Direct Observation of Phosphoranide Anions. Extremely Stable P–H Dioxyphosphoranes Containing Two C–P Bonds

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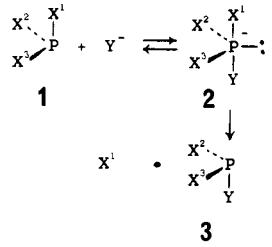
Abstract: Two very stable P–H phosphoranes, **13** and **19**, each containing two aryl and two alkoxy ligands, are prepared by $LiAlH_4$ reduction of spirobicyclic phosphonium salt **12** or reaction of PCl_3 with the Grignard reagent made from bromo alcohol **18**, respectively. Evidence is presented for the intermediate formation of tetracoordinate trigonal bipyramidal phosphoranide anions, conjugate bases of the P–H phosphoranes, in these syntheses. The phosphoranide anions **9** and **24**, produced by deprotonation of P–H phosphorane **13** or **19** with $LiAlH_4$, are directly observed by ^1H and ^{31}P NMR spectroscopy. Phosphoranide **9** is alkylated by benzyl bromide to give phosphorane **17**. The lithium derivative of phosphoranide **9** is not air sensitive but the sodium derivative is rapidly air oxidized to give the sodium phosphoranoxide **7**. The P–H phosphoranes (**13** and **19**) are not oxidized by H_2O_2 in $CHCl_3$, in contrast to the easy oxidation of tetraoxy or tetraaryl P–H phosphoranes, suggesting that essentially none of the open-chain tricoordinate phosphorus tautomers are in equilibrium with the P–H phosphoranes. We present ^1H, ^{19}F, and ^{31}P NMR, infrared spectroscopic, and mass spectrometric data in support of these findings.

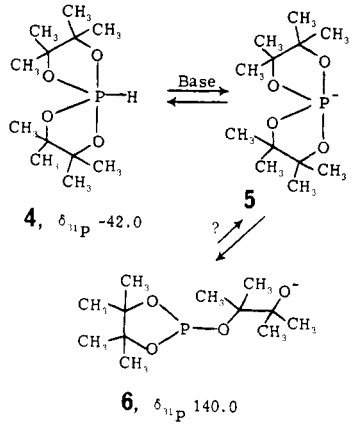
Nucleophilic displacements at tetracoordinate phosphorus have been extensively studied,[2] but little is known about the mechanism of the synthetically useful nucleophilic displacement at tricoordinate trivalent phosphorus,[3] such as that converting **1** to **3**. Tetracoordinate trigonal bipyramidal (TBP)



1 **2** **3**

intermediates or transition states, such as **2**, have been suggested.[4] A detailed study aimed at finding evidence for such an intermediate could find no evidence requiring its involvement in such substitution reactions.[5]

Two cyclic phosphoranide anions, e.g., **5**,[6] conjugate bases of the corresponding P–H phosphoranes, have been postulated as the products of deprotonation of P–H phosphoranes.[6,7] An equilibrium, e.g., of **5** and **6**, has been suggested.[6,7] In the single

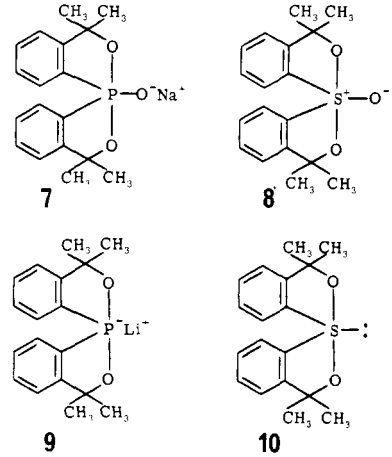


4, $\delta_{^{31}P}$ -42.0 **5** **6**, $\delta_{^{31}P}$ 140.0

study[6] in which ^{31}P NMR data were collected, the P^{III} alkoxide structure **6** ($\delta_{^{31}P}$ 140.0) appears to be the principal species present if there is indeed a fast equilibrium between **5** and **6**.

Most of the known P–H phosphoranes are oxyphosphoranes.[8] Nitrogen ligands are also common,[9] especially oxazaphosphoranes containing a P–H bond.[8] Carbon ligands are quite rare in this series,[10] and the only known tetraaryl P–H phosphorane is sensitive to light and base.[7] In general, the known P–H phosphoranes exhibit an equilibrium between P^V and tautomeric P^{III} structures, such as that suggested for **5** and **6**. The reversible intramolecular oxidative addition of O–H or N–H to P^{III} is characteristically a rapid process at ambient temperature.

