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Facile and Reversible Conversion of an Ammonium Tetraphenylborate Salt, $Fe(NO)_2[PhP(OCH_2CH_2)_2NH_2^+]_2[BPh_4^-]_2$, into an Amine–Triphenylborane Adduct, $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)\cdot BPh_3]_2$

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The iron dinitrosyl bis(phosphane ammonium tetraphenylborate) $Fe(NO)_2[PhP(OCH_2CH_2)_2NH_2^+]_2[BPh_4^-]_2$ (**2**) is converted, at room temperature, into the corresponding bis(phosphane amine–triphenylborane) adduct $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)\cdot BPh_3]_2$ (**3**), in which cleavage of one of the phenyl rings of the tetraphenylborate anion has occurred. Compound **2** is obtained (i) by direct protonation of $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ (**1**) and subsequent reaction with $NaBPh_4$, (ii) indirectly from the reaction of $NaBPh_4$ with the trimetallic complex $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)Fe(NO)_2I]_2$ (**4**), or (iii) from the reaction of $NaBPh_4$ with the nonisolated adduct formed by mixing $[Fe(NO)_2I]_2$ (**6**) with the bicyclic aminophosphorane $PhP(OCH_2CH_2)_2N$ (**7**). Complex **3** was also obtained directly by complexation of adduct **1** by BPh_3. The reaction of **3** with HCl and then with $NaBPh_4$ easily regenerates complex **2**. Variable-temperature ^{31}P NMR spectroscopy of **3** in DMF reveals a stepwise and reversible dissociation of the two BPh_3 groups.

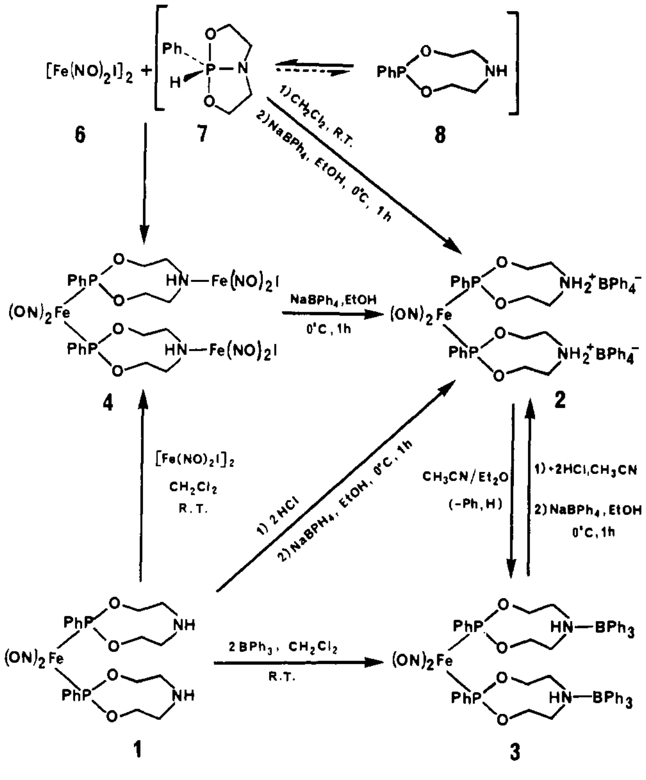
Introduction

The tetraphenylborate anion has been routinely used as a means of facilitating the crystallization, isolation and characterization of cationic transition-metal complexes and of ammonium cations. Although this counterion is usually considered as chemically inert, complications have now been reported in several instances, notably in relation to redox reactions,[2,3] complexation of one phenyl ring by the metal,[3] and transfer of phenyl[4] or biphenylyl[5] groups to an organic ligand. In this paper we report the surprisingly facile and reversible conversion of the tetraphenylborate ammonium salt $Fe(NO)_2[PhP(OCH_2CH_2)_2NH_2^+]_2[BPh_4^-]_2$ (**2**) into the triphenylborane adduct $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)\cdot BPh_3]_2$ (**3**), exemplifying another situation where this anion does not assume its expected passivity.

