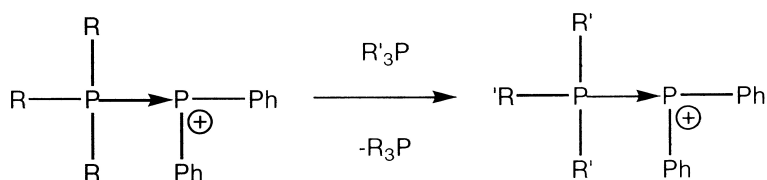Article

# Phosphine Coordination Complexes of the Diphenylphosphenium Cation: A Versatile Synthetic Methodology for P–P Bond Formation

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# Phosphine Coordination Complexes of the Diphenylphosphenium Cation: A Versatile Synthetic Methodology for P–P Bond Formation

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***Abstract:*** A series of phosphine−diphenylphosphenium donor−acceptor cationic complexes have been synthesized and comprehensively characterized (phosphine = diphenylchlorophosphine, triphenylphosphine, trimethylphosphine, and tricyclohexylphosphine). The complexes involve homoatomic P−P coordinate bonds that are susceptible to ligand exchange reactions highlighting a versatile new synthetic method for P−P bond formation. Phosphenium complexes of 1,2-bis(diphenylphosphino)benzene and 1,2-bis(*tert*-butylphosphino)benzene undergo unusual rearrangements to give a "segregated" diphosphine−phosphonium cation and a cyclic di(phosphino)phosphonium cation, respectively. The rearrangement products reveal the kinetic stability of the phosphine−phosphenium bonding arrangement.

## Introduction

Adducts of phosphorus(III) Lewis acids have been reported for a range of Lewis bases,[1a] but the homoatomic coordinate bonding imposed in examples of phosphine ligands on phosphorus(III) Lewis acceptors (e.g., **1a**, referred to here as phosphine−phosphenium[1b] cations) represents an important new development in coordination chemistry. The recent report of a stibine-stibenium salt[4] indicates the potential for diversification of homoatomic coordination, but phosphorus complexes are more readily evaluated by virtue of $^{31}$P NMR spectroscopy. Indeed, cations with the general structure **1b**, first alluded to as the product of reactions between alkyl/aryl halides (R−X) and a diphosphine,[5] were identified by $^{31}$P NMR spectroscopic studies of reaction mixtures containing chlorophosphines with AlCl$_3$[3,6,7] or GaCl$_3$.[3,8] Although P−E coordinate bonding [i.e., R$_2$(Cl)P−ECl$_3$; E = Al or Ga] is observed in some examples,[8] preferential interaction of the Lewis acid (AlCl$_3$ or GaCl$_3$) with the chlorine center of the chlorophosphine often effects heterolytic P−Cl cleavage to give phosphenium salts.[9] Consequential

or coincident phosphine to phosphine nucleophilic attack is expressed as phosphine−phosphenium coordination **1a**.[2,10]



**1a**   **1b**   **2a**: R=Ph, R'=Cl
**2b**: R=R'=Ph
**2c**: R=R'=Cyclohexyl
**2d**: R=R'=Me



**3**   **4**
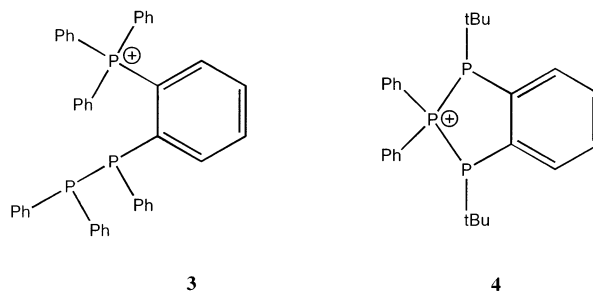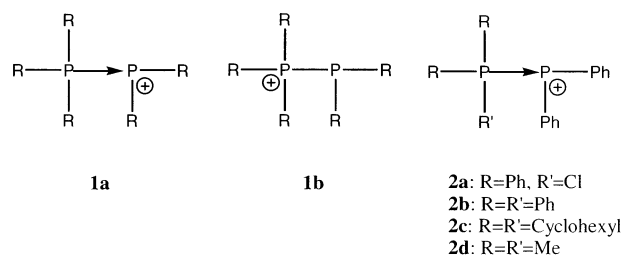
We now report the isolation and comprehensive characterization of phosphine-diphenylphosphenium (**2a** and **2b**) salts and their utility as a source of the diphenylphosphenium cation via ligand exchange reactions to arrive at triphenylphosphine−diphenylphosphenium **2b**, tricyclohexylphosphine−diphenylphosphenium **2c**, and trimethylphosphine−diphenylphosphenium **2d** derivatives. In addition, ligand exchange reactions involving 1,2-di(phosphino)benzene derivatives result in unusual rearrangements that implicate the kinetic stability of the isolated phosphine−phosphenium **1** cations with respect to the thermo-

