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Characterization of the first hexacoordinate phosphorus compound with S→P←S bonds

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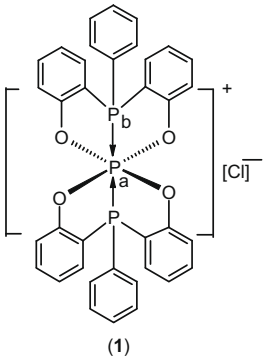
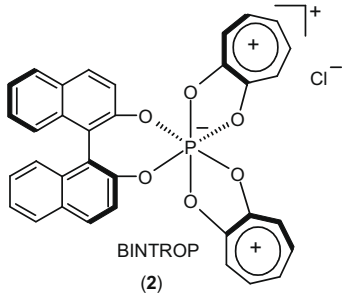
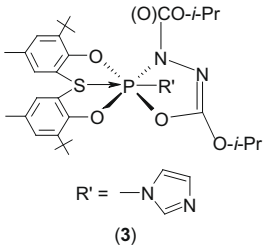
ABSTRACT

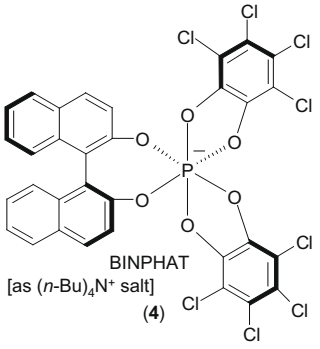
The first example of a hexacoordinate phosphorus compound $[S\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2]_2P^+(Cl^-\cdot C_3H_4N_2)$ with two S→P bonds is reported. This compound can be construed as an oxophosphonium salt with double intramolecular coordination by sulfur atoms. X-ray structure reveals a facial arrangement of the ligands with two coordinating sulfur atoms *cis* to each other. The S→P distance of 2.334 (1) Å is one among very short coordinate bond distances between sulfur and phosphorus.

Cyclic phosphorus compounds bearing hexacoordinate phosphorus [1] are much less numerous in number than analogous hexacoordinate metal complexes. However, there are several interesting examples of this class of compounds wherein phosphorus is cationic (e.g. **1**–**2**), neutral (e.g. **3**) or anionic (e.g. **4**). Compound **1**, reported by Cavell and coworkers several years ago, is a unique example in which two *trans* oriented $P^{III}\rightarrow P^{V}$ coordinate bonds exist [2]. Compounds **2** and **4**, reported by Lacour and coworkers, are useful as efficient NMR chiral shift reagents [3]. The neutral species **3** was synthesized by our group in connection with our efforts to check the reaction of P^{III} compounds with dialkylazodicarboxylates while probing the nature of intermediate species present in the first stage of the Mitsunobu reaction [4]. Numerous neutral hexacoordinate compounds with the $S\rightarrow PO_5$ or PO_4N skeleton have also been reported during the past decade by Holmes and coworkers [5]. These compounds are all formally hypervalent and we have been interested in such phosphorus derivatives [6]. In this context, we report herein the synthesis of a novel S→P←S compound with double coordination at phosphorus. Although the coordination can occur at acidic phosphonium center, coordination by two sulfur atoms onto a phosphorus, as reported here, is unprecedented.