We have recently reported[11] the synthesis of the novel sodium phosphoranoxide **7**, the stability of which was predicted by analogy with the stable sulfurane oxide[12] **8** which is isoelectronic with the anion of **7**. We were also successful in extending this analogy to bromoalkoxyphosphoranes,[13] and very



7 **8** **9** **10**

recently we have directly observed[14a] lithium phosphoranide **9**, which is isoelectronic with stable sulfurane **10**.[14b] We now report details of this study and additional syntheses and reactions centered around two stable P–H phosphoranes which bear two carbon and two oxygen ligands.

Results and Discussion

Synthesis and Reactivity. Hydroxyphosphorane[11] **11**, the conjugate acid of **7**, or the olefin phosphine oxide[11b] **14** reacts with trifluoromethanesulfonic (triflic) acid to give the stable spirobicyclic dioxyphosphonium triflate **12**.[11b] This dioxyphosphonium salt is reduced by lithium aluminum hydride to produce the tetracoordinate TBP lithium phosphoranide, **9**. Protonation of **9** gives stable P–H phosphorane **13** (Scheme I).

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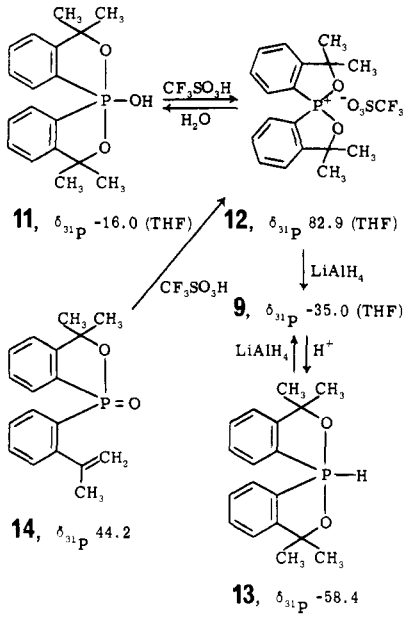
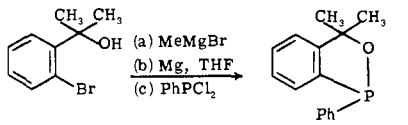
Scheme I



No spectroscopic evidence was found for the presence at equilibrium with either **9** or **13** of any detectable amount of the tautomeric open-chain P^{III} structures. This is evidenced even more convincingly by the inertness of **13** toward oxidation by H_2O_2 in $CHCl_3$. Tetraoxy P–H phosphoranes are oxidized even by a mild oxidizing agent such as dimethyl sulfoxide,[15] presumably through reaction of the open-chain P^{III} tautomer.

A suitable model for the possible P^{III} open-chain tautomer of either **9** or **13** is prepared from phenylphosphonous dichloride as shown below.[13] The cyclic phosphinite **15** (δ_{31P} 113.0)

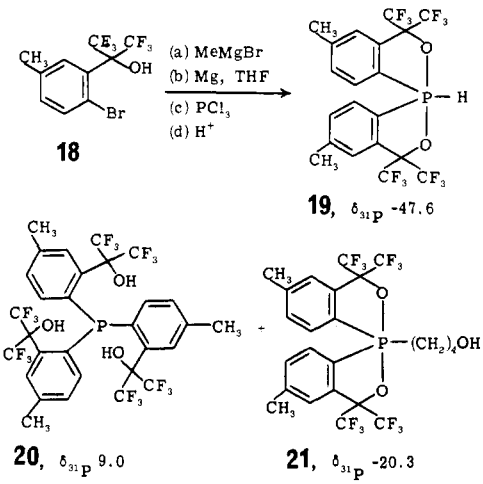


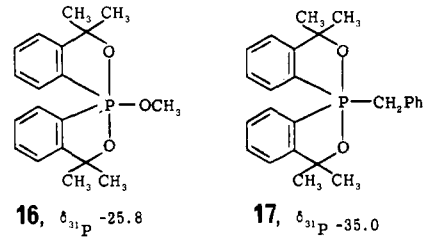
15, δ_{31P} 113.0

is, as expected, sensitive to air oxidation, giving the corresponding phosphinate.[13] The low-field ^{31}P chemical shift of **15** provides clear confirmation of the postulated tetracoordinate and pentacoordinate structures of **9** and **13**, respectively.

