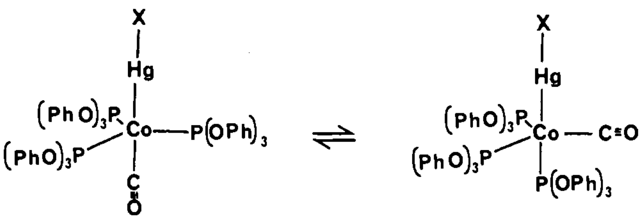
Scheme I



The method involves the direct reaction of the appropriate mercury halide salt with hydridotetrakis(triphenyl phosphite)cobalt(I) in acetone according to reaction 1.

$$HgX_2 + HCoL_3L' \rightarrow XHgCoL_3L' + HX \qquad (1)$$

Although the reaction appears to be the same as that used by MacDiarmid et al.[9] to prepare $Hg[Co(CO)_2(PF_3)_2]_2$, our reactions of $HCo[P(OC_6H_5)_3]_3L$ with mercuric halides provided no evidence for formation of the symmetrical mercurials, $Hg\{Co[P(OC_6H_5)_3]_3L\}_2$, even when large excess of $HCo[P(OC_6H_5)_3]_3L$ were used. Furthermore, it was reported that $HCo(CO)_2(PF_3)_2$ did not react with HgI_2 and no mention was made of reaction with $HgBr_2$, while we find that both react quickly and cleanly with $HCo[P(OC_6H_5)_3L]_2L$ according to reaction 1.

The yield of $XHgCo[P(OC_6H_5)_3]_4$ was found to be independent of whether or not anaerobic techniques were used. The respective monocarbonyl-substituted $XHgCo[P(OC_6H_5)_3]_3CO$ complexes were prepared in an analogous manner. The dicarbonyl substituted $XHgCo[P(OC_6H_5)_3]_2(CO)_2$ complexes were, however, prepared with standard airless ware techniques since the starting hydride $HCo[P(OC_6H_5)_3]_2(CO)_2$ was extremely air sensitive.[11] All of the resulting mercury salts are yellow to orange, air- and moisture-stable, crystalline solids.

Thermal decomposition occurred during melting (see Table I) for all the reported complexes. The noncarbonyl-containing complexes decomposed slowly even at room temperature; however, all complexes appeared to be stable indefinitely when stored in a freezer.

All of the complexes are highly soluble in benzene, dichloromethane, acetone, and tetrahydrofuran but only sparingly soluble in alcohols and nonhalogenated saturated hydrocarbon solvents. On standing for several hours, solutions of the complexes in chloroform were found to decompose to unidentified products.

The solution infrared of analytically pure samples of the monocarbonyl complexes (e.g., $XHgCo[P(OC_6H_5)_3]_3CO$) all exhibited two carbonyl absorptions (see Table I) of approximately equal intensity. The lower frequency absorption was found to be much broader than the higher frequency absorption. Several possible explanations exist for the two carbonyl stretching frequencies with only one carbonyl group in the molecule. The possibility of the presence of a dimer with halogen bridges between mercury atoms or a molecular dissociation into ionic species was shown to be incompatible with molecular weight determinations in benzene.[12] The results are, in fact, consistent with the presence of undissociated monomers in solution.

A dynamic equilibrium between two isomeric structures with the carbonyl either axial or equatorial to the mercury (Scheme I) seems most consistent with the existing data.[13] It would be expected that two different carbonyl stretching frequencies would result, one for each isomer since the force constants for the carbonyl bonds in $(C_6H_5)_3PFe(CO)_4$ and $(C_6H_5)_3MCo(CO)_4$ (where M = Sn or Pb) have been shown to be different for the axial and equatorial carbonyls. Indeed the work of Darensbourg and Darensbourg[14] has clearly shown that the axial carbonyl force constant is consistently larger than the equatorial for $LM(CO)_4$ type molecules. Therefore, one might speculate that the higher frequency absorption ($\sim$2004 cm^{-1}), in our solution spectra, corresponds to the axial isomer while the lower frequency absorption ($\sim$1967 cm^{-1}) is the equatorial isomer.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Thanks are due to David DeMarco and Dr. R. A. Walton for their assistance.