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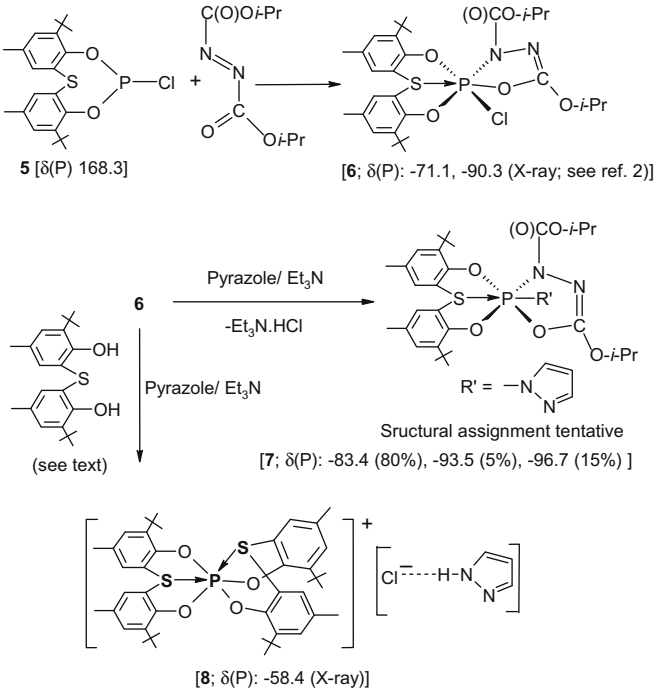
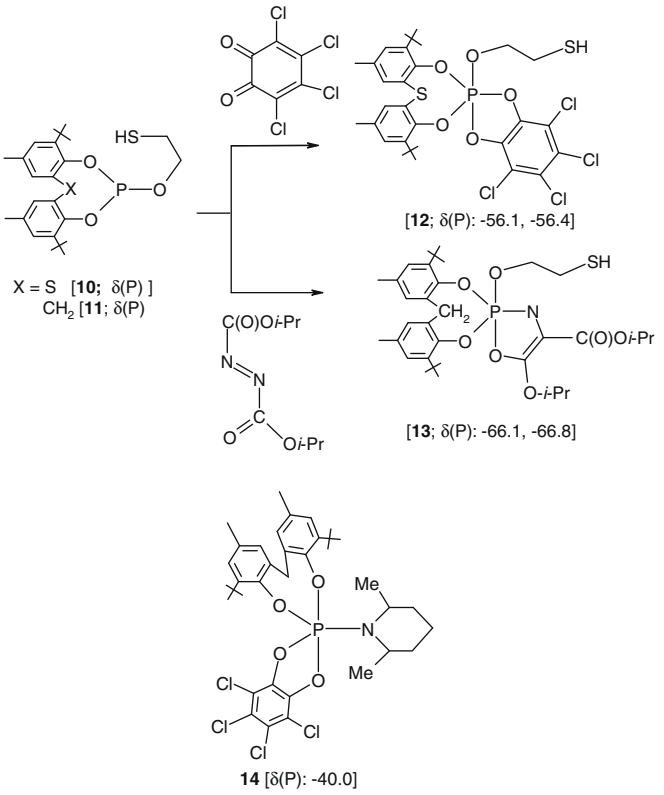
When S(6-*t*-Bu-4-Me-$C_6H_2O)_2PCl$ (**5**) [7,5c] was treated with DIAD, the hexacoordinate phosphorus compound **6** was formed [7]. When this *in situ* generated **6** was reacted with pyrazole, we obtained a crystalline compound **8** and subsequently another solid (labeled as **7**). The additional diol moiety in **8** must have come from ligand reorganization for which literature precedence is available [8]. The crystalline compound **8** [ca 10%; δ(P) −58.4] *exhibits two unusual coordinate* S→P *linkages* (Scheme 1; see below for X-ray structure). The phosphorus in this species can be termed as hypervalent [9]. This novel compound gave clean spectra with a single ^{31}P NMR signal at δ −58.4. In comparison to the P→P←P bonded **1** [δ ($P_{hexacoordinate}$) −107.8], this value for hexacoordinate phosphorus in **8** is much downfield, but it is known that sulfur connected phosphoranes do appear downfield [10]. In principle it should be possible to prepare compound **8** by starting with PCl_5 and two moles of the diol in the presence of pyrazole. However, we could not isolate it by this means (even in the presence of excess of pyrazole to drive the reaction forward) probably because of hydrolytic instability of the intermediates [^{31}P NMR evidence] [11].