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(1) (a) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307−4315. (b) Phosphine−phosphenium[2] **1a** is the most appropriate term to describe the reactivity of the compounds, although the Lewis drawing **1b** has been referred to as phosphinophosphonium[1] or diphosphonium.[3]

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dynamically preferred "segregated" diphosphine-phosphonium cation **3** and the cyclic di(phosphino)phosphonium cation **4**.

## Results and Discussion

Phosphorus centers bearing a lone pair of electrons are one of the most recognizable classical ligands. Less obvious is their potential as Lewis acids,[1] although a range of complexes have been isolated that are composed of a phosphorus(III) acceptor site with an arene,[11] carbene,[12] amine,[6,13–15] imine,[13,16,17] phosphine,[2,8,18–22] or gallane ligand.[23] Most complexes are formed at room temperature by simple addition of the ligand to a preformed cation or by displacement of an anion (Cl or $OSO_2CF_3$) from phosphorus, but they represent unique examples in each case.

Lewis acidity at phosphorus is enhanced for coordinatively unsaturated (coordination number < 3) centers and by the presence of a cationic molecular charge. Nevertheless, examples of aminophosphenium **5** salts[9] have been isolated, as the Lewis acidity is mediated by effective $\pi$-interaction between nitrogen and the coordinatively unsaturated, formally electron-deficient phosphorus center (illustrated in **5**). The resonance allowable



**5**            **6**
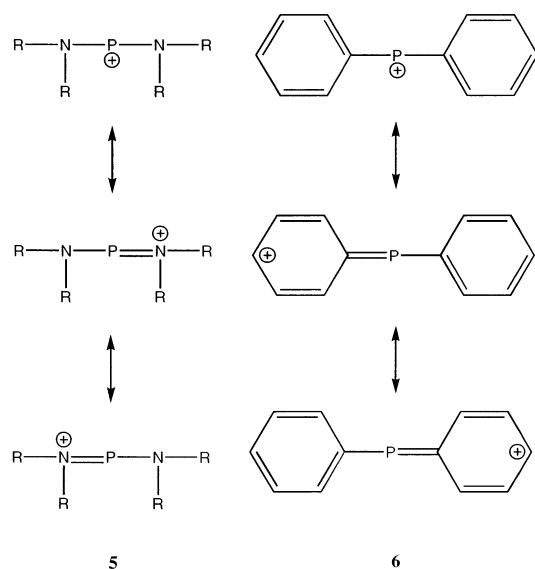
by the $\pi$ electron density of phenyl substituents in **6** is perhaps insufficient to enable isolation of the free Lewis acid, but the base-stabilized diphenylphosphenium cation is a potentially valuable synthetic moiety. A series of phosphine−diphenylphosphenium complexes have been prepared by ligand exchange, exploiting the homoatomic coordinate nature and lability of the P−P interaction.

**Table 1.** $^{31}P\{^{1}H\}$ NMR Data for Derivatives of **2**, **3**, and **4** and Related Species

| complex | δ (ppm) $^{31}P\{^{1}H\}$ | | $J_{PP}^{d,e}$ (Hz) | | reference |
|---|---|---|---|---|---|
| | rt (soln) | CP-MAS | rt (soln) | CP-MAS | |
| **2a**GaCl$_4$ | 78 / 3 | b | a | b | this work[10] |
| **2b**OSO$_2$CF$_3$ | 15 / −10 | 13 / −22 | a | 350 | this work[10] |
| **2b**GaCl$_4$ | 13 / −12 | 15 / −17 | 340 | 323 | this work[10,30] |
| Ph$_2$PPPh$_2$ | −15 | | | | 31 |
| Ph$_3$P | −5 | | | | 31 |
| Ph$_4$P$^+$ | ∼20$^f$ | | | | 31 |
| **2c**OSO$_2$CF$_3$ | 25 / −21 | 31 / −21 | 361 | 372 | this work |
| **2d**OSO$_2$CF$_3$ | 15 / −23 | 17 / −29 | 289 | 281 | this work |
| **3**GaCl$_4$ | 23 / −7 / −21 | c | 26$^e$ / 190$^d$ / 190,$^d$ 26$^e$ | c | this work |
| **4**OSO$_2$CF$_3$ | 25 / 18 | c | 321 | c | this work |
| **7**AlCl$_4$ | 30 / −174 | | 502 | | 20 |
| **8a**AlCl$_4$ | 23 / −28 | | 358 | | 26 |
| **9**OSO$_2$CF$_3$ | 139 / −6 | | 504 | | 2 |
| **10**AlCl$_4$ | 317 / 20 | | 455 | | 28 |
| **11**OSO$_2$CF$_3$ | a | 71 / −1 | a | 405 | 19 |
| **12**BPh$_4$ | 334 / 25 | | 384 | | 21 |