Registry No. $ClHgCo[P(OC_6H_5)_3]_4$, 80907-37-5; $BrHgCo[P(OC_6H_5)_3]_4$, 80907-38-6; $IHgCo[P(OC_6H_5)_3]_4$, 80907-39-7; $ClHgCo[P(OC_6H_5)_3]_3(CO)$, 80907-40-0; $BrHgCo[P(OC_6H_5)_3]_3(CO)$, 80907-41-1; $IHgCo[P(OC_6H_5)_3]_3(CO)$, 80907-42-2; $ClHgCo[P(OC_6H_5)_3]_2(CO)_2$, 80907-43-3; $BrHgCo[P(OC_6H_5)_3]_2(CO)_2$, 80907-44-4; $BrHgCo[P(OC_6H_5)_3]_3P(OCH_3)_3$, 80907-45-5; $HCo[P(OC_6H_5)_3]_4$, 41089-90-1; $HCo[P(OC_6H_5)_3]_3CO$, 29189-83-1; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; $HCo[P(OC_6H_5)_3]_2(CO)_2$, 57574-48-8; $HCo[P(OC_6H_5)_3]_3P(OCH_3)_3$, 80907-46-6.

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(12) Molecular weights determined in benzene: calcd for $ClHgCo[P(OC_6H_5)_3]_3CO$ 1253, found 1194; calcd for $BrHgCo[P(OC_6H_5)_3]_3CO$ 1298, found 1260.

(13) The ^{13}C NMR spectrum of $ClHgCo[P(OC_6H_5)_3]_3CO$ in acetone-d_6 was determined in the hope of confirming the presence of two isomers. However, no resonance signal for the carbonyl carbon was observed possibly due to the broadening effect of the nuclear quadrupole of cobalt.

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Crystal and Molecular Structure of Tris[*P*,*P*,*P'*,*P'*-tetraphenylamidobis(phosphine sulfido)-*S*,*S'*]bismuth(III)

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A number of structural studies have been reported for AX_6E[1] complexes of Pb(II),[2,3] As(III),[4,5] Sb(III),[6-8] Te(IV),[9] Se(IV),[10] and Bi(III).[8,11,12] In some instances, the molecular geometry conforms to VSEPR[13] expectations, whereas in other cases, the geometry is octahedral about the central atom A with no evidence for the nonbonded pair of electrons (E). The lone pair of electrons appears to be stereoactive in structures where X is a hard donor in the HSAB definition[14] or a donor atom associated with a "narrow bite" bidentate ligand such as dialkyldithiocarbamates or alkyl xanthates. On the other hand, the lone pair is stereoinactive in complexes where X is a soft donor as first noted by Wynne.[15]

We have been probing this relationship further by preparing AX_6E complexes in which X is either a hard or soft donor of a bidentate ligand which forms six-membered rings with the central atom. Little structural work has been done with these ligands in hypervalent main-group complexes as the examples cited earlier contain monodentate ligands or bidentate ligands which form four- (narrow bite) or five-membered rings with the central atom.

In this study we present the crystal and molecular geometry of $Bi(SPPh_2NPh_2PS)_3$ which is the first structural example

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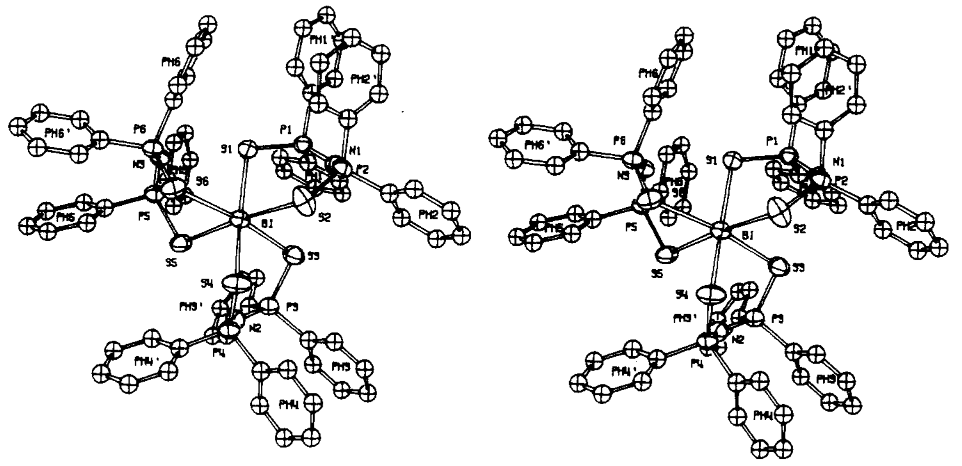

Figure 1. Stereoview of $Bi(SPPh_2NPh_2PS)_3$. Atoms are plotted at 50% thermal probabilities.