Results and Discussion

In order to prepare a crystalline derivative of the quaternary ammonium salt of the iron dinitrosyl complex **1** (Scheme I), ethanolic solutions of **1** were acidified with aqueous HCl and subsequently treated with an excess of sodium tetraphenylborate. The crude bis(phosphane ammonium borate) complex **2** precipitated readily as a powder, retaining ethanol molecules even after prolonged pumping under vacuum. Unexpectedly, this new complex proved to be labile. Upon simple recrystallization in acetonitrile–ether at room temperature, a mixture of two crystalline products was obtained, which could be separated by solubility differences. One, in the form of light orange needles, had spectroscopic properties identical with those of the initial precipitate and was identified as salt **2** with ethanol and acetonitrile as molecules of solvation. The second compound, present as red parallelepipedic crystals, was identified as the bis(amine–triphenylborane) adduct **3** solvated with CH_3CN. The latter was further characterized by its independent direct preparation through the reaction of compound **1** with triphenylboron. While complex **2** is readily soluble in a variety of solvents (CH_2Cl_2, THF, CH_3CN), compound **3** was soluble only in DMF, thus allowing the separation of the two compounds to be easily achieved by selective solubilization of **2** in CH_3CN. In a typical experiment, where the recrystallization procedures were repeated several times, 80% of the iron originally present in complex **1** was eventually found in complex **3**; this unambiguously identifies salt **2** as its progenitor. Benzene was detected by gas chromatography in the mother liquors, thus elucidating the fate of the cleft phenyl ring and identifying the other product of the redox process.

Scheme I



The transformation of **2** into **3** also took place, at a variable rate, when **2** was dissolved in pure CH_3CN or CH_2Cl_2 (**3** precipitates upon standing); it was even observed to occur in the solid state, sometimes overnight. Moreover, this process can easily be reversed, as **3** could be converted back into **2** in high yields by protonation, followed by precipitation with $NaBPh_4$.

As well as by their solubility properties, the two interconvertible compounds **2** and **3** are easily differentiated by their

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(1) (a) University of Nice. (b) University of Ottawa.

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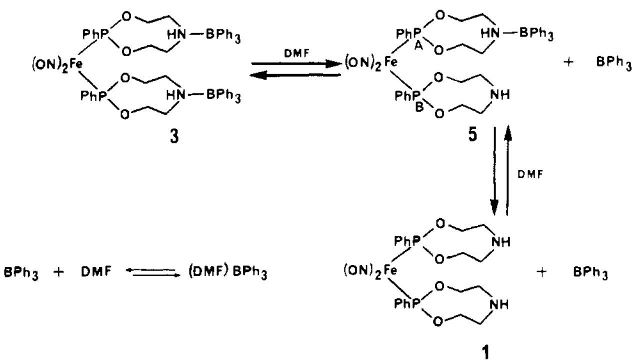
Scheme II



spectroscopic features, in particular NMR. The presence of BPh_4^- in **2** is readily established by ^{11}B NMR spectroscopy, confirming its ionic nature; the spectrum, obtained in DMF, consists of a sharp singlet at −6.5 ppm, a value close to that of −6.7 ppm found for $NaBPh_4$ in the same solvent (−6.4 ppm reported in CH_3CN[6]). On the other hand, **3** is characterized by a very broad signal at +7.4 ppm. The ^{31}P NMR spectrum of **2** at 25 °C consists of a sharp singlet at 209.7 ppm whose downfield position relative to the ^{31}P resonance of complex **1** at 202.0 ppm is in line with our previous observations on polymetallic complexes such as **4** (Scheme I), in which similar downfield shifts were consistently noted for phosphorus upon quaternization of the transannular nitrogen of the aminophosphane ligand.[9,10]

In sharp contrast, the ^{31}P NMR spectrum of complex **3** is temperature and dilution dependent and can be rationalized in terms of temperature-dependent dynamic equilibria between complex **3** and its stepwise dissociation products **5** and **1**, triphenylborane being in part taken up by the solvent (Scheme II). The best resolved spectra are obtained around −7 °C. They then consist (Figure 1) of three sets of signals: singlet a at 202.3 ppm is assigned to the uncomplexed compound **1**, and singlet b, at lower field, to compound **3**, in which the phosphorus atoms are also magnetically equivalent, both having quaternized transannular nitrogen atoms, while the doublet of doublets c is attributed to the intermediate mono(amine–borane) adduct **5**. The low-field doublet (208.0 ppm; $J_{P_A-P_B} \sim 5$ Hz) of this last set is assigned to P_A, which has a tetracoordinated transannular nitrogen atom, and the higher field doublet (227 ppm) is assigned to P_B with a tricoordinated transannular nitrogen atom. When the temperature is increased, a decrease in intensity of signal b with respect to the other signals is observed, as well as a broadening of all resonances, which coalesce above 50 °C into a single signal, indicating that the exchange of the BPh_3 groups among the available donor sites is rapid on the NMR time scale. The reverse trend is observed upon cooling, and at −52 °C, signal b accounts for more than 80% of the total peak area. The relative intensity of signal b also decreases upon dilution with DMF, with which compound **1** is in competition for the coordination of BPh_3. Further support for this interpretation of the spectra was obtained by adding various amounts of BPh_3 to solutions of compound **1** in DMF. With 2 molar equiv of BPh_3, the spectra of the solutions are identical with those of **3** measured under the same temperature and dilution conditions. With only 1 equiv of BPh_3, the same sets of lines are obtained but with, as expected, an inversion of the intensities of signals a and b (Figure 1).

