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A Phosphoranide (10-P-4) Anion Coordinating to Transition Metals, as a Lewis Base and a π-Acceptor

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ABSTRACT

The reaction of 10-P-5 hydridophosphorane **6** *with KH provides the 10-P-4 potassium phosphoranide anion* **7a**. *Anion* **7a** *reacts with* $CpFe(CO)_2I$ *and* $BrAu(PEt_3)$ *to replace the halide with the phosphoranide as a monodentate ligand forming* **8** *and* **9**. *The X-ray structure of* **8** *shows that the equatorial* —$Fe(CO)_2Cp$ *ligand of* **8** *makes the apical P—O bonds (1.824 Å) longer than the P—O bonds (1.80 Å) of the phosphoranide oxide anion* **10**. *The P—O bonds (1.75 Å) of* **6**, *with an equatorial proton ligand, are still shorter. This provides evidence that the* —$Fe(CO)_2Cp$ *ligand is not only a sigma-acceptor Lewis acid ligand, but also a pi-donor that transfers electrons into the O—P—O three-center bond's antibonding orbital to increase its P—O bond lengths. It is a better pi-donor than the* —O^- *pi-donor of phosphoranide oxide* **10**.

INTRODUCTION

Phosphoranides, 10-P-4 anionic species [1], have been postulated as intermediates or as transition states for nucleophilic substitution reactions at three-coordinate phosphine centers [2]. The first organophosphoranide anion, **1**, was earlier prepared in our laboratory by the deprotonation reaction of the neutral hydridophosphorane with lithium aluminumhydride [3]. Schomburg et al. [4] reported the first X-ray crystal structure for an organophosphoranide anion **2**. The X-ray structure showed a highly distorted pseudotrigonalbipyramidal (ψ-TBP) structure of this phosphoranide, with a lone pair of electrons in the equatorial position. However, phosphoranide **2** was in equilibrium with the monocyclic phosphite alkoxide in solution. A three-center four-electron (3c–4e) bond, such as the apical O—P—O 3c–4e bond of **1**, has negative charge on the two apical oxygens and a relatively positive charge on the electropositive central phosphorus [5]. This species is stabilized by the CF_3 groups adjacent to the negatively charged apical oxygens and by the two electropositive equatorial carbons of the bidentate ligands of **1**, which are coordinated to the positively charged phosphorus, providing a ψ-TBP geometry for this phosphoranide. Phosphoranide **2** has four electronegative oxygens from the bidentate ligands, so it is found to be in equilibrium with **2a**. The equatorial oxygens are more electronegative than the equatorial carbon of **1** and, therefore, provide less stabilization for the 3c–4e bond of **2** (Equation 1).

More recently a lithiated cyclenphosphoranide, **4**, was prepared by deprotonating cyclenphosphorane **3**, with *n*-butyllithium [6]. The X-ray crystal structure shows the geometry of the phosphoranide to be a distorted ψ-TBP geometry, with a lone pair of electrons in the equatorial position. Compound **4** was found [6] to be polymeric in the solid state with a Li^+(THF) unit bridging two cyclenphosphoranide nitrogen centers by coordination of two apical nitrogens (Equation 2).

Phosphoranide anions, other than the first one prepared (**1**), have been used as ligands to transition metals [7]. In most cases [8] the phosphoranide an-

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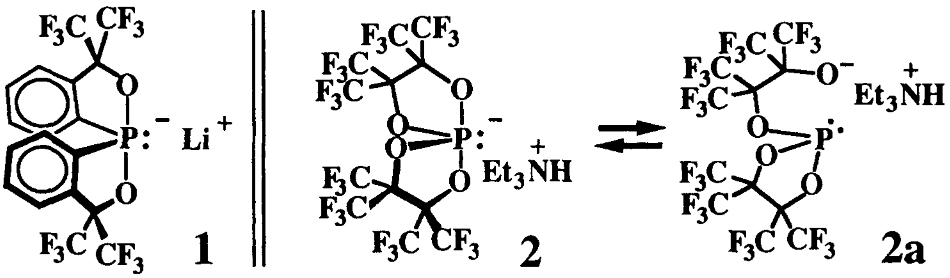
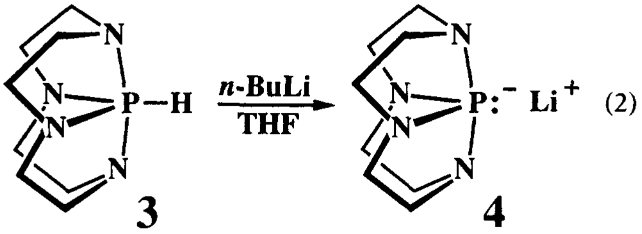
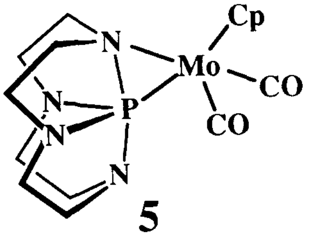


(1)



3 4 (2)

ions, with ligands having four oxygens or four nitrogens to coordinate to the phosphorus, act as bidentate ligands in coordinating to the transition metal as shown for **5**, as determined by Lattman et al. [8c], with similar species determined by Riess et al. [8a,b] (Scheme 1).



