bulky Mn(CO)$_5$ groups, they range from 106.9 (1) to 110.3 (1)°.

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Supplementary Material Available: Tables of hydrogen atom positional parameters for I–IV, cation positional parameters for [PPN][I], solvate positional parameters for III·CH$_2$Cl$_2$, and anisotropic thermal parameters and complete bond distances and angles for I–IV (33 pages); tables of observed and calculated structure factors for I–IV (72 pages). Ordering information is given on any current masthead page.

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and Department of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65401

Hydrotris[3-(2′-thienyl)pyrazol-1-yl]borate: A Ligand of Remarkably Low Steric Requirements

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Received September 26, 1990

The new ligand hydrotris[3-(2′-thienyl)pyrazol-1-yl)borate (=L*) was prepared and shown to have the second-lowest steric hindrance among the known poly(pyrazolyl)borates. It forms octahedral L^*_2M complexes with first-row transition-metal ions but fails to yield stable L*MX species, except with Zn(II). It also reacts with HB(3-Pr^i-4-Br-pz)$_3$CoCl to form octahedral HB(3-Pr^i-4-Br-pz)$_3$CoL*, having C_{3v} symmetry. The structure of L^*_2Co was determined by X-ray crystallography. Two different crystal forms of the molecule in different conformations are reported. Form A: monoclinic, $C2/c$ (No. 15), a = 21.577 (2) Å, b = 12.464 (1) Å, c = 18.298 (2) Å, β = 113.21 (1)°, T = −70 °C, V = 4522.6 Å^3, Z = 4. The structure was refined to R, R_w = 0.062, 0.065 by using 3670 diffractometer-collected data. Form B: triclinic, $P\bar{1}$ (No. 2), a = 10.148 (2) Å, b = 11.768 (2) Å, c = 12.241 (3) Å, α = 61.54 (1)°, β = 69.06 (1)°, γ = 67.19 (1)°, T = −70 °C, V = 1157.5 Å^3, Z = 1. The structure was refined to R, R_w = 0.044, 0.043 by using 4380 diffractometer-collected data. The Mössbauer effect hyperfine parameters for L^*_2Fe, obtained at 78 and 295 K, are typical of distorted high-spin octahedral iron(II) complexes, but the asymmetric line widths found in the quadrupole doublet indicate the presence of a reduced relaxation rate for the effective paramagnetic hyperfine field.

Introduction

In contrast to cyclopentadienide ligands, with which they have often been compared, the tris(pyrazolyl)borate ligands offer much greater opportunities for modifying their coordinative features.[1] Whereas only one substituent can be placed on C$_5$H$_5$ ($\rightarrow$C$_5$R$_5$) to yield a derivative ligand *with retention of the original ligand symmetry*, there are 15 ways of placing from one to ten identical substituents on the parent HB(pz)$_3$ ligand and still maintain its original C_{3v} symmetry.[2]

As has been shown earlier, effective space management around the coordinated metal in poly(pyrazolyl)borates can be achieved through regiospecific placement of selected substituents in the pyrazolyl 3-position.[3] In the HB(3-Rpz)$_3$ ligands, where R = phenyl, this hinders but does not prevent formation of L$_2$M complexes, and favors formation of tetrahedral LMX species, which can be solvated or complexed with a donor ligand. With R = Bu^t, the metal is quite inaccessible and remains in a tetrahedral or pseudotetrahedral environment for the first-row transition metals. By pseudotetrahedral we are referring to structures such as HB(3-Bu^{t}pz)$_3$Zn(OAc),[4] HB(3-Bu^{t}pz)$_3$Mg(OAc),[5] HB(3-Bu^{t}pz)$_3$Zn(NO$_3$),[6] and HB(3-Bu^t-5-Me-pz)$_3$Co(O$_2$),[7] where some degree of five-coordination could be present.

In the hierarchy of increasing steric hindrance around the metal in 3-substituted tris(pyrazolyl)borates, the currently known series is H < CH$_3$ < C$_6$H$_5$ < Pr^i < Bu^t. In terms of forming octahedral L$_2$M complexes, ligands with R = H and CH$_3$ do so readily, those with R = C$_6$H$_5$ do so reluctantly, and those with R = Pr^i do not form L$_2$M complexes.[8] The ligands with R = Pr^i will form octahedral complexes only with rearrangement of each L to HB(3-Pr^{i}pz)$_2$(5-Pr^{i}pz); they will also form mixed octahedral LML complexes, provided L is a relatively unhindered tris(pyrazolyl)borate ligand.[9] Finally, ligands with R = Bu^t do not form octahedral complexes at all with first-row transition metals.[10]

Conversely, in terms of formation of LMX (X = halide or pseudohalide) species, ligands with R = Bu^t form these stable complexes with ease; with R = Pr^i, LMX complexes are also readily formed, but they possess reactivity for solvation or for displacement of X with anionic nucleophiles; ligands with R = phenyl form LMX species, which are even more reactive toward solvation or substitution of X. When R = methyl, and even more so when R = H, the LMX species become progressively less stable and undergo transformation to the octahedral L$_2$M complexes.

To investigate the effect of reducing the ring size of the 3-substituent (as compared with a phenyl group), we prepared the HB[3-(2′-thienyl)pyrazol-1-yl]$_3$ ligand shown in I and studied its coordinative behavior to see where it fits in the series of tris(pyrazolyl)borates with different 3-substituents.

A priori, tris(pyrazolyl)borates with the 3-(2′-thienyl) substituent were expected to fit between those with 3-phenyl and those

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(2) Considering that the 3-, 4-, and 5-positions of the pyrazolyl group, as well as the boron atom, can be substituted, we have the possibilities of four mono-, six bis-, four tris-, and one tetrakis-substituted HB(pz)$_3$ ligands, all maintaining the original ligand symmetry. The number of possibilities is greatly increased, if substituents are nonidentical.

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