(SPMe$_2$MNe$_2$PS)$_2$[17] and leads to steric crowding through phenyl 1,3 axial–axial interactions. The crowding in Fe(SPMe$_2$NMe$_2$PS)$_2$ 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$_2$NPh$_2$PS)$_3$ presumably due to van der Waals repulsion between the phenyl rings. Also indicative of steric crowding are the relatively close C$\cdots$C nonbonded distances between phenyl carbons or different phosphorus atoms. Some examples are 3.35 [C(14)$\cdots$C(23)], 3.45 [C(21)$\cdots$C(56)], 3.49 [C(21)$\cdots$C(12)], and 3.56 Å [C(23)$\cdots$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$_2$NPh$_2$PS)$_3$ 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$_2$NPh$_2$PS)$_3$·C$_3$H$_6$O, 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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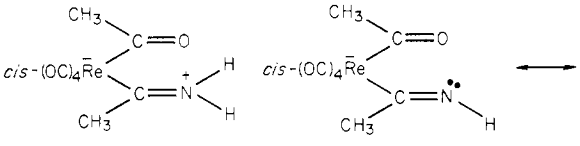
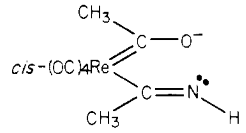
We reported recently that rhena- and ferra-β-diketones condense with the boron trihalides or BCl$_2$Ph to afford neutral (metalla-β-diketonato)B(X)(Y) complexes where X is a halogen and Y is either halogen or phenyl.[1,2] The X-ray structure of a (ferra-β-diketonato)BF$_2$ complex confirms the expected 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]



1



2

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen. Methylene chloride was distilled from P$_2$O$_5$ 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$_4$Si as an internal reference. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Preparation of {*cis*-(OC)$_4$Re[CH$_3$C(O)][CH$_3$CN(H)]}$^-$ (2) and the Boron Complexes [*cis*-(OC)$_4$Re(CH$_3$CO)(CH$_3$CNH)]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$_2$Cl$_2$/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*-(OC)$_4$Re(CH$_3$CO)(CH$_3$CNH)]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); ^{1}H NMR δ

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0020-1669/82/1321-2100$01.25/0

2.89 (s, 3, CH_3CN), 3.07 (s, 3, CH_3CO), 9.43 (br s, 1, NH). Anal. ($C_8H_7NBO_5Cl_2Re$) C, H, N.

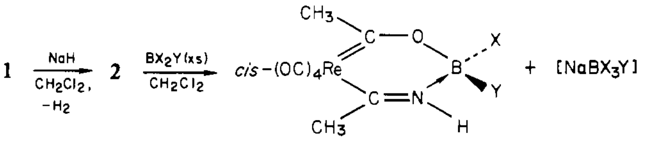
[*cis*-$(OC)_4Re(CH_3CO)(CH_3CNH)$]$BBr_2$ (4): bright yellow crystals (0.175 g, 40%); mp 117–118 °C; IR (CH_2Cl_2) ν(CO) 2100 (m), 2000 (vs), 1995 (vs), 1970 (s), ν(C$\overset{\cdots}{-}$O, C$\overset{\cdots}{-}$N) 1540 (br, m); ^{1}H NMR δ 2.92 (s, 3, CH_3CN), 3.10 (s, 3, CH_3CO), 9.57 (br s, 1, NH). Anal. ($C_8H_7NO_5BBr_2Re$) C, H, N.

[*cis*-$(OC)_4Re(CH_3CO)(CH_3CNH)$]$BI_2$ (5): dark yellow powder; IR (CH_2Cl_2) ν(CO) 2100 (m), 1995 (br, vs, 1970 (s); ^{1}H NMR δ 3.01 (s, 3, CH_3CN), 3.25 (s, 3, CH_3CO), 9.91 (br s, 1, NH).

[*cis*-$(OC)_4Re(CH_3CO)(CH_3CNH)$]B(Cl)(Ph) (6): colorless crystals (0.125 g, 31%); mp 155–158 °C; IR (CH_2Cl_2) ν(CO) 2100 (m), 2000 (vs), 1980 (br, s); ^{1}H NMR δ 2.85 (s, 3, CH_3CN), 3.10 (s, 3, CH_3CO), 7.35 (complex m, 5, C_6H_5), 9.51 (br s, 1, NH). Anal. ($C_{14}H_{12}NO_5BClRe$) C, H, N.

Results and Discussion

When the rhenaacetylacetonimine complex, **1**, is treated with NaH in CH_2Cl_2 solution, the rhenaacetylacetone iminato anion, **2**, is formed. Reaction of **2** with BCl_3, BBr_3, BI_3, or $PhBCl_2$ affords the (rhenaacetylacetone iminato)B (X)(Y) complexes **3–6**. Complexes **3–6** dissolve in benzene, and the mass spectrum of **3** shows a parent ion, principal fragmentation ions, and the correct isotopic pattern consistent with a neutral, monomeric structure, as shown.