Lithium phosphoranide **9** is stable toward air oxidation under normal conditions. Attempts to observe the sodium derivative of **9**, however, were unsuccessful in the presence of air. Deprotonation of **13** in THF by sodium amide (accompanied by NH_3 evolution) or sodium hydride (H_2 evolution) in an NMR tube without exclusion of air leads to the formation of the sodium phosphoranoxide **7**. Initially, a mixture of **7** and **13** is observed. In this mixture the typical ^{31}P NMR doublet of **13** has exactly the same δ and $^1J_{HP}$ values as the pure **13**. Our failure to observe line broadening in the ^{31}P NMR of this mixture, despite the large (23.4 ppm) chemical shift difference between **9** and **13** and the large (680 Hz) value of the ^{31}P–H coupling constant, provides clear evidence for the inability of the phosphoranoxide **7** to deprotonate **13** and points to a pK_a for **13** much greater than the pK_a (10–11) established for **7**. Phosphoranoxide **7** is obtained in a similar manner from phosphonium triflate **12** and sodium hydride in THF in the presence of air. These reactions are presumably mediated by the sodium analogue of phosphoranide **9** which is apparently very sensitive to air oxidation, leading eventually to **7**. This was confirmed both by ^{31}P NMR and by quenching the reaction with methyl iodide, giving the already known[11b] methoxyphosphorane **16**. It should be noted that H–D exchange of **13** with a tenfold excess of CH_3OD was complete at room temperature before the NMR spectrum was obtained (ca. 10 min).

Scheme II



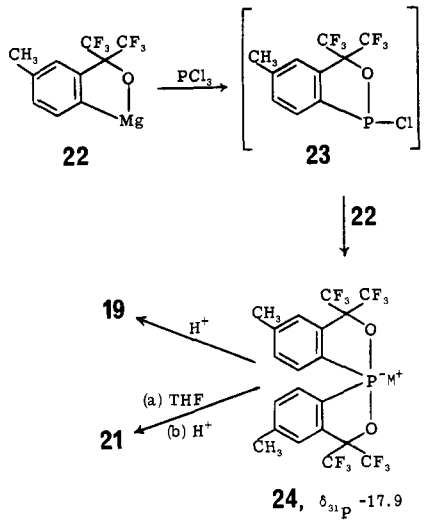


Lithium phosphoranide **9** is also obtained from the reaction of P–H phosphorane **13** and lithium aluminum hydride. This transformation can be reversed by hydrochloric acid. Lithium phosphoranide **9** is alkylated by benzyl bromide in THF at ambient temperature within 3 days. The benzylphosphorane **17** obtained in this reaction exhibits identical ^1H and ^{31}P NMR spectra with those of a sample made from phosphonium salt **12** and benzylmagnesium chloride. In the latter reaction, however, **17** is accompanied by ca. 30% of olefin **14**.

The Grignard reagent prepared from 1-methyl-1-(2-bromophenyl)ethanol[11] reacts with phosphorus trichloride to give a low yield of **13** (in an analogy to Scheme II). This synthetic route is not efficient for the synthesis of **13**. A complex mixture is produced which also contains olefin **14**. This synthetic approach, however, is much more successful in the preparation of another P–H phosphorane, **19** (Scheme II). The synthesis of the starting bromo alcohol **18** has recently been described.[11b] The Grignard reagent prepared from the bromo alcohol **18** (represented here as **22**, although other formulations are equally plausible) reacts with phosphorus trichloride in THF in a nucleophilic displacement at tricoordinate phosphorus to give products **19–21**, which were isolated and characterized.

Phosphine **20** is the conventional product one might expect in this reaction. The two phosphoranes, **19** and **21**, are more interesting in the context of our study of phosphoranide anions. It is reasonable to suggest that these two phosphoranes are formed from the phosphoranide anion (Scheme III) which is, in turn, formed by the reaction of **22** with intermediate **23**. This phosphoranide either reacts with the solvent THF by a nucleophilic attack at C-α to give **21** or acts as a base to abstract a proton from solvent to give P–H phosphorane **19**. This evidence for marked nucleophilicity of a phosphoranide has a parallel in the reaction of phosphides with epoxides to give hydroxyalkylphosphines.[16] Strongly basic or nucleophilic species are known[17] to either deprotonate THF to give fragmentation products or cleave this ether by α-attack leading to 4-substituted 1-butanols.