The solid labeled as **7** showed three peaks in the ^{31}P NMR spectrum [δ −83.4 (80%), −93.5 (5%) and −96.7 (15%)]. There was some broadening in ^{31}P NMR spectrum at low temperatures, but we could not conclude whether **7** is a pure product or a mixture of products (^{1}H NMR was complicated). Multiple ^{31}P NMR signals indicating the existence of geometrical isomerism in solution for structurally (X-ray) characterized compounds are not uncommon for this class of compounds as is evident in the case of **6**. We can only say that at least one of the isomers is likely to be a species analogous to **3** [δ −89.8].

In an effort to compare these compounds with other sulfur containing phosphoranes, we have also conducted the oxidative addition reactions using **10–11** as shown in Scheme 2 and isolated compounds **12–13** [12]. Looking at the data as represented by **14** [13] and related compounds [4,6b,14,15], it is difficult to ascertain whether **12** and **13** have S→P coordination or not, but because the $-OCH_2CH_2SH$ group may not be able to render the phosphorus sufficiently acidic to have the hexacoordination we assign pentacoordination to **12–13**. So far we have not succeeded in obtaining suitable crystals of **12–13** for X-ray structure determination.



Scheme 1.



Scheme 2.

Compound **8** represents the first example of a hexacoordinate phosphorus compound with S→P←S double coordination (Fig. 1, Table 1) [16,17]. All previously known compounds had only one P←S bond. The geometry is essentially octahedral with facial arrangement of the two fused rings, but the two sulfur atoms are *cis* to each other. This arrangement is different from that observed in **1** wherein the two coordinating phosphorus atoms are *trans* to each other. The molecule crystallizes in the *C*2/*c* space group with only half the molecule in the asymmetric unit. The two equivalent P←S coordinate bonds are quite strong [2.334 (1) Å] and are comparable to that in the chloro precursor **6** [2.317 (1) Å] [4], but much shorter than several other neutral hexacoordinate compounds with

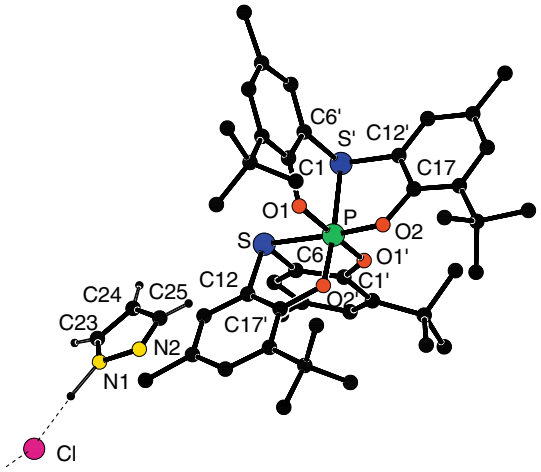


Fig. 1. Molecular structure of **8**, only selected atoms are labeled.

Table 1
Selected interatomic distances (Å) and angles (°) for 8 with esd's in parentheses.

P–O(1)	1.6694(16)	P–O(2′)	1.6351(17)
P–O(1′)	1.6694(16)	P–S	2.3343(9)
P–O(2)	1.6352(17)	P–S′	2.3343(9)
N1–H(N1)	0.86[a]	H(N1)···Cl	2.30[a]
N(1)···Cl	3.140(3)		
O(1)–P–O(1′)	173.59(12)	O(2)–P– S′	91.36(6)
O(1)–P–O(2)	94.20(8)	O(1′)–P–O(2′)	94.20(8)
O(1)–P–O(2′)	90.20(8)	O(1′)–P–S	88.71(6)
O(1)–P–S	86.53(6)	O(1′)–P– S′	86.53(6)
O(1)–P–S′	88.71(6)	S–P–O(2′)	91.36(6)
O(2)–P–O(1′)	90.20(8)	S–P–S′	83.90(4)
O(2)–P–O(2′)	93.39(12)	O(2′)–P–S′	175.19(7)
O(2)–P–S	175.19(7)		
N(1)–H(N1)···Cl	166.7[a]		