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SCHEME 1

A few transition metals have coordinated to phosphoranides, with four oxygens coordinated to the phosphorus. This maintains the phosphoranide as a monodentate ligand, with the metal coordinated only to the phosphorus [7].

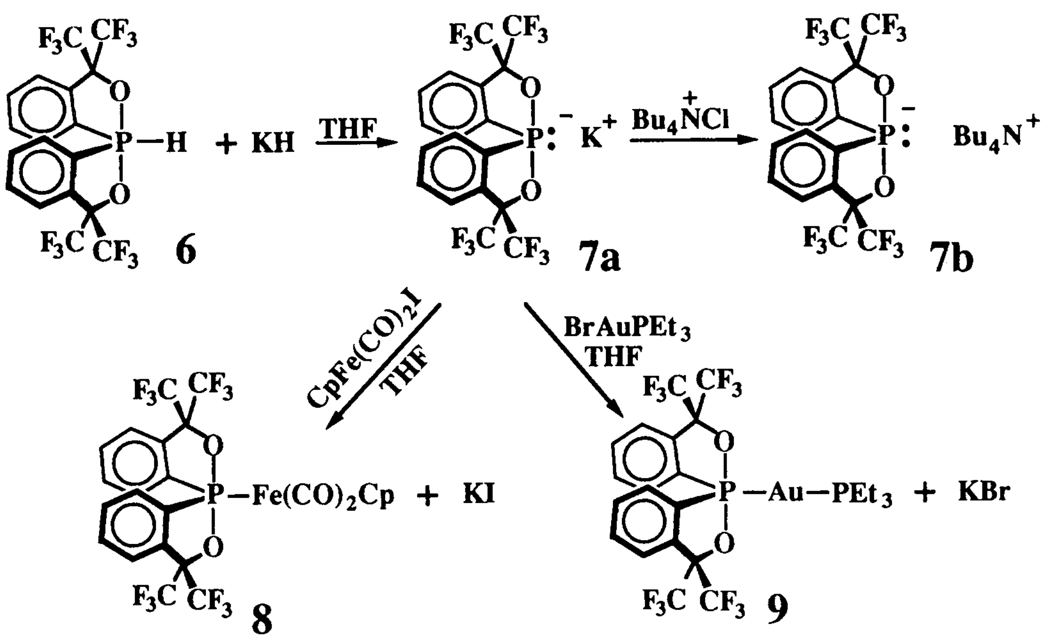
RESULTS

Phosphoranide anion **7a** was prepared by deprotonation of neutral hydridophosphorane **6** by KH, and was isolated as a stable compound in high yield, with the cation being the potassium cation (**7a**) or the tetrabutylammonium cation. The downfield shift observed in the ^{31}P NMR (δ +28.4) for anion **7b** or anion **7a** (δ +32.95), compared to that of the neutral hydridophosphorane **6** (δ −48.2), is not explained by the fact that **7a** is an anion, while **6** is neutral. The P—O bonds of anion **7a** must be increased in length to put more positive charge on the phosphorus than in neutral **6**. It is possible that anion **7** is unsymmetrical with one of the P—O bonds broken, although this must be rapidly equilibrating to exchange the two oxygens for coordination to the phosphorus to make the ^{19}F NMR provide only two quartets for the four CF_3 groups, even at low temperature. It has been found for other phosphoranides that the anion has lower field ^{31}P chemical shift than is seen for the neutral hydridophosphorane [4, 6].

The protons ortho to the phosphorus of the phenyl rings of hydridophosphorane have the NMR peak at δ 8.30 while they are at slightly higher field (δ 8.25) upon forming anion **7a**. The position of the ortho proton is determined largely by the dipole moment of the adjacent apical P—O bond [9b]. Although removal of the proton puts negative charge on the molecule, the dipole moment may increase to keep the proton in about the same NMR position.

Phosphoranide anion **7a** reacts with transition metal complexes, $Fe(CO)_2CpI$ and $AuBrPEt_3$, to form phosphoranes **8** and **9** (Scheme 2) in which the phosphoranide is acting as a monodentate ligand. Phosphoranide anion **7** has two bidentate ligands that were designed to stabilize the TBP species. The ligand has two electronegative trifluoromethyl groups adjacent to each apical oxygen and two electropositive carbon atoms in the equatorial plane stabilizing the 3c–4e bond. A five-membered ring linking apical, equatorial positions is known [10] to stabilize a large number of TBP 10-X-L species.