Scheme III



Direct observation of the lithium derivative of phosphoranide **24** by ^1H, ^{19}F, and ^{31}P NMR is achieved by deprotonation of the P-H phosphorane **19** with $LiAlH_4$ in THF. Evidence for a near-zero equilibrium concentration of the open-chain P^{III} tautomer is available for **19,** as for **13,** in the failure of 30% hydrogen peroxide to effect its oxidation to hydroxyphosphorane.

Spectroscopy and Structure. The two stable P-H phosphoranes **13** and **19** are chiral. Consequently, the two pairs of diastereotopic methyls in **13** are nonisochronous, as are the CF_3 groups in **19.** This is manifested in chemical shift nonequivalence of the diastereotopic groups. The CF_3 groups give rise to a quartet of doublets ($^4J_{FF}$ = 9, $^4J_{FP}$ = 3 Hz) and a quartet ($^4J_{FF}$ = 9, $^4J_{FP}$ = 0 Hz) in the ^{19}F NMR spectrum of **19.** The typical high-field $\delta_{^{31}P}$ values (−58.4 and −47.6)[18] and the characteristically large $^1J_{HP}$ (680 and 730 Hz) are all consistent with the P-H pentacoordinate TBP structures of **13** and **19,** respectively. Support for the suggestion that these structures may be considered to be near the TBP geometry which is illustrated, rather than a structure nearer the square pyramid extreme often seen,[19] stems from the low-field chemical shift of the protons ortho to phosphorus in the condensed benzene rings. Data accumulated in this laboratory[20] consistently show that such protons in TBP molecules centered around S,[20a] I,[20b] Si[20c] or P[11,13] are seen at a relatively low field. This deshielding is believed to arise from the close proximity of these protons to the axial hypervalent bond.

The larger P-H coupling constant in **19,** as compared with **13** (Δ^1J_{HP} = 50 Hz), is consistent with s character at P and a stronger P-H bond in **19** than in **13.** This is also supported by the observation of P-H stretching frequencies in the infrared spectra of **13** and **19** at 2360 and 2460 cm^{-1}, respectively.

The ^{31}P NMR chemical shift for phosphorane **13** (−60.1 ppm, THF) is 25.1 ppm to higher field than that for its conjugate base, phosphoranide **9.** This appears to imply a greater dependence of ^{31}P chemical shift on coordination number than on negative charge. A similar upfield shift is observed upon protonation of diphenylphosphide anion to yield diphenylphosphine.[18] The ^1H NMR spectra of phosphoranides **9** and **24,** when compared with those of **13** and **19,** show all the aromatic proton peaks at higher field, especially those for protons ortho and para to P (see Experimental Section). This is consistent with the assigned structures, and with negative charge delocalization into the aromatic rings. Completely analogous correlations are found in the ^{31}P and ^1H NMR spectra of **19** and of the lithium derivative of **24.**

The mass spectra[21] of stable phosphoranes **13** and **19** show the corresponding molecular ions (5% of the base peaks). All of the other derivatives we have prepared in the 1,1′-spirobi[3*H*-2,1-benzoxaphosphole] series show negligible M − 1 ions in their mass spectra. The M − 1 ions in the mass spectra of the P-H phosphoranes **13** and **19** are three to four times more abundant (15–20% of the base peak) than the molecular ions. This is a manifestation of the relative stability of the spirocyclic dioxyphosphonium cations derived from the P-H phosphoranes. The open-chain P^{III} tautomers of **13** and **19** are alcohols, which would be expected[22] to show negligible molecular and M-H ions. The mass spectra of **13** and **19** may therefore be taken as evidence for the same (P^V) structures in the gas phase as in solution.