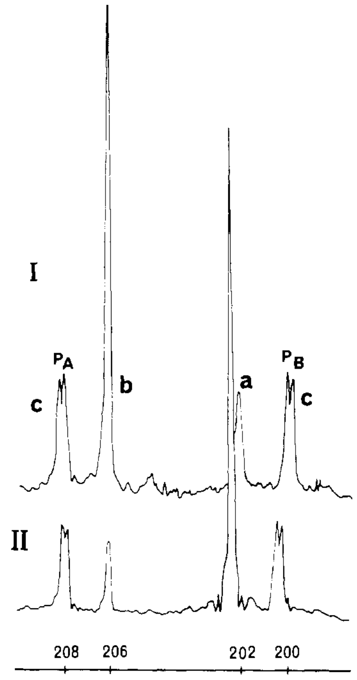


Figure 1. ^{31}P NMR spectra at −7 °C: I, spectrum of a 3×10^{-2} M solution of **3** in DMF; II, spectrum of a 3×10^{-2} M solution of **1** in DMF after addition of 1 equiv of BPh_3.

In the IR spectra (KBr), the amine–borane adduct **3** can also be readily differentiated from the ammonium salt **2** by the presence of a weak but sharp absorption at 3230 cm^{-1}, assigned to the coordinated NH (for comparison, piperidine–triphenylborane has ν_{NH} at 3226 cm^{-1}[7]). It is of interest also that the ionic complex **2** and the nonionic **3** have identical ν_{NO} vibration frequencies (1740, 1690 cm^{-1}), which rules out the localization of a positive charge at the metal fragment for the former.

Mixtures of **2** and **3** were also obtained, albeit in much lower yield (14%), in the reaction of the trimetallic compound **4** with $NaBPh_4$ in ethanol (Scheme I). In this case direct alcoholysis of the Fe–I bonds, and/or their $NaBPh_4$-assisted ionization to yield cationic intermediates prone to nucleophilic reaction with the solvent at the NO's,[8] may account for the proton-generating step required for the formation of **2**.

Worthy of mention is also the reaction between the iron dinitrosyl iodide dimer **6** and the bicyclic aminophosphorane **7**. Our initial aim was to prepare dissymmetrical iron dinitrosyl chelates with the open tautomeric form **8** of **7**. A range of such chelates, with diverse metal carbonyls, have been prepared recently[9,10] and proved to have unusual properties, probably owing to the transannular location of the P and N atoms.[10] In the present case no chelate formation was detected when the reactants were taken in a 1:1 ratio. Instead, the experimental data indicate that trimetallic complex **4** is the main reaction product, as shown by the very close similarities between the IR and ^{31}P NMR spectra of the isolated powder and those of an independently prepared sample of **4**.[11] Every attempt to induce a clean crystallization from solutions of **4** having failed, CH_2Cl_2 was replaced by ethanol and the solution was allowed to react with $NaBPh_4$. Complexes **2** and **3** were then the sole reaction products that could be identified in the solution and isolated. Formation of $Fe(NO)_2L_2$ derivatives containing an $\{Fe(NO)_2\}^{10}$ fragment[12] has already been re-

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ported to occur in the reactions of a variety of phosphanes and phosphites with dimer **6**, an $\{Fe(NO)_2\}^9$ complex, or its chloro and bromo analogues.[13-16]