Complex **8** has been characterized by different spectroscopic techniques. This complex is stable in both air and moisture. A downfield shift in the ^{31}P NMR compared to both **6** and **7**, with only a single



SCHEME 2

pair of quartets in the ^{19}F NMR and a downfield shift of the proton ortho to phosphorus on the phenyl ring, is consistent with the formation of a TBP structure. The downfield chemical shift of protons ortho to phosphorus on the bidentate ligands of the metal complexes, δ 8.00 to 8.60, is characteristic of such protons and is observed in closely related phosphoranes [9], sulfuranes [11], iodinanes [12], and siliconates [13], and is due to the proximity of these protons to the dipolar X—O bond. The expected structure of complex **8** was further established by X-ray crystallography. The structure of this complex in the solid state is a distorted trigonal bipyramid (TBP) with electronegative two trifluoromethyl groups adjacent to the apical oxygens. There are two carbon atoms of the phenyl ring and the iron metal in the equatorial positions adjacent to phosphorus. Figure 1 shows the crystal structure

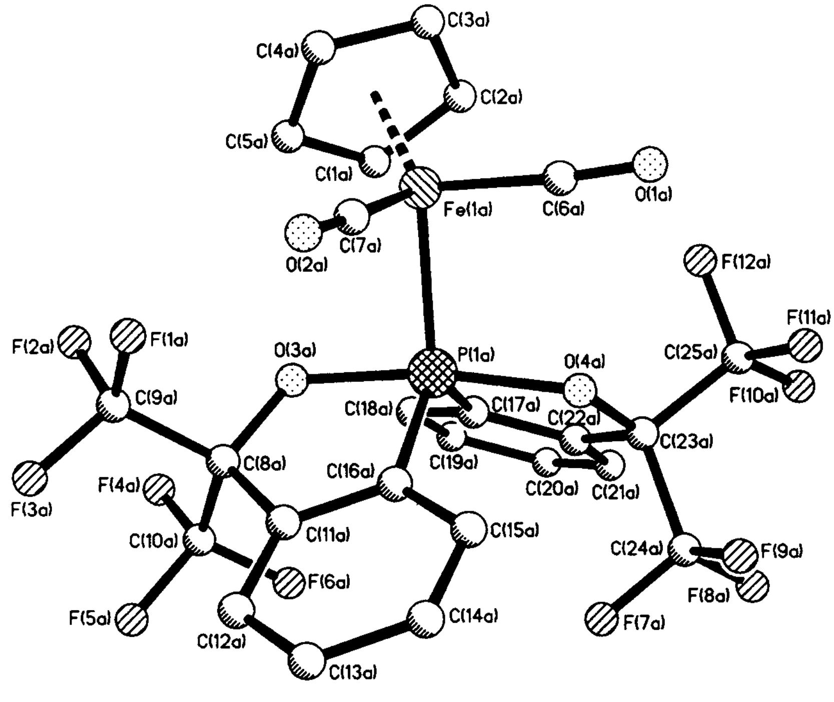


FIGURE 1 The X-Ray Structure of **8**.

TABLE 1 Bond Lengths and Angles for Phosphorane **8**

Bond Lengths	
Fe(1A)-C(1A)	2.116(7)
Fe(1A)-C(2A)	2.095(7)
Fe(1A)-C(3A)	2.102(6)
Fe(1A)-C(4A)	2.102(6)
Fe(1A)-C(5A)	2.105(6)
Fe(1A)-C(6A)	1.791(6)
Fe(1A)-C(7A)	1.768(7)
Fe(1A)-P(1A)	2.300(2)
C(1A)-C(2A)	1.406(7)
C(1A)-C(5A)	1.400(8)
C(2A)-C(3A)	1.419(9)
C(3A)-C(4A)	1.392(7)
C(4A)-C(5A)	1.403(8)
C(6A)-O(1A)	1.134(7)
C(7A)-O(2A)	1.150(9)
P(1A)-O(3A)	1.819(3)
P(1A)-C(16A)	1.839(6)
P(1A)-C(17A)	1.843(5)
P(1A)-O(4A)	1.829(3)
Bond Angles (°)	
Fe(1A)-P(1A)-C(16A)	118.5(2)
Fe(1A)-P(1A)-C(17A)	121.9(2)
C(16A)-P(1A)-C(17A)	119.6(2)
O(3A)-P(1A)-O(4A)	170.3(2)
C(17A)-P(1A)-O(4A)	85.1(2)
Fe(1A)-P(1A)-O(3A)	93.6(1)
O(3A)-P(1A)-C(16A)	85.4(2)
O(3A)-P(1A)-C(17A)	90.4(2)
Fe(1A)-P(1A)-O(4A)	96.0(1)