Table I. Crystal Data[a]

formula: $C_{72}H_{60}BiN_3P_6S_6 \cdot C_3H_6O$
$a = 17.200\ (5)$ Å[a]
$b = 11.451\ (2)$ Å
$c = 37.320\ (8)$ Å
$\beta = 95.17\ (2)^\circ$
crystal faces: $\{100\}$,[b] $\{\bar{1}00\}$,[b] $\{011\}$[b] and $\{00\bar{1}\}$, $\{010\}$, $\{0\bar{1}0\}$

fw: 1612
radiation: Cu Kα
space group: $P2_1/c$, $Z = 4$
$\rho_{calcd} = 1.455$ g cm^{-3}
$\rho_{obsd} = 1.46\ (1)$ g cm^{-3}
$\mu = 82.67$ cm^{-1}, $\lambda = 1.54509$ Å
$T = 295$ K
$V = 7302$ Å^3

[a] The figures in parentheses are the standard deviation of the least significant digit here and throughout this paper. [b] Most prominent.

of a main-group element coordinated to this particular ligand. Furthermore, this is the first structural example of a tris complex of any metal with this ligand, although a few examples of bis complexes with transition metals have been reported.[16-18]

Table II. Positional Parameters of Nongroup Atoms

	10^4x	10^4y	10^4z
Bi	−2724 (1)	1872 (1)	1342 (1)
P(1)	8444 (2)	427 (2)	627 (1)
P(2)	9153 (2)	2651 (2)	862 (1)
P(3)	8128 (2)	336 (2)	2162 (1)
P(4)	7293 (2)	2473 (2)	2348 (1)
P(5)	5511 (2)	−26 (2)	124 (1)
P(6)	5377 (2)	2162 (2)	715 (1)
S(1)	7311 (2)	734 (2)	687 (1)
S(2)	8422 (2)	3498 (2)	1166 (1)
S(3)	8502 (2)	648 (2)	1607 (1)
S(4)	7299 (2)	3524 (2)	1916 (1)
S(5)	6181	355 (2)	1584 (6)
S(6)	5875 (2)	3274 (2)	1078 (1)
N(1)	9091 (4)	1267 (6)	821 (2)
N(2)	7439 (4)	1120 (6)	2285 (2)
N(3)	5537 (4)	797 (6)	780 (2)
SC1	5318 (13)	862 (19)	314 (6)
SC2	6001 (12)	249 (16)	330 (5)
SC3	5940 (11)	918 (17)	3499 (4)
SO1	6617 (13)	−538 (17)	3282 (5)

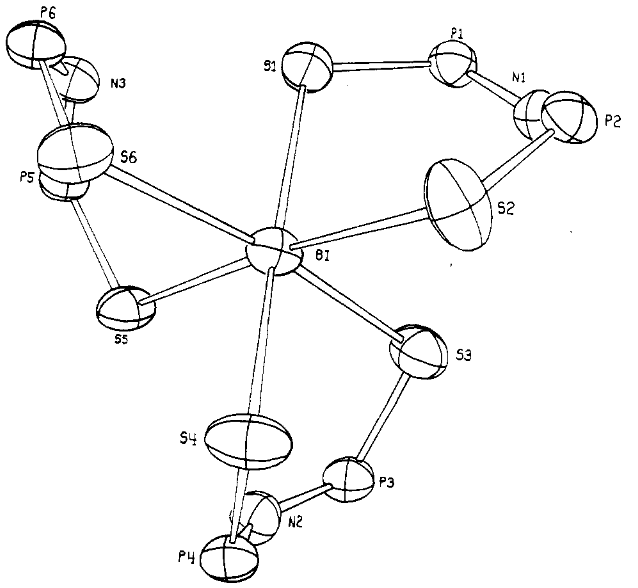

Figure 2. A 50% probability plot showing geometry about Bi with phenyl rings omitted.

Experimental Section

The synthesis and characterization of $Bi(SPPh_2NPh_2PS)_3$ have been previously reported.[19] X-ray quality crystals were grown by evaporation from acetone–ethanol. Crystallographic data are summarized in Table I. The instrumentation used, methods for data reduction, computer program used, and scattering factor sources are described in a previous publication.[20] No decomposition was noted during data collection.