The most remarkable result is the facility with which the bis(ammonium tetraphenylborate) salt **2**, whatever its mode of preparation, is converted into the bis(amine–triphenylborane) complex **3**. Although the decomposition of such a tetraphenylborate salt into the corresponding amine–triphenylborane adduct has already been reported, it usually required more drastic conditions such as pyrolysis at elevated temperatures.[17] On the other hand, at least two papers are available that report the instability of ammonium tetraphenylborate derivatives at room temperature. A cationic hydrazido tungsten complex, $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$, when allowed to react with $NaBPh_4$, was shown to yield small amounts of a diazene–triphenylborane adduct (11%) along with the expected tetraphenylborate salt (58%).[18] It was not reported, however, whether or not the latter salt, once formed, showed signs of facile degradation. More directly comparable to the present case is the decomposition of several BPh_4^- salts of cationic cyclopentadienyl iron complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2LH^+][BPh_4^-]$, containing protonated imidazole or vicinal triazole ligands (symbolized as LH in the above formula).[19] These compounds also retained molecules of solvents in the solid state and were converted into the amine–triphenylborane adducts in refluxing THF (32–92% yields) within a matter of hours. Benzene was also reported to form during this reaction.

In the above azole complexes, the instability of the ammonium salts increased parallely to the acidity of the protonated nitrogen atom.[19,20] The smooth transformation of compound **2** into **3** under very mild conditions now allows the acidity factor as a key requirement for a facile degradation to be discarded.[23] The presence of molecules of solvents in the solid state of both types of tetrafluoroborate salts remains the only common feature that can be identified. In the azole series, a suitably arranged molecule of solvent was proposed to act as an efficient proton relay between the protonated nitrogen atom and BPh_4^-.[19] The detection of benzene, an expected product in such a reaction, during the conversion of complex **2** into complex **3** indicates that a similar reaction pathway may indeed be a likely one in the present case.

In conclusion, the instability of several tetraphenylborate salts of ammonium derivatives containing a transition metal stands as a possible complication associated with the use of BPh_4^- as a counterion. With respect to ligand **8**, whose ability to act as an assembling ligand between two transition elements had already been established,[11] the formation of compound **3** serves to illustrate the possibility of using it in the elaboration of mixed transition metal/main group element complexes.

Experimental Section

All manipulations were carried out under dry argon or vacuum with carefully dried reactants and solvents. $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ (**1**) and $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)Fe(NO)_2I]_2$ (**4**) were prepared as described previously,[11] and dimer **6** was prepared according to the literature.[25] IR spectra were recorded on Unicam SP 1100 and Perkin-Elmer 577 spectrometers, calibrated with a polystyrene film. ^{31}P and ^{11}B NMR spectra were recorded in DMF on Varian FT 80 and Bruker WH-90 spectrometers. An external D_2O lock was used. Chemical shifts are given in ppm positively downfield from H_3PO_4 for phosphorus and from $BF_3 \cdot Et_2O$ for boron and are considered to be accurate to ca. 0.3 ppm. Ca. 3 × 10^{-2} M solutions in DMF were used in the NMR experiments with complexes **2** and **3**. Mass spectra were obtained on Nermag R-1010 and 7070 VG analytical mass spectrometers. Elemental analyses were performed by the Service Central de Microanalyse (CNRS, France), MWH Laboratories, Phoenix, AZ, and Canadian Microanalytical Service Ltd., Vancouver, British Columbia, Canada. Melting points were measured in capillary tubes sealed under argon. Unless otherwise noted, percentage yields were calculated with respect to the total amount of iron present in the initial reagent.

Synthesis of the Iron Dinitrosyl Bis(phosphane ammonium tetraphenylborate) 2. (a) From $Fe(NO)_2[PhP(OCH_2OCH_2)_2NH]_2$ (1), HCl, and $NaBPh_4$. Aqueous HCl (1 mL, 1.20 mmol) was added dropwise to a stirred solution of **1** (0.3 g, 0.557 mmol) in EtOH (15 mL) at room temperature. After 5 min, the temperature was lowered to 0 °C and a solution of $NaBPh_4$ (0.571 g, 1.67 mmol) in EtOH (15 mL) was added. An orange precipitate formed immediately. After 1 h of stirring, the mixture was filtered. The solid was washed with 3 × 20 mL of EtOH and then with 4 × 20 mL of Et_2O and dried under vacuum without heating to yield crude **2** (confirmed by IR and NMR spectroscopy) retaining molecules of EtOH (confirmed by ^1H NMR spectroscopy). The solid was redissolved in 2 mL of CH_3CN, and 20 mL of Et_2O was added on top of the CH_3CN solution. Crystallization occurred overnight at room temperature, affording a mixture of **2** (0.173 g, 23%) and **3** (0.356 g, 60%), which were separated by selective dissolution of **2** into CH_3CN.