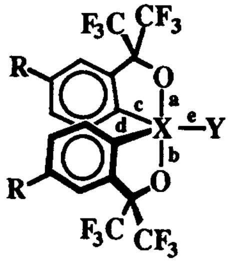
of **8**. Table 1 provides selected bond lengths and bond angles for the structure of **8**. The equatorial C—P—C and C—P—Fe angles have values between 118.5° and 121.9° respectively. The exocyclic and endocyclic apical–equatorial angles are in the range of 85.1° to 96.0°. The apical–apical O—P—O bond angle of 170.3° is a bit distorted from the ideal value of 180° of a TBP structure, and the distortion of the two oxygens away from the iron metal with the Fe—P—O bond angles as 93.6° and 96.0° is compatible with this decision.

A summary of the important structural information for comparison between **6** and **8** and phosphoranide oxide anion **10** is given in Table 2. In the case of hydridophosphorane **6** the distortion of the O—P—O bond from linearity is very slightly toward the equatorial hydrogen and the bigger opposite effect is observed for the structurally analogous potassium phosphoranoxide **10** [14] and sulfurane oxide **11** [15] (Scheme 3). This is rationalized by considering the repulsive interactions between π-donor equatorial ligands (the equatorial P—O bond in **10** and S—O bond in **11**) and the electrons of the 3c–4e hypervalent bond. Since the C—P—O bond angles in the five-membered rings are less than 90°, this makes it easy to distort the O—P—O angle away from the equatorial ligand with *p*-electron pairs that are repulsive to the electrons of the 3c–4e bond. Previously this deviation from linearity of the axial O—P—O bond in case of transition metal-substituted phosphoranes has been interpreted as being related to the steric requirements of the ligands attached to the metal, with bonds nonlinear to that of the phosphorus–metal bond [7, 16]. In the crystal structure of **8**, the bulkiness of FeCp(CO)$_2$ may also contribute to the distortion of the apical O—P—O angle. The decreased angle of the equatorial C—P—C angle from the expected 120° expected for an undistorted TBP geometry could be partly contributed to this same effect. The mean equatorial P—C bond length of **8** is 1.841 Å. The P—Fe bond length is 2.3 Å, which is comparable to the P—Fe bond lengths observed for other iron complexes [17] using triaryl or trialkylphosphine ligands.

The averaged apical P—O bond lengths of **8** are 1.824 Å. These are considerably longer than those for hydridophosphorane **6** and phosphoranoxide anion **9**. This can be explained by invoking an interaction of the filled d-orbitals or p-orbitals of the metal (HOMO) with the vacant antibonding molecular orbital on the three-center four-electron hypervalent bond (LUMO). An increase in electron donation from the equatorial ligand to the apical 3c–4e bond could lead to longer apical bond lengths and is observed in **6**, **10**, and **8** in Table 2. A similar apical bond elongation has also been observed between phosphoranes **6**, **10**, and **8** and is reflected with a downfield shift of ^{31}P NMR of these complexes with increased apical P—O bond lengths, as shown in Table 2.

Phosphoranide **7a** also reacts with BrAuPEt$_3$ in tetrahydrofuran to form a monodentate transition metal substituted phosphorane **9**. The ^{31}P NMR of **9** shows two peaks at δ 48.3 and 38.3 for the pentacoordinated phosphorus and tetracoordinated phosphorus species respectively. A single pair of quartets in the ^{19}F NMR suggests a symmetrical structure. Although it could be a rapidly equilibrating conversion of an unsymmetrical species, with one P—O bond broken and O$^-$ quickly attacking the phosphorus to cleave the opposite P—O bond, no evidence for this is observed. However, the ^{31}P NMR results (**6**, δ −48.2; **10**, δ −14.8; **8**, δ 14.7; and **9**, δ 48.3) are compatible with the symmetrical structures, such as that shown by the X-ray structures of **6**, **8**, and **10**. An X-ray structure will be obtained for **9**. A downfield shift in ^{31}P NMR and upfield shift in the ^{19}F NMR compared to the iron complex **8** suggests that the phosphoranide ligand in **9** is a better pi-acceptor than in **8**. The gold metal complex is probably a stronger pi-donor than the iron complex. The downfield shift in ^{31}P NMR of the tetracoordinated phosphorus in **9** (δ 38.3) is comparable to BrAuPEt$_3$ (δ 35.55). This may suggest that phosphines in general are good sigma-

TABLE 2 A Comparison of Bond Lengths (Å) and Bond Angles (Deg.) for Similar Phosphoranes **6**, **8**, and **10** and Sulphurane Oxide **11**