3, X = Y = Cl
4, X = Y = Br
5, X = Y = I
6, X = Cl, Y = Ph

Solution-phase IR spectra of **3–6** show terminal carbonyl stretching bands at the frequencies expected for a neutral complex with a relative intensity pattern which is consistent with a *cis*-$(OC)_4Re$ fragment. The ν(CO) frequencies of **3–6** are ca. 20 cm^{-1} lower in energy than those of the corresponding [*cis*-$(OC)_4Re(CH_3CO)_2$]BX_2 complexes.[1] This shift apparently reflects a more electron-rich rhena ligand when an NH group is substituted for an oxygen atom. The ν(C$\overset{\cdots}{-}$O, C$\overset{\cdots}{-}$N) stretching frequencies at ca. 1540 cm^{-1} are 15 cm^{-1} lower in energy than the corresponding band of **1**. This shift may result from a slight decrease in the intra chelate ring C=O and C=N bond orders upon coordination to the boron moieties.

The ^{1}H NMR spectra show N–H resonances in the range of 9.43–9.91 ppm, which indicates that the N–H hydrogen atom and the iminium–ligand methyl group are syn relative to the C$\overset{\cdots}{-}$N multiple bond.[4-6] An unusual feature in each of these spectra is that the iminium methyl resonance appears at *higher* field than the acetyl methyl resonance. In complexes **3–6**, the iminium methyl resonances appear in the range 2.85–3.01 ppm, while the acetylmethyl resonances appear in the range of 3.07–3.25 ppm. The average anisochronism[9] for these two methyl resonances is 21 Hz. In complex **1**, the iminium and acetyl methyl resonances appear at 2.86 ppm and 2.68 ppm, respectively. However, in the symmetrical [*cis*-$(OC)_4Re(CH_3CO)_2$]B(X)(Y) complexes, which are analogous to **3–6**, the acetyl methyl resonances appear in the range of 3.09–3.18 ppm. Therefore, in the comlexes **3–6**, the iminium methyl resonances have chemical shifts similar to that of the iminium methyl resonance of **1** (i.e., as if the NH group were protonated), and the acetyl methyl resonances have chemical shifts similar to those of the acetyl groups in (rhenaacetylacetonato)B(X)(Y) complexes [i.e., where the acetyl ligand is coordinated to a B(X)(Y) moiety]. These chemical shift data for complexes **3–6** are entirely consistent with the proposed structure where *both* the oxygen and the nitrogen atoms of the rhenaacetylacetone iminato ligand are coordinated to the boron atom. Unfortunately, single crystalline samples of these complexes have not been isolated yet to permit an X-ray structural determination.

Complexes **3–6** are rhena analogues to the known neutral (2-pentanone-4-iminato)BZ_2 complexes (or related derivatives) where Z can be alkyl, aryl, or F.[10,11] Interestingly, anion **2** does not react with BF_3 to afford a (rhenaacetylacetone iminato)BF_2 complex. Also, ionic boronium salts of the type [(rhenaacetylacetone iminato)$_2$B]$^+$X$^-$ are not observed. Complexes **3–6** decompose slowly in ether solutions. This effect is not observed with the (rhenaacetylacetonato)BX_2 complexes. However, organic (β-diketonato)BZ_2 complexes are, presumably, slightly more stable than the corresponding Schiff base complexes, also.[10]

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Registry No. **1**, 66808-78-4; **2**, 80719-67-1; **3**, 80720-91-8; **4**, 80720-92-9; **5**, 80720-93-0; **6**, 80720-94-1; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $PhBCl_2$, 873-51-8; BI_3, 13517-10-7.

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Molecular Structure of $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$, a Compound with a Dangling Dithiophosphate Ligand

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The structure of $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$, a compound prepared[1] by the oxidation of $Mo(CO)_4Cl_2$ by *p*-tolyl azide in the presence of $(NH_4)S_2P(OC_2H_5)_2$, is important because it is a d^1 complex with a potential coordination number of 7 and a potential 19-electron configuration. No precedents exist. Additional importance arises because this compound is the precursor[1] of an unusual tetranuclear cluster, [$Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)$]$_4$.[2] Although we have considered several possible structures for the mononuclear compound, accumulated ESR, infrared, and chemical evidence led us to a bias in favor of a cis octahedral structure with a linear arylimido ligand, two bidentate dithiophosphate ligands, and a third monodentate dithiophosphate ligand.[1] Severe twinning of the crystals from the original preparation prevented a meaningful determination of the structure at that time. However, recrystallization from a different mixture of solvents has provided the crystals which were used in the study described herein.

Experimental Section

Orange-brown crystals of $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$ were obtained by recrystallization from benzene/petroleum ether. Although the compound has a bronze color when it is recrystallized from CH_2Cl_2/CH_3OH,[1] the infrared and ESR spectra of both samples are

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