A Patterson function revealed the positions of the Bi, P, and S atoms. Successive series of least-squares refinement and difference maps yielded the positions of the nonhydrogen atoms. Table II gives the final atomic coordinates, and Table S2 (supplementary material) lists

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(1) Abbreviations: A = central atom, X = ligand, E = nonbonded pair of electrons.
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Table III. Selected Bond Distances (Å) and Angles (Deg) for $Bi(SPPh_2NPh_2PS)_3$ with Estimated Standard Deviations

Bi–S(1)	2.770 (3)	Bi–S(2)	2.832 (3)
Bi–S(3)	2.728 (3)	Bi–S(4)	2.851 (3)
Bi–S(5)	2.772 (3)	Bi–S(6)	2.986 (3)
P(1)–S(1)	2.014 (3)	P(4)–S(4)	2.009 (4)
P(2)–S(2)	2.014 (4)	P(5)–S(5)	2.025 (3)
P(3)–S(3)	2.025 (3)	P(6)–S(6)	1.994 (4)
P(1)–N(1)	1.594 (7)	P(4)–N(2)	1.591 (8)
P(2)–N(1)	1.595 (8)	P(5)–N(3)	1.594 (7)
P(3)–N(2)	1.586 (7)	P(6)–N(3)	1.602 (7)
P(1)–C(11)	1.819 (5)	P(2)–C(12′)	1.815 (5)
P(1)–C(11′)	1.827 (5)	P(3)–C(13)	1.827 (5)
P(2)–C(12)	1.805 (5)	P(3)–C(13′)	1.820 (5)
P(4)–C(14)	1.817 (5)	P(5)–C(15′)	1.819 (5)
P(4)–C(14′)	1.801 (5)	P(6)–C(16)	1.806 (5)
P(5)–C(15)	1.821 (5)	P(6)–C(16′)	1.833 (5)
S(1)···S(2)	4.03 (1)	S(2)···S(6)	4.37 (1)
S(1)···S(3)	4.03 (1)	S(3)···S(4)	4.03 (1)
S(1)···S(5)	4.04 (1)	S(3)···S(5)	3.99 (1)
S(1)···S(6)	4.16 (1)	S(4)···S(5)	4.24 (1)
S(2)···S(3)	3.76 (1)	S(4)···S(6)	3.80 (1)
S(2)···S(4)	3.54 (1)	S(5)···S(6)	3.85 (1)
S(1)–Bi–S(2)	92.0 (1)	S(2)–Bi–S(6)	97.4 (1)
S(1)–Bi–S(3)	94.3 (1)	S(3)–Bi–S(4)	92.7 (1)
S(1)–Bi–S(4)	166.3 (1)	S(3)–Bi–S(5)	93.0 (1)
S(1)–Bi–S(5)	93.5 (1)	S(3)–Bi–S(6)	172.6 (1)
S(1)–Bi–S(6)	92.5 (1)	S(4)–Bi–S(5)	97.8 (1)
S(2)–Bi–S(3)	85.1 (1)	S(4)–Bi–S(6)	81.1 (1)
S(2)–Bi–S(4)	77.0 (1)	S(5)–Bi–S(6)	83.8 (1)
S(2)–Bi–S(5)	174.4 (1)		
Bi–S(1)–P(1)	106.2 (2)	Bi–S(4)–P(4)	101.6 (2)
Bi–S(2)–P(2)	107.2 (2)	Bi–S(5)–P(5)	102.2 (1)
Bi–S(3)–P(3)	101.5 (2)	Bi–S(6)–P(6)	99.4 (2)
S(1)–P(1)–N(1)	119.2 (3)	S(4)–P(4)–N(2)	117.0 (3)
S(2)–P(2)–N(1)	119.6 (3)	S(5)–P(5)–N(3)	119.8 (3)
S(3)–P(3)–N(2)	117.8 (3)	S(6)–P(6)–N(3)	117.6 (3)
P(1)–N(1)–P(2)	132.9 (5)	P(5)–N(3)–P(6)	133.0 (5)
P(3)–N(2)–P(2)	136.5 (5)		
S(1)–P(1)–C(11′)	104.5 (2)	S(4)–P(4)–C(14)	108.5 (2)
S(1)–P(1)–C(11)	108.4 (2)	S(4)–P(4)–C(14′)	108.3 (2)
S(2)–P(2)–C(12)	105.5 (2)	S(5)–P(5)–C(15)	103.6 (2)
S(2)–P(2)–C(12′)	107.9 (2)	S(5)–P(5)–C(15′)	108.3 (2)
S(3)–P(3)–C(13)	104.0 (2)	S(6)–P(6)–C(16)	109.9 (2)
S(3)–P(3)–C(13′)	110.3 (2)	S(6)–P(6)–C(16)	109.8 (2)
N(1)–P(1)–C(11)	106.9 (2)	N(2)–P(4)–C(14′)	106.4 (2)
N(1)–P(1)–C(11′)	111.4 (2)	N(2)–P(5)–C(14)	110.9 (2)
N(1)–P(2)–C(12)	105.3 (2)	N(3)–P(5)–C(15′)	105.8 (2)
N(1)–P(2)–C(12′)	111.0 (2)	N(3)–P(5)–C(15)	110.2 (2)
N(2)–P(3)–C(13′)	104.9 (2)	N(3)–P(6)–C(16)	106.4 (2)
N(2)–P(3)–C(13)	112.8 (2)	N(3)–P(6)–C(16′)	109.4 (2)
C(11)–P(1)–C(11′)	105.6 (2)	C(14)–P(4)–C(14′)	105.2 (2)
C(12)–P(2)–C(12′)	106.8 (2)	C(15)–P(5)–C(15′)	108.7 (2)
C(13)–P(3)–C(13′)	106.6 (2)	C(16)–P(6)–C(16′)	102.5 (2)