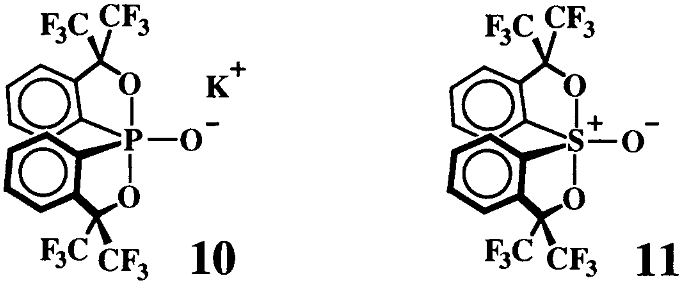


Bond Lengths and Angles	**6** (*X* = *P*, *Y* = *H*, *R* = *H*)^a	**10** (*X* = *P*, *Y* = *O*, *R* = *H*)^a	**11** (*X* = *S*, *Y* = *O*, *R* = t-*Bu*)^b	**8** (*X* = *P*, *Y* = *FeCp(CO)$_2$*, *R* = *H*)
a (Å)	1.748(3)	1.803(3)	1.78(5)	1.819(3)
b	1.743(2)	1.797(4)	1.777(5)	1.829(3)
c	1.804(4)	1.813(5)	1.784(5)	1.839(6)
d	1.809(4)	1.826(4)	1.796(6)	1.843(5)
e	1.32(3)	1.492(4)	1.439(4)	2.300(2)
∠ab (deg.)^c	178.47(13)	188.7(2)	187.7(2)	189.7(2)
∠ae	89.75(12)	94.6(2)	94.3(2)	93.6(1)
∠ac	88.48(14)	86.2(2)	88.0(2)	85.4(2)
∠cd	127.6(2)	121.0(2)	117.7(3)	119.6(2)
∠ed	114.5(11)	120.5(2)	120.7(2)	121.9(2)
^{31}P NMR	−48.2	−14.8		14.7

[a] Ref. 14.

[b] Ref. 15.

[c] In this table angle ∠ab is measured from the side of ligand Y.



SCHEME 3

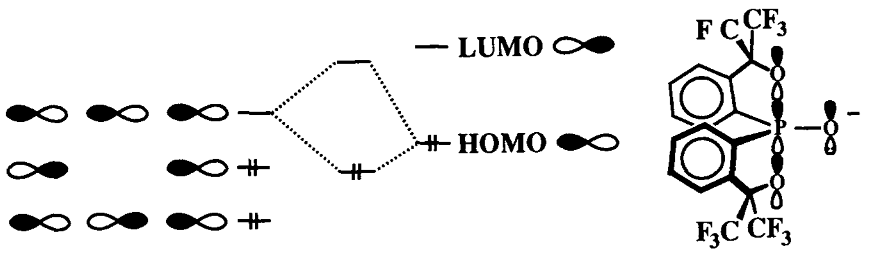
donor ligands making the gold metal more electron rich. A large coupling constant, $^2J_{PP}$ = 544 Hz, suggests that the P—Au—P bond is essentially linear.

DISCUSSION

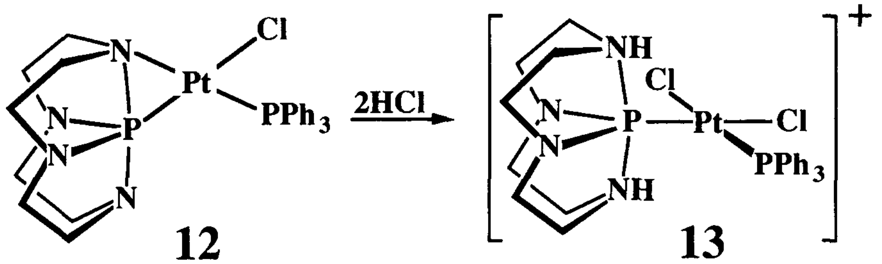
It has been known for some time [3, 14] that replacement of the equatorial hydrogen of **6** by the negatively charged oxygen of **10** makes the apical P—O bonds increase in length from 1.75 Å to 1.80 Å. This suggests that the electron pair on the equatorial O$^-$ is high enough in energy to introduce electrons into the antibonding orbital of the 3c–4e O—P—O bond as approximately suggested by the orbitals shown in Scheme 4.

Coordination of phosphoranide **7a** to the iron Lewis acid to form **8** provides longer apical P—O bonds (1.824 Å, avg.) than were observed for phosphorane oxide anion **10**. This does suggest that the iron species is not only a Lewis acid coordinating to the electron pair of the phosphoranide. It is also a better pi-donor to the O—P—O antibonding orbital than is the O$^-$ of **10**.