(b) From $[Fe(NO)_2I]_2$ (6), Bicyclic Aminophosphorane 7, and $NaBPh_4$. Two molar equivalents of **7** (1.28 g, 6.08 mmol) in CH_2Cl_2 (15 mL) was added dropwise, at room temperature, to a stirred solution of **6** (1.48 g, 3.04 mmol) in CH_2Cl_2 (15 mL). After evaporation of the solvent, the black residue was redissolved in 30 mL of EtOH. After the mixture was cooled to 0 °C, a solution of $NaBPh_4$ in 15 mL EtOH (2.93 g, 8.29 mmol) was added dropwise. An orange precipitate formed immediately. After 1 h, the solid was filtered, washed with 3 × 10 mL of EtOH and then 5 × 15 mL of Et_2O, and dried under vacuum without heating, to yield 2.32 g of crude **2**, retaining molecules of EtOH (confirmed by IR and NMR spectroscopy). The product was rapidly crystallized in CH_3CN/Et_2O (1:10) as orange needles (1.67 g, 20%). Crystalline **2**, readily soluble in CH_2Cl_2, THF, and CH_3CN, retained CH_3CN and EtOH, as shown by its ^1H NMR spectrum in CD_2Cl_2. Elemental analyses, when performed within a short period of time, were consistent with the presence of two EtOH and two CH_3CN molecules per iron. Anal. Calcd for $C_{76}H_{86}B_2FeN_6O_8P_2$ (**2**, 2 EtOH, 2 CH_3CN): C, 67.46; H, 6.50; N, 6.21. Found: C, 67.53; H, 6.24; N, 6.41. Mp: 100–102, 180–183 °C (see below). IR (KBr), cm^{-1}: ν_{OH} (tentative) 3600–3300 (w, br) with three maxima at 3590, 3460, and 3400;[26] $\nu_{NH_2^+}$ (tentative) 3100 (m) and several weak absorptions between 2900 and 2500;[27] ν_{CH_3CN} 2295, 2265 (w); ν_{NO} 1740 (s), 1690 (vs); weak bands comparable to those

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(12) $\{M(NO)_2\}^m$ represents a metal dinitrosyl complex in which the nitrosyl ligand is formally considered as NO^+ and the metal to have *m* d electrons. See, for example: Enemark, J. H.; Feltham, R. S. *Coord. Chem. Rev.* **1974**, *13*, 339.

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found in the spectrum of **3** but with differences in relative intensities in the 1500-1400 region, very similar to those found in the spectra of $NaBPh_4$ and $TlBPh_4$ near 1280 (w, br) and 1235 (w);[28] 1200-1100 region very close to those of $CuBPh_4$ and $AgBPh_4$;[28] ν_{CH} 750 (s), 710 (vs).[28] NMR (DMF), ppm: ^{11}B, -6.5; ^{31}P, 209.7.

(c) From the Trimetallic Complex 4 and $NaBPh_4$. **4** (0.539 g, 0.528 mmol) was treated with $NaBPh_4$ (0.458 g, 1.43 mmol) in EtOH (30 mL) according to the same procedure as above. The crude orange-red product **2** (0.360 g) crystallized as orange-red needles (0.346 g, 16%) from CH_3CN/Et_2O (1:10).

Synthesis of the Iron Dinitrosyl Bis(phosphane amine-triphenylborane) 3 by Reversible Transformation of 2 or Directly from 1 and BPh_3. The only method that led to *crystalline* **3** was the decomposition of **2** in a CH_3CN/Et_2O solution. The compound dissolved only in DMF (slowly at room temperature); attempts to recrystallize **3** in this solvent resulted in its precipitation as an amorphous solid. Elemental analysis and IR spectra of ground single crystals of **3** were consistent with the presence of 0.5 CH_3CN/Fe. Anal. Calcd for $C_{57}H_{59.5}B_2FeN_{4.50}O_6P_2$ (**3**, 0.5 CH_3CN): C, 65.61; H, 5.71; N, 6.04. Found: C, 65.09; H, 5.63; N, 5.99. Mp: 179-180 °C. IR (KBr), cm^{-1}: ν_{NH} 3230 (w); ν_{NO} 1740 (s), 1690 (vs), 1200-1100 region similar to those of $CuBPh_4$ and $AgBPh_4$,[28] with an additional medium-intensity band at 1160; ν_{CH} 730 (s), 710 (vs).[28] NMR (DMF), ppm: ^{11}B, +7.4 (very broad); ^{31}P, see Discussion.