final thermal parameters for the structure determination. The parameters are the result of full-matrix least-squares refinement with 10 070 reflections with $I \geq 2\sigma(I)$. The data were corrected for absorption and Lorentz and polarization effects. A linear absorption coefficient of 82.67 cm^{-1} was calculated with transmission coefficients ranging from 0.36 to 0.65. Refinement was based on F with the function minimized being $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. Final consistency indices R_1 and R_2 were 0.055 and 0.085, respectively, where $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Phenyl rings were refined as rigid groups. Supplementary material includes a structure factor tabulation (Table S1), anisotropic thermal parameters (Table S2), group parameters for rigid phenyl rings (Table S3), and generated positions and isotropic thermal parameters of group atoms (Table S4).

Results and Discussion

Table IV.[11] Selected Bi–S and S···S Intermolecular Distances (Å) for $Bi(dtp)_3$

	Set a		
Bi–S(1)	2.714 (6)	Bi–S(5)	2.609 (6)
Bi–S(3)	2.702 (6)		
S(1)···S(3)	3.751 (7)	S(1)···S(5)	3.923 (9)
S(3)···S(5)	3.935 (9)		
	Set b		
Bi–S(2)	2.886 (6)	Bi–S(6)	2.858 (6)
Bi–S(4)	2.878 (6)		
S(2)···S(4)	4.424 (9)	S(2)···S(6)	4.603 (8)
S(4)···S(6)	4.192 (9)		

Atomic coordinates are listed in Table II, and selected bond distances and angles are found in Table III. Figure 1 is a stereoscopic drawing of the complexes while Figure 2 shows the coordination sphere with phenyl rings omitted.

The coordination geometry of $Bi(SPPh_2NPPh_2S)_3$ is best described as a distorted octahedron. The distortion is complex and does not mimic the trigonal C_{3v} distorition noted by Lawton for $Bi(dtp)_3$[11] (dtp = *S,S′*-diisopropylphosphorodithioate) although there are some notable similarities. Table IV lists nonbonded S...S and Bi–S bond distances for $Bi(dtp)_3$. Both complexes have two distinct sets of Bi-S bond distances with one set longer than the other. In $Bi(SPPh_2NPh_2PS)_3$, the shorter bonds corresponding to set a in Table IV are Bi–S(1), Bi–S(3), and Bi–S(5) with an average value and root mean square (rms) deviation of 2.76 (3) Å. The longer set corresponding to set b in Table IV consists of Bi–S(2), Bi–S(4), and Bi–S(6) with an average value and rms deviation of 2.89 (8) Å.