The ligand with four nitrogens usually acts as a bidentate ligand, as in **5** or **12**. It was found [7d] that protonation of the two apical nitrogens of **12** made the phosphoranide a monodentate ligand in **13** (Equation 3). The added chloride also made the platinum tetracoordinate in **13**. Protonation of the two apical nitrogens of the phosphorus in **13** makes these apical nitrogen ligands more electronegative than the equatorial nitrogen ligands, making the ligand more similar to the bidentate ligands we



SCHEME 4

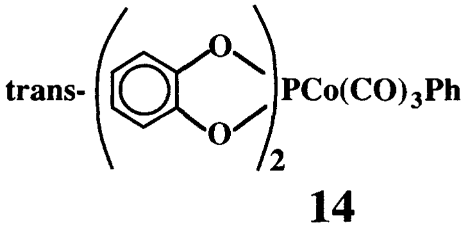


(3)

have used in **8** and **9**, etc., with apical oxygens and equatorial carbons.

Phosphoranides with equivalent apical and equatorial ligands usually act as bidentate ligands to the metals. The metallophosphorane (**14**), studied by Lattman et al. [7b, 7c] has four identical oxygens attached to the phosphorus, but are sufficiently stable between TBP and square pyramidal geometries to make the phosphoranide ligand monodentate (Scheme 5).

A variety of transition metal species have been found to react with phosphoranide **7a** to form a monodentate phosphoranide ligand to an isolated metal species. These will be published later. We are also considering that if another equatorial pi-donor ligand of a 10-P-5 species would be a stronger donor than the metal species, it could become unsymmetrical by breaking one of the apical P—O bonds. An example has been observed for a sulfur analog [18]. Sulfurane oxide **16** is treated with base changing the TBP 10-S-5 species to 8-S-4 species **17** because the —CH_2^- ligand is a very good pi-donor, putting enough electron density into the antibonding O—S—O orbital to cleave one of the S—O apical bonds (Equation 4). No such example has yet been seen for the phosphorus analogs.



14

SCHEME 5

EXPERIMENTAL

General Remarks

All reactions are carried out under an atmosphere of dry nitrogen in a dry box. Chemical shifts are reported on the δ scale, parts per million downfield from tetramethylsilane (for ^1H) or fluorotrichloromethane (for ^{19}F) or from an external standard 85% H_3PO_4 in H_2O (for ^{31}P). Elemental analyses are within 0.4% of the theoretical values calculated for the listed elements.

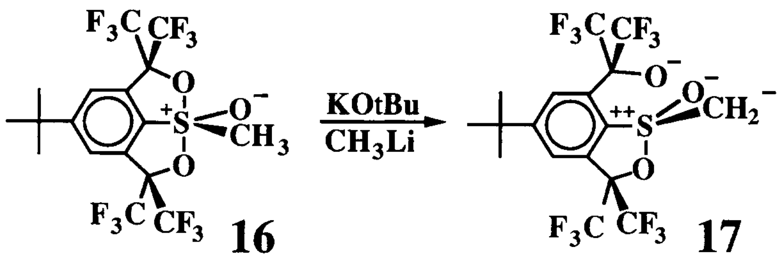
Solvents and Starting Materials

Hydridophosphorane was prepared as described previously [3]: ^1H NMR ($CDCl_3$) δ 8.38 (d, 1, J = 728.4 Hz, PH), 8.30 (dd, 2, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 12 Hz, PCCH), 7.75 (m, 6, PCC(R)CH and PCCCHCH); ^{19}F NMR ($CDCl_3$) δ −75.06 (q, 6, J = 9.49 Hz), −76.32 (dq, 6, $^4J_{PF}$ = 3.4 Hz, $^4J_{FF}$ = 9.49 Hz); ^{31}P NMR ($CDCl_3$) δ −48.2 (d, J_{PH} = 728.4 Hz).

Ether, hexane, and tetrahydrofuran were dried by distillation from sodium–benzophenone. Pentane was dried over a Na/K alloy and methylene chloride was distilled from calcium hydride.

Tetrabutylammonium Bis[α,α-bis(trifluoromethyl)benzenemethanolato (2 –)-C^2,O]-Phosphoranide (1 –), 7b

Hydridophosphorane **6** (0.251 g, 0.486 mmol) was dissolved in 3 mL of tetrahydrofuran and KH (0.24 g, 0.599 mmol) was added. Potassium phosphoranide, **7a**, was filtered off after 10 min: ^1H NMR (THF-d_8) δ 8.21 (d, 2, J = 7.25 Hz, PCCH), 7.44 (d, 2, J = 7.25 Hz, PCC(R)CH), 7.29 (t, 2, J = 7.25 Hz,



(4)

PCCCCH), 7.24 (t, 2, J = 7.25 Hz, PCCCH); ^{19}F NMR (THF-d_8) δ -73.41 (q, 6, J = 9.4 Hz), -75.84 (dq, 6, $^4J_{PF}$ = 13.8 Hz, $^4J_{FF}$ = 9.46 Hz); ^{31}P NMR (THF-dg) δ 32.95 (sep, $^4J_{PF}$ = 13.8 Hz).