The unusual stability of P-H phosphoranes **13** and **19** and their conjugate bases, phosphoranides **9** and **24,** stems from a combination of stabilizing effects which are discussed for related hydroxyphosphoranes in the preceding paper.[11b]

The markedly enhanced stability of diaryldialkoxy P-H phosphoranes (**13, 19**) or phosphoranides (**9, 24**), when compared with that of their tetraoxy (**4** or **5**)[6,7] or tetraaryl[7] analogues, can be explained by suggesting that the less symmetrical substitution pattern in **13, 19, 9,** and **24** enhances the difference in electronegativity between the central phosphorus atom and the apical substituents. Such a difference in electronegativity is a factor favorable to the formation of three-center four-electron bonds.[23]

Experimental Section

A description of the general procedures used for spectra, analyses, and purifications is to be found in the preceding paper.[11b]

3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (13). Phosphonium salt **12** (4.5 g) was suspended in dry THF (70 mL) and $LiAlH_4$ was added in five portions (a total of 1 g) with external cooling. Hydrogen was immediately evolved. This mixture was stirred for 0.5 h at ambient temperature, then absolute EtOH (5 mL) was added dropwise at 0 °C, followed by 1:1 HCl (10 mL). The organic layer and a $CHCl_3$ (50 mL) extract were combined and washed with aqueous $NaHCO_3$ to give crude **13,** which was chromatographed on neutral alumina, eluting with benzene–ethyl acetate, 10:1. The crude product, however, was mounted on the column and left there for 16 h before further elution. After an unidentified impurity, phosphorane **13** was eluted (2.0 g, 57%), mp 99 °C: R_f 0.65 (neutral alumina–benzene); IR 2360 cm^{-1} (P-H); ^1H NMR δ 1.56 (6 H, s, Me), 1.62 (6 H, s, Me), 7.22–7.48 (6 H, m, HAr), 8.08–8.28 (2 H, m, H ortho to P), 8.48 (1 H, d, $^1J_{HP}$ = 680 Hz, HP); ^{31}P NMR δ −58.4 (d, $^1J_{HP}$ = 680 Hz); ^{31}P NMR (THF) δ −60.1 (d, $^1J_{HP}$ = 680 Hz); MS *m/e* 300 (M^+, 5%), 299 (M − H, 15%), 285 (M − Me, 100%), 267 (M − Me − H_2O, 15%), 147 (11%), 135 (18%). Anal. ($C_{18}H_{21}O_2P$) C, H, P.

Direct Observation of Lithium 3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (9). A. Phosphonium triflate[11b] **12** (36 mg) was added to THF-d_8 (0.4 mL), followed by $LiAlH_4$ (13 mg). ^1H NMR showed that the reaction was complete within 20 min: ^1H NMR (THF-d_8) δ 1.52 (6 H, s, Me), 1.83 (6 H, s, Me), 6.75–7.60 (8 H, m, HAr); ^{31}P NMR (THF) δ −35.0.

Treatment of **9** with concentrated HCl gave **13** (vide infra).

B. Phosphorane **13** (30 mg) was dissolved in THF-d_8: ^1H NMR δ 1.49 (6 H, s, Me), 1.56 (6 H, s, Me), 7.20–7.56 (6 H, m, HAr), 8.08–8.19 (2 H, m, H ortho to P), 8.36 (1 H, d, $^1J_{HP}$ = 680 Hz, HP). $LiAlH_4$ (10 mg) was added to the above solution and the ^1H and ^{31}P NMR spectra were identical with those described under A above. Protonation with 18% HCl regenerated **13** (^1H NMR).

1-Benzyl-3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (17). A. Phosphorane **13** (60 mg) was dissolved in THF-d_8 (0.4 mL) and $LiAlH_4$(20 mg) was added, followed by benzyl bromide (100 mg). After 3 days, the ^1H NMR confirmed the formation of **17:** ^1H NMR (THF-d_8) δ 1.28 (6 H, s, Me), 1.42 (6 H, s, Me), 3.57 (2 H, d, $^2J_{HP}$ = 18 Hz, CH_2), 6.80–7.40 (11 H, m, HAr), 8.13–8.36 (2 H, m, H ortho to P).

Partition of this solution between 1:1 HCl (5 mL) and $CHCl_3$ (8 mL) yielded phosphorane **17** (42 mg, 70%), mp 118 °C (pentane): ^1H NMR δ 1.31 (6 H, s, Me), 1.47 (6 H, s, Me), 3.64 (2 H, d, $^2J_{HP}$ = 18 Hz, CH_2), 6.90–7.40 (11 H, m, HAr), 8.15–8.37 (2 H, m, H ortho to P); ^{31}P NMR δ −36.0; MS *m/e* 390 (M^+, 0.01%), 375 (M − Me,

3%), 299 (M − C_7H_7, 8%), 182 (20%), 91 (100%); field desorption MS *m/e* 390 (M^+, 4%), 375 (M − Me, 30%), 299 (M − C_7H_7, 100%).