[a] H(N1) is fixed by geometry and hence for the corresponding distances/angles esd's are not given.

only one P←S bond [5]. Between the two sets of the P–O bonds, with O *trans* to S and O *trans* to O, the distances to the former are shorter. The essential difference in geometry between this S→P←S bonded compound **8** and Cavell's P→P←P compound **1** is that while the coordinating P atoms in **1** are *trans*, the coordinating sulfur atoms in our compound **8** are *cis* to each other as shown in Fig. 2. Both these compounds can be construed as oxophosphonium salts with additional two coordinate bonds for which there is no precedence. The stability of **8** is slightly enhanced by the hydrogen bonded chloride (to pyrazole NH) ion.

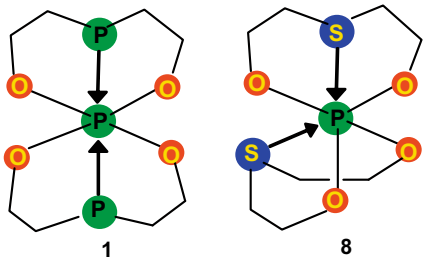


Fig. 2. A drawing showing the disposition of coordinating phosphorus atoms in **1** and sulfur atoms in **8**.

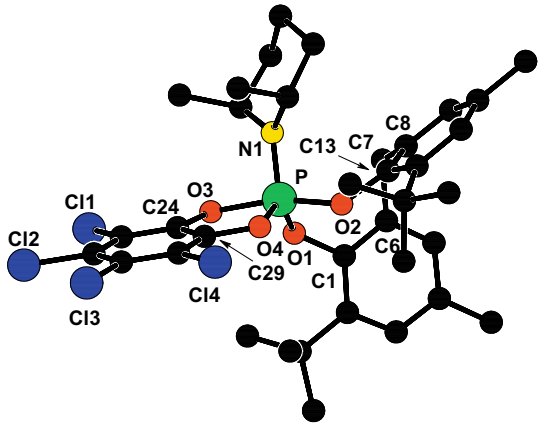


Fig. 3. Molecular structure of **14**·3/2C_4H_8O showing all non-hydrogen atoms; solvent atoms are not shown. Selected bond lengths (Å) and bond angles (°) P–O(1) 1.5966(18), P–O(2) 1.6505(18), P–O(3) 1.8012(18), P–O(4) 1.6587(18), P–N(1) 1.644(2), O(1)–P–O(2) 94.83(9), O(1)–P–O(3) 81.03(9), O(1)–P–O(4) 124.99(10), O(2)–P–O(3) 166.02(9), O(2)–P–O(4) 83.94(9), O(2)–P–N(1) 101.05(10), O(3)–P–O(4) 87.53(9), O(1)–P–N(1) 118.85(11), O(3)–P–N(1) 92.60(10), O(4)–P–N(1) 115.25(11).

The X-ray structural analysis of **14** (Fig. 3) was performed mainly for comparison of the solution state ^{31}P NMR and solid state structures as mentioned above [16–18]. Here, the phosphorus has highly distorted trigonal bipyramidal geometry (more towards square pyramidal). It is likely that the two methyl groups of the 2,6-lupetidine group projecting in the same direction have distorted the geometry at phosphorus significantly.

To summarize, the first example of a hexacoordinate phosphonium salt **8** with two S→P bonds is reported. Apart from the characterization of a new type of structural entity, this observation should be helpful in assessing the coordination tendencies of phosphorus to form a hexacoordinate state that might assist in describing the mechanistic action of phosphoryl transfer enzymes [19].

Acknowledgements

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Appendix A. Supplementary material

CCDC 722265 and 722394 contain the supplementary crystallographic data for compounds **8** and **14**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.04.013.