Interconversion of the Ammonium Tetraphenylborate 2 into the Amine-Triphenylborane 3. (a) Transformation 2 → 3. **2** can be converted into **3** by repeated crystallizations in CH_3CN/Et_2O (1:10). In a typical experiment, 0.720 g (0.533 mmol) of **2** was dissolved in 1 mL of CH_3CN; 10 mL of Et_2O was carefully added. The Et_2O layer was allowed to diffuse slowly into the CH_3CN solution at room temperature; the precipitate that formed overnight was filtered, washed twice with 15 mL of CH_3CN and then three times with 20 mL of Et_2O, and dried. The filtrate was evaporated, and the process was repeated twice to yield altogether 0.494 g (87%) of **3** as red parallelepipedic crystals. Benzene was detected by gas-liquid chromatography (SE 30, 80 °C) in the CH_3CN/Et_2O filtrate after transformation of **2** and identified by comparison with an authentic sample. The conversion of **2** into **3** was also observed to occur spontaneously (i) within $^1/_2$ h in pure CH_3CN, when solutions of **2** were concentrated under vacuum at ca. 40 °C, (ii) in CH_3CN or CH_2Cl_2 when solutions of **2** were left overnight at room temperature, and (iii) in the solid state; in one experiment, the decay could be monitored by IR spectroscopy as occurring within 2 h.

(b) Reverse Transformation of 3 to 2. Aqueous HCl (1.20 mmol) was added dropwise to a stirred suspension of **3** (0.64 g, 0.580 mmol) in CH_3CN (15 mL). The crystals slowly dissolved, and after 10 min at room temperature a homogeneous solution was obtained. The solvent was then evaporated under vacuum and the residue redissolved in EtOH (15 mL). The addition of $NaBPh_4$ (0.645 g, 1.88 mmol) in EtOH (15 mL) afforded a precipitate, which was filtered and washed with EtOH (3 × 10 mL) and Et_2O (5 × 15 mL), to yield 0.610 g (73%) of crystalline **2**.

Direct Synthesis of 3 by Reaction of $Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ (1) with BPh_3. Triphenylboron (0.37 g, 1.530 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of **1** (0.413 g, 0.766 mmol) in CH_2Cl_2 (30 mL). After 10 min, the solvent was removed and the ochre solid residue was washed (3 × 10 mL of CH_2Cl_2 and then 3 × 15 mL of Et_2O) and dried for several hours under vacuum, to yield 0.653 g (78%) of **3**, mp 175-180 °C. Anal. Calcd for $C_{57}H_{60}B_2FeN_4O_6P_2Cl_2$ (**3**, CH_2Cl_2): C, 61.80; H, 5.42; N, 5.05; P, 5.60. Found: C, 61.90; H, 5.46; N, 5.09; P, 5.66.

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Registry No. **1**, 84988-36-3; **2**, 92958-55-9; **3**, 92984-17-3; **4**, 84988-35-2; **6**, 15002-08-1; **7**, 57680-64-5; BPh_4^-, 4358-26-3.

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Preparation and Crystal Structure of Hg_3NbF_6 and Hg_3TaF_6: Mercury Layer Compounds

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The reaction of mercury with $Hg(MF_6)_2$ (M = Nb, Ta) dissolved in SO_2 gives rise to golden crystals of tetragonal $Hg_{3-\delta}MF_6$, which are subsequently transformed into silver crystals of trigonal Hg_3MF_6. The former are isostructural with the M = As, Sb analogues, but the latter have layer structures that are reported here for the first time. They consist of hexagonal sheets of Hg atoms that are separated by sheets of MF_6^- ions.

Introduction

In previous papers we have reported the preparation, structure and properties of the new homopolyatomic cations of mercury, Hg_3^{2+} and Hg_4^{2+}, formed by oxidation of mercury with SbF_5 and AsF_5. With excess oxidant the mercurous cation Hg_2^{2+} is formed, but with smaller amounts of oxidant the linear cations, Hg_3^{2+} and Hg_4^{2+}, are obtained.[1-4] With a still smaller amount of oxidant, the final product is the metal-like compound $Hg_{3-\delta}MF_6$ (M = As ($\delta = 0.18$) and Sb ($\delta = 0.10$)). Neutron and X-ray diffraction studies have shown that these compounds contain two nonintersecting mutually perpendicular sets of chains of mercury atoms that are incommensurate with the host lattice of MF_6^- anions.[5-7] Because of their unusual structure and anisotropic conductivity, these compounds have been of considerable interest to solid-state physicists. The extensive literature on the physical properties of these compounds has recently been reviewed.[8]

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