$^a$ Not observed. $^b$ Not measured. $^c$ Not resolved. $^{d\ 1}J_{PP.}$ $^{e\ 3}J_{PP.}$ $^f$ This chemical shift can vary depending on the solvent and counterion.

A 2:1 stoichiometric reaction mixture of Ph$_2$PCl with GaCl$_3$ at room temperature shows a single product in the $^{31}P\{^{1}H\}$ NMR spectra that has been isolated and comprehensively characterized as **2a**GaCl$_4$ (Table 1). Reaction mixtures of **2a**GaCl$_4$ with Ph$_3$P show a singlet at δ = 82 ppm in the $^{31}P\{^{1}H\}$ NMR spectra assigned to Ph$_2$PCl and two doublets (Table 1) assigned to **2b**GaCl$_4$, that has also been isolated and comprehensively characterized. The corresponding trifluoromethanesulfonate salt, **2b**OSO$_2$CF$_3$ has been isolated in high yield from the reaction of Ph$_2$PCl, Ph$_3$P, and Me$_3$SiOSO$_2$CF$_3$. Identical $^{31}P\{^{1}H\}$ NMR spectra are observed for the analogous mixture of Ph$_2$PCl, Ph$_3$P, and GaCl$_3$ suggesting that salts of **2b** engage in minimal cation/anion interaction in solution.

The triphenylphosphine-diphenylphosphenium trifluoromethanesulfonate **2b**OSO$_2$CF$_3$ represents a valuable synthetic source of diphenylphosphenium. Reactions with the more basic phosphines Cy$_3$P and Me$_3$P give **2c**OSO$_2$CF$_3$ and **2d**OSO$_2$CF$_3$, respectively (Table 1). $^{31}P\{^{1}H\}$ NMR spectra of these reaction mixtures show quantitative release of Ph$_3$P (δ = −5 ppm), and both salts have been isolated and characterized. The facile interchange between derivatives of **2** by means of phosphine

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**Table 2.** Crystal Data for Derivatives of **2**, **3**, and **4**