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[7] (a) *S(6-t-Bu-4-Me-C_6H_2O)$_2$PCl* (***5***): This was prepared by treating PCl_3 with the diol in the presence of Et_3N {1:1:2 molar ratio] in toluene or by simply heating PCl_3 with the diol {1:1 molar ratio) under neat conditions with stirring at 100 °C (purity >95%). Mp: 174–176 °C {lit 174–176 °C [5c]}; ^{31}P NMR: δ 168.3 {lit 168.4 [5c]}.;
(b) *[S{6-t-Bu-4-Me-C_6H_2O}$_2$]$_2$P$^+$Cl$^-$.($C_3H_4N_2$)* (***8***) *[and the solid **7**]*: To a stirred solution of **5** (0.92 g, 2.2 mmol) in toluene (20 mL) at −78 °C was added DIAD (0.45 g, 2.2 mmol) through a syringe over a period of 5 min. The reaction mixture was brought to room temperature and stirred for 12 h; then the solvent was evaporated and the residue crystallized from heptane-dichloromethane (2 + 0.5 mL) mixture. This reaction mixture showed δ (^{31}P) 71.0, −90.3 (br) corresponding to **6**. When the reaction was performed in the presence of pyrazole (2.2 mmol) using the *in situ* generated **6**, compound **8**

separated out, followed by **7** (ca 0.5 g). Yield (**8**): 0.2 g (ca 10%). ^{1}H NMR: δ 1.02 and 1.53 (2 s, 36 H, Ar-C(CH_3)$_3$), 2.36 (s, 12 H, ArCH_3), 4.83 (m, 2 H, OC*H*(CH_3)$_2$), 6.38 (br s, 1 H, pyrazolyl-*H*) 7.23-7.64 (m, 5 H, Ar-*H*), 8.03 and 8.12 (2 br s, 2 H, pyrazolyl-*H*); ^{13}C NMR: δ 21.6 (s, ArCH_3), 29.0 and 29.4 (2 s, C(CH_3)$_3$), 34.9 and 35.3 (2 s, *C*(CH_3)$_3$), 129.0, 129.1, 129.5, 133.1, 133.7, 134.4, 135.5, 137.8; ^{31}P NMR: δ −58.4; Anal. Calcd. for $C_{50}H_{64}ClN_4O_4PS_2$: C 65.53; H, 6.99; N, 6.11, S 6.99. Found: C, 65.42; H, 7.04; N, 6.04; S, 6.88. Although this compound could be detected in another reaction containing additional diol, isolation of a pure material could not be accomplished in that case.

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[11] For the reaction using 1:2:1 and 1:2:5 stoichiometry of PCl_5, diol and pyrazole, the ^{31}P NMR spectrum [δ(P): −3.4, −13.7, −18.4 with the last one predominating when a higher stoichiometry of pyrazole was used] of the resulting mixture showed peaks only in the tetracoordinate region.

[12] [a] *[X{6-t-Bu-4-Me-C_6H_2O}$_2$]POCH$_2$CH$_2$SH [X = S (**10**), CH$_2$ (**11**)]*: Compound [CH_2{6-*t*-Bu-4-Me-C_6H_2O}$_2$]PCl (**9**) was prepared by a method reported by us before [6a]. Compounds **10** and **11** were prepared in ⩾80% yield by treating **5** or **9** with 2-mercapto ethanol in the presence of Et_3N in toluene. *Compound **10***: Semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 18H, 2CH(CH_3)$_3$), 2.28 (s, 6H, ArCH_3), 2.89–2.91 (m, 2H, SCH_2), 4.26–4.28 (m, 2H, OCH_2), 7.12–7.34 (4H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 26.2 (d, *J* = 5.7 Hz), 30.0, 35.2, 65.9 (d, *J* = 27.4 Hz), 123.0 (d, *J* = 2.8 Hz), 128.3, 129.1 (d, *J* = 26.0 Hz) 133.5, 140.6, 153.4 (d, *J* = 7.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ = 142.7; LC/MS *m/z* 464 [M+1]$^+$. *Compound **11***: mp 160–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 18H, 2CH(CH_3)$_3$), 2.29 (s, 6H, ArCH_3), 2.93–2.99 (m, 2H, SCH_2), 3.35–3.38 (m, 1H, CH_ACH$_B$), 4.27–4.31 (m, 1H, CH$_A$CH_B), 4.53–4.58 (m, 2H, OCH_2), 7.01–7.28 (4H, Ar *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.5, 31.0, 34.7 (d, *J* = 5.7 Hz), 45.5, 64.7 (d, *J* = 4.9 Hz), 126.8, 128.8, 133.7, 136.2 (d, *J* = 3.7 Hz), 142.0 (d, *J* = 3.5 Hz), 145.8 (d, *J* = 7.4 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ = 129.2; LC/MS *m/z* 445 [M+1]$^+$.;