The major evidence cited by Lawton[11] for a stereoactive lone pair in $Bi(dtp)_3$ is in part the elongation of the Bi–S bonds of set b (Table IV). He attributes the elongation to lone pair–bonded pair repulsion with the bonds oriented in the same direction as the lone pair. The shorter bonds (set a) are those oriented in the opposite direction of the lone pair. This is supported by the opening of the corresponding S–Bi–S bond angles which straddle the lone pair. For the "long set" the average S–Bi–S bond angle in $Bi(dtp)_3$ is 100.6°. Consequently S···S nonbonded distances on the trigonal face made up by S(2), S(4), and S(6) are also much longer than those making up the other faces (Table IV).

While there are two distinct sets of Bi–S bond distances in $Bi(SPPh_2NPPh_2S)_3$, the S···S nonbonded distances do not strongly suggest a lone pair. As in $Bi(dtp)_3$, the face corresponding to the elongated S bond distances is made up of S(2), S(4), and S(6), but only one of these distances, S(2)···S(6), is opened up (4.37 Å) with a corresponding S(2)–Bi–S(6) angle of 97.4°. The other two distances are actually two of the shortest edges found in the distorted octahedron (3.80 and 3.54 Å). In fact, S(2)···S(4) is significantly less than the sum of the van der Waals radius (3.60 Å).[21] If the lone pair is displaced toward the S(2)···S(6) edge, this does not explain the other long S···S nonbonded distances of 4.24 [S(4)···S(5)] and 4.16 Å [S(1)···S(6)] which are not exclusively associated with the longer Bi–S bonds.

The further effect of ligand steric bulk and its influence on molecular geometry must also be considered. For the structure of $Mn(SPPh_2NPPh_2S)_2$[16] in which there is no evidence of steric crowding, the six-membered ring formed by the ligand with the metal is in a twisted-boat conformation with a sulfur atom and a phosphorus atom at the apices. This conformation give the energetically favored 1,3 axial–equatorial arrangement of the phenyl rings situated on the same ligand but on different phosphorus atoms. As Figures 1 and 2 clearly show, the chelate ring conformation for $Bi(SPPh_2NPh_2PS)_3$ is a twisted boat with the metal and nitrogen at the apices. This conformation is similar to that observed for Fe-

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[21] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

$(SPMe_2MNe_2PS)_2$[17] and leads to steric crowding through phenyl 1,3 axial–axial interactions. The crowding in $Fe(SPMe_2NMe_2PS)_2$ is reflected in the average N–P–C(ax)[22] angle and rms deviation of 111.0 (1.2)°, which is significantly larger than the average value of 106.0 (8)° for N–P–C(eq)[22] in $Bi(SPPh_2NPh_2PS)_3$ presumably due to van der Waals repulsion between the phenyl rings. Also indicative of steric crowding are the relatively close C···C nonbonded distances between phenyl carbons or different phosphorus atoms. Some examples are 3.35 [C(14)···C(23)], 3.45 [C(21)···C(56)], 3.49 [C(21)···C(12)], and 3.56 Å [C(23)···C(21)], all of which are within range of the sum of the van der Waals radii normally taken for a phenyl ring (3.48 Å).[23] The degree of interaction for the hydrogen atoms cannot be assessed since they were not located in this study. Due to the bulky nature of this ligand it is difficult to envision any of seven-coordinated structure such as a pseudopentagonal bipyramid (C_{5v}) as seen for $Sb(ox)_3$[3,6] or a trigonally distorted octahedron (C_{3v}) like that observed for $Bi(dtp)_3$.[11] Both the C_{5v} and C_{3v} structures would force ligands closer together than that expected for O_h site symmetry. In fact, the enigmatic distortion pattern observed for $Bi(SPPh_2NPh_2PS)_3$ may be a result of two opposing effects. The longer set of Bi–S bonds may indeed be due to electrostatic repulsions between bonded pairs and the lone pair while the bulky ligands are forcing near octahedral symmetry to minimize ligand–ligand repulsions, thus partially overriding the influence of the lone pair. Such a possibility has already been pointed out by Gillespie.[24] At present, we may conclude that the steric crowding is severe in this complex, but its affect on the stereochemistry is uncertain. Further studies using the methyl derivatives of these ligands are being pursued.

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Registry No. $Bi(SPPh_2NPh_2PS)_3 \cdot C_3H_6O$, 80822-48-6.