Tetrabutylammonium chloride (0.135 g, 0.486 mmol) in 3 mL of tetrahydrofuran was added to **7a** at room temperature. After 1 h, the mixture was filtered in the dry box to remove KCl. Solvent was removed by vacuum and white solid was recrystallized from tetrahydrofuran/hexane to give **7b** (0.3 g, 0.396 mmol, 81.5%): mp 153.5–154.5°C; ^{1}H NMR (THF-d_8) δ 8.25 (d, 2, J = 7.5 Hz, PCCH), 7.40 (d, 2, J_{HH} = 7.5 Hz, PCC(R)CH), 7.23 (t, 2, J_{HH} = 7.5 Hz, PCCCCH), 7.15 (t, 2, J_{HH} = 7.5 Hz, PCCCH), 3.26 (m, 8, NCH_2), 1.61 (m, 8, $NCCH_2$), 1.30 (m, 8, $NCCCH_2$), 0.91 (t, 12, CH_3); ^{19}F NMR (THF-d_8) δ -73.32 (A_3B_3, 6, J = 9.4 Hz), -75.32 (dq, 6, $^4J_{PF}$ = 15.2 Hz, $^4J_{FF}$ = 9.4 Hz); ^{31}P NMR (THF-d_8) δ 28.41 (sep, $^4J_{PF}$ = 15.2 Hz). Anal. ($C_{34}H_{44}NF_{12}O_2$) C, H, N.

Metal Species Used to Form **8** *and* **9**

$CpFe(CO)_2I$ was purchased from Alfa Products. ^{1}H NMR ($CDCl_3$) δ 5.05 (s, Cp); ^{13}C (THF-d_8) δ 214.85 (s, CO), 85.58 (s, Cp).

$BrAu(PEt_3)$ was purchased from Strem Chemicals. ^{1}H NMR ($CDCl_3$) δ 1.86 (dq, 6H, $^3J_{HH}$ = 7.6 Hz, $^2J_{PH}$ = 10.2 Hz), 1.21 (dt, 9H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 18.84 Hz).

Dicarbonyl(cyclopentadienyl) Bis[α,α-bis(trifluoromethyl)benzenemethanolato (2−)-C^2,O]Phosphoranide iron (2+), **8**

Potassium phosphoranide **7a** (0.39 g, 0.62 mmol was dissolved in 4 mL of ether and dicarbonyl(cyclopentadienyl)iodo iron in 2 mL of ether was added. The reaction mixture was filtered after 1 h and solvent was removed by vacuum. A yellowish red solid was recrystallized from methylene chloride/hexane to give **8** (0.35 g, 0.51 mmol, 82.3%): mp 180–181°C; ^{1}H NMR ($CDCl_3$) δ 8.45 (t, 2, J = 8.7 Hz, PCCH), 7.6 (m, 6, PCC(R)CH, PCCCHCH), 4.86 (s, 5, Cp); ^{19}F NMR ($CDCl_3$) δ -74.07 (A_3B_3, J = 9.93 Hz), -74.46 (A_3B_3, J = 9.93 Hz); ^{31}P NMR ($CDCl_3$) δ 14.7 (s); ^{13}C (THF-d_8) δ 213.43 (s, $^2J_{CP}$ = 39.64 Hz, CO), 210.56 (s, $^2J_{Cp}$ = 28.65 Hz, CO), 141.88 (d, $^1J_{CP}$ = 101.1 Hz, $^2J_{CH}$ = 6.7 Hz, PC), 136.7 (d, $^1J_{CH}$ = 167 Hz, $^3J_{CH}$ = 9.1 Hz, PCC(R)C), 134.22 (d, $^2J_{CP}$ = 12.9 Hz, PCC(R)), 131.56 (d, $^1J_{CH}$ = 161.85 Hz, $^2J_{CP}$ = 12.6 Hz, $^3J_{CH}$ = 7.3 Hz, PCC), 132.29 (s, $^1J_{CH}$ = 162.3 Hz, PCC(R)CC), 125.55 (d, $^1J_{CH}$ = 164.8 Hz, $^3J_{CP}$ = 8.1 Hz, PCCC), 124.54 (dq, $^1J_{CF}$ = 289.7 Hz, $^3J_{CP}$ = 5.3 Hz, CF_3), 124.12 (dq, J_{CF} = 289.7 Hz, $^3J_{CP}$ = 5.3 Hz, CF_3), 87.52 (s, 5C, J_{CH} = 182.79 Hz, Cp), 83.77 (d sep, $^2J_{CF}$ = 30.44 Hz, $^2J_{CP}$ = 9.39 Hz, POC), IR ($CHCl_3$) MCO (cm^{-1}); 2045, 1992. Anal. ($C_{25}H_{13}O_4F_{12}PFe$) C, H.