[b] *Compound **12***: To a stirred solution of **10** (0.69 g, 2.80 mmol) in dry toluene (10 mL), was added *o*-chloranil (1.30 g, 2.80 mmol) at room temperature and the reaction was continued until the color of *o*-chloranil disappeared (12 h). Removal of solvent *in vacuo* to gave **12** as a gummy solid. Yield 1.39 g (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 18H, 2 CH(CH_3)$_3$), 2.26 (s, 6H, 2 PhCH_3), 2.79–2.84 (m, 2H, SCH_2), 2.95–2.96 (m, 1H, CH_ACH$_B$), 4.28–4.30 (m, 2H, OCH_2), 4.40–4.42 (m, 1H, CH_ACH$_B$), 7.00–7.41 (4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.5, 25.3, 25.4, 29.4, 35.0, 39.1, 46.0, 65.6, 68.7 (d, *J* = 8.0 Hz), 114.8 (d, *J* = 20.0 Hz), 119.2 (d, *J* = 9.0 Hz), 124.2, 125.3, 128.2, 129.0, 129.8, 131.0, 131.6 (d, *J* = 6 .0 Hz), 137.9 (d, *J* = 8.0 Hz), 140.4 (d, *J* = 6.0 Hz), 151.4 (d, *J* = 9.0 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ = −56.1 and −56.4; LC/MS *m/z* 663 [M+1]$^+$.;

[c] *Compound **13***: To a stirred solution of 162 (0.20 g, 0.45 mmol) in dry toluene (10 mL), was added DIAD (0.09, 0.45 mmol) through syringe slowly at room temperature and the reaction was continued until the color of DIAD disappeared (12 h). The solvent was removed *in vacuo* to obtain **13**. Yield 0.61 g (75%); mp 160–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, *J* = 6.0 Hz, CH(CH_3)$_2$), 1.32 for major isomer (s, 18H, 6C(CH_3)$_3$), 1.41 for minor (s, 18H, 6C(CH_3)$_3$), 2.28 for major isomer (s, 6H, PhCH_3), 2.36 for minor isomer 2.89–2.91 (s, 6H, PhCH_3) 2.91 (m, 2H, SCH_2), 3.44–3.47 (m, 1H, CH_ACH$_B$), 4.34–4.39 (m, 1H, CH$_A$CH_B), 4.45–4.47 (m, 2H, OCH_2), 4.95–5.03 (m, 1H, C*H*(CH_3)$_2$), 6.98–7.27 (m, 4H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 21.7, 22.0, 30.7, 34.8, 70.0, 125.3, 126.8, 127.2, 128.2, 128.7, 129.0, 133.2, 140.2, 146.2, 156.1; ^{31}P NMR (160 MHz, $CDCl_3$) δ = −66.0 and −66.8; LC/MS *m/z* 650 [M+1]$^+$.