Supplementary Material Available: Listings of structure factor amplitudes (Table S1), final positional and thermal parameters (Table S2), group parameters for the rigid phenyl rings (Table S3), and generated positions and isotropic thermal parameters (Table S4) (79 pages). Ordering information is given on any current masthead page.

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[22] Axial and equatorial phenyl carbons are abbreviated as C(ax) and C(eq), respectively. These refer specifically to the carbon atom bonded directly to phosphorus. The axial carbons are C(11′), C(12′), C(13), C(14), C(15), and C(16′). The equatorial carbons are C(11), C(12), C(13′), C(14′), and C(15′), and C(16).

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Reactions of Coordinated Molecules. 32. Rhena β-Keto Iminato Complexes of Boron

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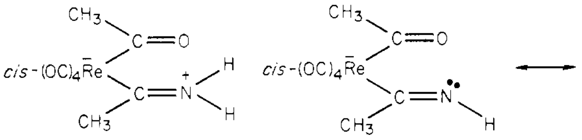
We reported recently that rhena- and ferra-β-diketones condense with the boron trihalides or BCl_2Ph to afford neutral (metalla-β-diketonato)B(X)(Y) complexes where X is a halogen and Y is either halogen or phenyl.[1,2] The X-ray structure of a (ferra-β-diketonato)BF_2 complex confirms the expected bidentate, chelating coordination of the ferra-β-diketonato ligand to the boron atom.[3]

Condensation of rhena-β-diketones with NH_3 or primary amines also affords the well-characterized rhena β-keto imines such as the rhenaacetylacetone imine complex **1**.[4-6] Deprotonation of the iminium ligand of this zwitterionic molecule might generate a rhenaacetylacetone iminato anion, **2**, which could act as a bidentate, chelating ligand analogous to organic Schiff bases. We now report the facile generation of anion **2** and its complexation to several boron halide moieties. The α-enolate anions of these (rhena β-keto iminato)B(X)(Y) complexes, or their N-alkyl derivatives, may also undergo transannular C–C bond formation between the adjacent acylic and iminium sp^2-hybridized carbon atoms, as shown recently for a (ferra-β-diketonato)BF_2 complex.[7]



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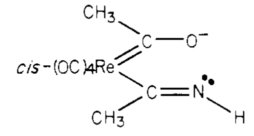

2

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen. Methylene chloride was distilled from P_2O_5 prior to use. All boron halide compounds were used as purchased without further purification. Complex **1** was prepared by a literature procedure.[8]

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are recorded in cm^{-1}. Proton NMR spectra were recorded on a JEOL MH-100 NMR spectrometer as $CDCl_3$ solutions using Me_4Si as an internal reference. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Preparation of $\{cis\text{-}(OC)_4Re[CH_3C(O)][CH_3CN(H)]\}^-$ (2) and the Boron Complexes $[cis\text{-}(OC)_4Re(CH_3CO)(CH_3CNH)]B(X)(Y)$ (3–6). To a solution of 0.30 g of **1** in 20 mL of methylene chloride was added 1 molar equiv of NaH. Hydrogen gas was evolved instantaneously, affording a colorless solution of anion **2**. The reaction solution was cooled to −78 °C, and an excess of 2 molar equiv of the appropriate boron halide reagent was added to the reaction solution as a gas (BCl_3), liquid (BBr_3 or $PhBCl_2$), or solid (BI_3). The product complexes formed upon mixing the reagents. The reaction solution was stirred at −78 °C to 20–60 min, and then it was warmed slowly to room temperature. The solvent was removed at reduced pressure. Extraction of the reaction residue with a CH_2Cl_2/hexane solution and cooling the extractant solution, after filtration, to −20 °C afforded the solid products. All of the products were relatively stable thermally, except for the iodide complex which underwent slow thermal decomposition at room temperature even in the solid state. Complexes **3**, **4**, and **6** are air stable for at least several minutes, while complex **5** is not stable upon exposure to air. The detailed characterization of each complex is provided below.

$[cis\text{-}(OC)_4Re(CH_3CO)(CH_3CNH)]BCl_2$ (3): pale yellow crystals (0.10 g, 27%); mp 107–108 °C; IR (hexane) ν(CO) 2100 (m), 2000 (vs), 1990 (vs), 1975 (s), ν(C⋯O, C⋯N) 1540 (br, m); ^1H NMR δ

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