Triethylphosphine Bis[α,α-bis(trifluoromethyl)benzenemethanolato (2−)-C^2,O]Phosphoranide Gold (1+), **9**

Hydridophosphorane **6** (0.5 g, 0.969 mmol) was dissolved in 5 mL of tetrahydrofuran and KH (0.047 g, 1.2 mmol) was added. The mixture was filtered after 10 min. The $BrAuPEt_3$ (1+) (0.39 g, 0.987 mmol) in 5 mL of tetrahydrofuran was added dropwise to the phosphoranide solution at room temperature. The reaction mixture was filtered after 35 min and solvent was removed by vacuum. The white solid was recrystallized from methylene chloride/hexane to give **9** (0.65 g, 0.78 mmol, 80.8%): mp 206–208°C; ^{1}H NMR ($CDCl_3$) δ 8.33 (t, 2, J = 8.8 Hz, PCCH), 7.65 (brd, 2, J_{HH} = 6.7 Hz, PCC(R)CH), 7.53 (m, 4, PCCCHCH), 1.75 (dq, 2, $^2J_{PH}$ = 15.8 Hz, $^3J_{HH}$ = 7.66 Hz, $^4J_{PH}$ = 2.9 Hz, PCH_2), 1.12 (dt, 3, $^3J_{PH}$ = 17.05 Hz, $^3J_{HH}$ = 7.66 Hz, $^5J_{PH}$ = 1.0 Hz, PCH_3); ^{19}F NMR ($CDCl_3$) δ -74.36 (q, 6, J = 9.5 Hz), -75.37 (dq, 6, J_{FF} = 9.5 Hz, J_{PF} = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ 48.3 (d sep, 1, $^4J_{PF}$ = 6.10 Hz, $^2J_{PP}$ = 544.05 Hz), 38.3 (d, 1, $^2J_{PP}$ = 544.05 Hz). Anal. ($C_{24}H_{23}O_2P_2F_{12}Au$) C, H.

X-Ray Structure Determination

Crystal Growth. Crystals of **8** were obtained by recrystallization from methylene chloride/hexane and slow cooling.

Crystal Data. The information on the crystal data and summary of the structure determination method are given in Table 3. The X-ray data were obtained by the Siemens Facility in Madison, Wisconsin by Dr. Charles F. Campana.

The complete data obtained for the X-ray structure of **8**, which is not all included in this paper, is being deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW England, from whom a copy can be obtained.

TABLE 3 Structure Determination Summary

Crystal Data	
Empirical Formula	$C_{25}H_{13}O_4F_{12}PFe$
Color; Habit	Orange prism
Crystal Size (mm)	0.40 × 0.20 × 0.20
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	a = 17.907(10) Å b = 16.818(6) Å c = 18.930(11) Å β = 115.10(4)°
Volume	5133(4) Å^3
Z	8
Formula Weight	692.2
Density (calc.)	1.791 Mg/m^3
Absorption Coefficient	0.764 mm^{-1}
F(000)	2752
Data Collection	
Diffractometer used	Siemens R3m/V
Radiation	Mo$K\alpha$ (λ = 0.71073 Å)
Temperature (K)	295
Monochromator	Highly oriented graphite crystal
2θ Range	3.0° to 45.0°
Scan Type	Wyckoff
Scan Speed	Variable; 4.00° to 15.00°/min. in ω
Scan Range (ω)	1.00°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	2 measured every 98 reflections
Index Ranges	$0 \leq h \leq 21, 0 \leq k \leq 20, -22 \leq l \leq 20$
Reflections Collected	9821
Independent Reflections	9152 (R_{int} = 3.02%)
Observed Reflections	5138 ($F > 6.0\,\sigma(F)$)
Absorption Correction	N/A
Solution and Refinement	
System Used	Siemens SHELXTL PLUS (MicroVAX II)
Solution	Direct methods
Refinement Method	Full-matrix least-squares
Quantity Minimized	$\Sigma w(F_o - F_c)^2$
Absolute Configuration	N/A
Extinction Correction	$\chi = 0.00009(2)$, where $F^* = F\,[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0004F^2$
No. of Parameters Refined	776
Final R Indices (obs. data)	R = 4.29%, wR = 4.88%
R Indices (all data)	R = 9.25%, wR = 6.68%
Goodness-of-Fit	1.34
Largest and Mean Δ/σ	0.173, 0.028
Data-to-Parameter Ratio	6.6:1
Largest Difference Peak	0.32 eÅ^{-3}
Largest Difference Hole	−0.29 eÅ^{-3}

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REFERENCES AND NOTES

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