[13] *Compound [CH_2(6-t-Bu-4-Me-C_6H_2O)$_2$P(NC_7H_{14})(1,2-OC_6Cl_4O)] (**14**)*: This was prepared by treating [CH_2(6-*t*-Bu-4-Me-C_6H_2O)$_2$P(NC_7H_{14}) [Mp: 222–224 °C; δ(P): 142.1] with an equimolar quantity of *o*-chloranil. Mp: 276–278 °C (dec); ^{1}H NMR: δ 1.14 (d, ^3J(H–H) = 7.6 Hz, 6 H, CHCH_3), 1.31 (s, 18 H, Ar-C(CH_3)$_3$), 1.20–1.80 (br, 6 H, (CH_2)$_3$), 2.27 (s, 6 H, ArCH_3), 3.41 (d, ^2J(H–H) = 13.9 Hz, 1 H, (Ar)$_2$CH_AH$_X$), 4.08 (br m, 2 H, C*H*-N), 4.66 (d, ^2J(H–H) = 13.9 Hz, 1 H, (Ar)$_2$CH$_A$H$_X$), 6.88 and 6.99 (2 s, 4 H, Ar-*H*); ^{31}P NMR: δ −40.0; Anal. Calcd for $C_{36}H_{44}Cl_4NO_4P$: C, 59.43; H, 6.10; N, 1.94. Found: C, 59.65; H, 6.14; N, 1.98.

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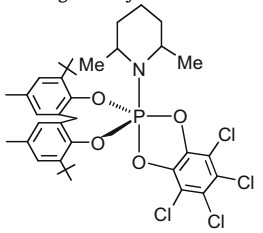
[16] X-ray data for **8** and **14** were collected on Bruker AXS SMART diffractometer at 296 K using Mo K$_\alpha$ (λ = 0.71073 Å) radiation and capillary mounting. The structures were solved by direct methods [17]; all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms, a riding model was used. *Compound **8***: Mol. formula $C_{25}H_{32}Cl_{0.50}N_2O_2P_{0.50}S$; Formula weight 951.61; crystal system monoclinic; space group *C*2/*c*; *a* = 22.8081(13) Å; *b* = 15.0379(9) Å; *c* = 16.0253(10) Å; β = 113.1990(10)°; *V* = 5052.0(5) Å^3; *Z* = 4; D_{calc} = 1.204 g cm^{-3}; μ = 0.236 mm^{-1}; *F*(0 0 0) = 1952; Data/restraints/parameters 4452/0/289; *S* = 1.055; R_1 [$I > 2\sigma(I)$] = 0.0501; wR_2 [all data] = 0.1480; Max./min. residual electron dens. = 0.484/−0.265 eÅ^{-3}. *Compound **14***·3/2C_4H_8O: Mol. formula $C_{84}H_{112}Cl_8N_2O_{11}P_2$; formula weight 1671.30; crystal system monoclinic; space group *C*2/*c*; *a* = 21.978(5) Å; *b* = 13.464(3) Å; *c* = 31.081(7) Å; β = 96.074(4)°; *V* = 9146(4) Å^3; *Z* = 4; D_{calc} = 1.214 g cm^{-3}; μ = 0.336 mm^{-1}; *F*(0 0 0) = 3536; Data/restraints/parameters 8026/7/493; *S* = 1.067; R_1 [$I > 2\sigma(I)$] = 0.0598; wR_2 [all data] = 0.1944; Max./min. residual electron dens. = 0.708/−0.412 eÅ^{-3}.

[17] [a] G.M. Sheldrick, SHELX-97 – A Program for Crystal Structure Solution and Refinement, University of Göttingen, 1997;
[b] G.M. Sheldrick, SADABS, Siemens Area Detector Absorption Correction, University of Göttingen, Germany, 1996;
[c] G.M. Sheldrick, SHELXTL NT Crystal Structure Analysis Package, Bruker AXS, Analytical X-ray System, WI, USA, 1999, version 5.10.

[18] We had assigned a different geometry **14′** for this compound before Ref. [6b].



14' (disposition of groups as assigned earlier)

[19] R.R. Holmes, Acc. Chem. Res. 37 (2004) 746.