B. Phosphonium triflate[11b] **12** (0.1 g), dry THF (10 mL), and benzylmagnesium chloride [made from benzyl chloride (0.4 g) and Mg (0.1 g) in ether (8 mL)] were stirred for 10 min at ambient temperature, then treated with aqueous NH_4Cl (5 mL, 4 N). The organic layer and a $CHCl_3$ (10 mL) extract gave a mixture of **17** and **14** in the ratio of 5:2, determined from both the ^1H and ^{31}P NMR spectra. **17:** ^1H NMR δ 1.31 (6 H, s, Me), 1.47 (6 H, s, Me), 3.64 (2 H, d, $^2J_{HP}$ = 18 Hz, CH_2), 7.03–7.40 (11 H, m, HAr), 8.15–8.37 (2 H, m, H ortho to P); ^{31}P NMR −35.6. **14:** ^1H NMR δ 1.58 (3 H, s, Me), 1.64 (3 H, s, Me), 2.17 (3 H, m, MeC=C), 5.02 (1 H, M, CH), 5.24 (1 H, m, CH), 7.04–7.78 (8 H, m, HAr); ^{31}P NMR δ 44.2. This mixture was not further purified.

Reaction of 12 or 13 with Sodium Hydride. Addition of excess NaH to a suspension of **12** (100 mg), or a solution of **13** (100 mg) in dry THF (5 mL) gave reactions which were followed by ^{31}P NMR. Reaction of **13** with NaH was slow enough to allow observation of a mixture of **13** (δ_{31P} −60.1, d, $^2J_{HP}$ = 680 Hz) and the air oxidation product **7** (δ_{31P} −26.9).[11a] After 2 days the ^{31}P NMR spectrum indicated complete conversion of **13** to phosphoranoxide **7.** After excess CH_3I was added, and the mixture was left in the dark for 5 days, ^{31}P NMR showed complete conversion of **7** to methoxyphosphorane[11b] **16** (δ_{31P} −25.8). Filtration and evaporation of the solvent followed by extraction of the residue with pentane gave pure **16** (50–60 mg, 55–58%), identical with an authentic sample.[11b]

Attempted Synthesis of 13 from Phosphorus Trichloride. Methylmagnesium bromide (33 mL, 3.1 M in ether) was added to a THF (150 mL) solution of 1-methyl-1-(2-bromophenyl)ethanol (21.6 g), followed by magnesium turnings (2.5 g). This mixture was boiled for 2.5 h and cooled and PCl_3 (6.3 g) in THF (10 mL) was added dropwise. The mixture was boiled for 0.5 h, cooled, and treated with aqueous NH_4Cl (80 mL, 4 N). The organic layer and $CHCl_3$ (100 mL) extract were subjected to column chromatography on silica, eluting with 1:1 benzene–ethyl acetate, to give first crude **13** (0.8 g), contaminated with at least two unidentified byproducts. Next, the olefin **14** (2.4 g, 18%), mp and mmp 126 °C,[11b] was eluted. Crude **13** was characterized, without further purification, by its ^{31}P NMR (δ −58.4, d, $^1J_{HP}$ = 680 Hz), which collapsed to a singlet upon proton decoupling.

5,5′-Dimethyl-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*,2,1-benzoxaphosphole] (9), Tris[2-(1-trifluoromethyl-2,2,2-trifluoroethyl)phenyl]phosphine (20), and 5,5-Dimethyl-3,3,3′,3′-tetrakis(trifluoromethyl)-1-(ω-hydroxybutyl)-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (21). Methylmagnesium bromide (17.6 mL, 3.1 M in ether) was added to a THF (70 mL) solution of 1-(2-bromo-5-methylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol[11b] (**18,** 18.2 g), followed by magnesium turnings (1.32 g). This mixture was boiled for 4 h and cooled, and PCl_3 (3.4 g) in THF (10 mL) was added dropwise. The resulting mixture was boiled for 12 h, cooled, and treated with 1 N H_2SO_4 (25 mL). The organic layer and $CHCl_3$ (50 mL) extract gave crude product. Recrystallization from benzene (20 mL) gave phosphine **20** (3 g, 15%), mp 187–188 °C: ^1H NMR δ 2.48 (9 H, s, Me), 6.78 (3 H, dd, $^3J_{HH}$ = 9, $^3J_{HP}$ = 15 Hz, H ortho to P), 7.15–7.35 (3 H, m, HAr), 7.25 (3 H, s, OH), 7.61–7.78 (3 H, m, HAr); ^{31}P NMR δ +9.0; MS *m/e* 802 (M^+, 2%), 543 (M − H − ArH, 100%), 475 (M − Ar − CF_3, 80%), 222 (17%), 203 (10%), 189 (11%), 171 (11%), 151 (12%), 119 (18%), 91 (17%). Anal. ($C_{30}H_{21}F_{18}O_3P$) C, H, P.

The mother liquor from the recrystallization of **20** was chromatographed on neutral Al_2O_3, eluting with benzene. The first compound coming off the column was the P–H phosphorane **19** (2.4 g, 18%), mp 190 °C (pentane): R_f 0.9 (neutral alumina–benzene); IR 2460 cm^{-1} (P–H); ^1H NMR δ 2.50 (6 H, s, Me), 7.35–7.55 (4 H, m, HAr), 8.13 (2 H, dd, $^3J_{HH}$ = 8 Hz, H ortho to P), 8.40 (1 H, d, $^1J_{HP}$ = 725 Hz, HP); ^1H NMR (THF-d_8) δ 2.50 (6 H, s, Me), 7.50–7.65 (4 H, m, HAr), 8.13 (2 H, dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 12 Hz, H ortho to P), 8.40 (1 H, d, $^1J_{HP}$ = 725 Hz, HP); ^{19}F NMR (THF) ϕ 74.32 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3), 75.58 (6 F, dq, $^4J_{FF}$ = 9, $^4J_{FP}$ = 3 Hz, CF_3); ^{19}F NMR ϕ 74.90 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3), 76.17 (6 F, dq, $^4J_{FF}$ = 9, $^4J_{FP}$ = 3 Hz, CF_3); ^{31}P NMR (THF) δ −47.6 (d, $^1J_{HP}$ = 730 Hz); MS *m/e* 544 (M^+, 5%), 543 (M − H, 20%), 475 (M − H − CF_3, 20%), 181 (11%), 169 (13%), 131 (18%), 119 (21%), 69 (CF_3, 100%). Anal. ($C_{20}H_{13}F_{12}O_2P$) C, H, P.

The second compound eluted was phosphorane **21** (1.7 g, 10%), contaminated with ca. 10% of **9** (by ^{31}P NMR spectroscopy), which was not purified further: R_f 0.50 (neutral alumina–benzene); ^1H NMR δ 1.50 (4 H, m, CH_2), 2.30 (2 H, m, CH_2P), 2.47 (s, 6 H, Me), 2.76 (1 H, br s, HO), 3.50 (2 H, t, $^3J_{HH}$ = 6 Hz, CH_2O), 7.18–7.50 (4 H, m, HAr), 8.21 (2 H, dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 11 Hz, H ortho to P); ^{31}P NMR (THF) δ −20.3; field desorption MS *m/e* 616 (M^+).

***Direct Observation of Lithium* 5,5-Dimethyl-3,3,3′,3′-tetrakis(trifluoromethyl)-1,1′-spirobi[3*H*-2,1-benzoxaphosphole] (24, M = Li).** Phosphorane **19** (29 mg) was dissolved in THF-d_8 (0.4 mL): ^1H NMR δ 2.50 (6 H, s, Me), 7.50–7.65 (4 H, m, HAr), 8.15 (2 H, dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 12 Hz, H ortho to P), 8.40 (1 H, d, $^1J_{HP}$ = 725 Hz, HP). $LiAlH_4$ (10 mg) was added to this solution, which evolved molecular hydrogen: ^1H NMR δ 2.25 (6 H, s, Me), 6.89 (2 H, d, $^3J_{HH}$ = 8 Hz, H meta to P), 7.33–7.50 (4 H, m, HAr); ^{31}P NMR (THF) δ −17.9; ^{19}F NMR (THF) ϕ 73.80 (6 F, q, $^4J_{FF}$ = 9 Hz, CF_3), 75.10 (6 F, dq, $^4J_{FF}$ = 9, $^4J_{FP}$ = 3 Hz).

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