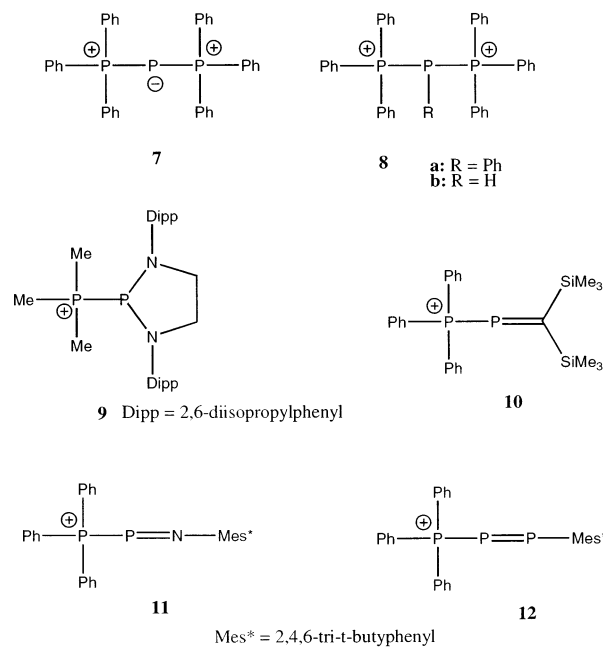| | 2aGaCl$_4$ | 2bOSO$_2$CF$_3$ | 2bGaCl$_4$ | 2cOSO$_2$CF$_3$ | 2dOSO$_2$CF$_3$ | 3GaCl$_4$·0.5CH$_2$Cl$_2$ | 4OSO$_2$CF$_3$ |
|---|---|---|---|---|---|---|---|
| empirical formula | C$_{24}$H$_{20}$Cl$_5$Ga$_1$P$_2$ | C$_{31}$H$_{25}$F$_3$O$_3$P$_2$S$_1$ | C$_{30}$H$_{25}$Cl$_4$Ga$_1$P$_2$ | C$_{31}$H$_{43}$F$_3$O$_3$P$_2$S$_1$ | C$_{16}$H$_{19}$F$_3$O$_3$P$_2$S$_1$ | C$_{42}$H$_{34}$Cl$_4$Ga$_1$P$_3$ | C$_{27}$H$_{32}$F$_3$O$_3$P$_3$S$_1$ |
| formula weight | 617.35 | 596.51 | 659.01 | 614.65 | 410.31 | 885.48 | 586.50 |
| crystal system | orthorhombic | triclinic | monoclinic | orthorhombic | monoclinic | monoclinic | triclinic |
| space group | *Pbca* | *P*$\bar{1}$ | *C2/c* | *Pna*2$_1$ | *P*2$_1$/*n* | *P*2$_1$/*n* | *P*$\bar{1}$ |
| *a* (Å) | 18.482(6) | 10.474(3) | 24.656(3) | 18.934(3) | 11.569(3) | 9.881(1) | 10.039(2) |
| *b* (Å) | 27.662(8) | 11.002(3) | 9.818(4) | 10.451(2) | 8.265(2) | 14.605(1) | 10.638(2) |
| *c* (Å) | 10.744(5) | 14.140(4) | 25.714(2) | 15.711(2) | 19.965(5) | 28.467(3) | 10.648(2) |
| $\alpha$ (deg) | 90 | 78.083(5) | 90 | 90 | 90 | 90 | 102.735(3) |
| $\beta$ (deg) | 90 | 73.302(5) | 103.076(7) | 90 | 97.214(5) | 91.502(2) | 107.407(3) |
| $\gamma$ (deg) | 90 | 68.632(5) | 90 | 90 | 90 | 90 | 100.374(3) |
| *V* (Å$^3$) | 5493(3) | 1421.5(7) | 6063(2) | 3108.8(8) | 1893.9(8) | 4106.7(7) | 1404.2(4) |
| *Z* | 8 | 2 | 8 | 4 | 4 | 4 | 2 |
| $D_C$ (mg m$^{-3}$) | 1.493 | 1.394 | 1.444 | 1.313 | 1.439 | 1.432 | 1.387 |
| radiation, $\lambda$ (Å) | Cu K$\alpha$ (1.54178) | Mo K$\alpha$ (0.71071) | Cu K$\alpha$ (1.54178) | Mo K$\alpha$ (0.71071) | Mo K$\alpha$ (0.71071) | Mo K$\alpha$ (0.71071) | Mo K$\alpha$ (0.71071) |
| diffractometer | Rigaku AFC5R | Bruker PLATFORM/ SMART 1000 CCD | Rigaku AFC5R | Bruker PLATFORM/ SMART 1000 CCD | Bruker PLATFORM/ SMART 1000 CCD | Bruker PLATFORM/ SMART 1000 CCD | Bruker PLATFORM/ SMART 1000 CCD |
| temp (K) | 296(1) | 193(2) | 296(1) | 193(2) | 193(2) | 193(2) | 193(2) |
| *R* (*I* > 2$\sigma$(*I*)) | 0.0512$^a$ | 0.0703$^a$ | 0.049$^b$ | 0.0410$^a$ | 0.0956$^a$ | 0.0829$^a$ | 0.0508$^a$ |
| *wR* (*I* > 2$\sigma$(*I*)) | 0.1329$^a$ | 0.1723$^a$ | 0.056$^b$ | 0.0850$^a$ | 0.2418$^a$ | 0.2272$^a$ | 0.1179$^a$ |
| goodness-of-fit *S* | 0.971$^a$ | 1.024$^a$ | 1.33$^b$ | 1.020$^a$ | 1.038$^a$ | 1.024$^a$ | 1.024$^a$ |

$^a$ $R(F [I > 2\sigma(I)]) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2 [\text{all data}]) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S(\text{all data}) = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ ($n$ = no. of data; $p$ = no. of parameters varied, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and $a$ and $b$ are constants suggested by the refinement program [see Supporting Information]). $^b$ $R(F [I > 3\sigma(I)]) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F[I > 3\sigma(I)]) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o^2|]^{1/2}$; $S(I > 3\sigma(I)) = [\Sigma w(|F_o| - |F_c|)^2/(o - p)]^{1/2}$ ($o$ = no. of observed data; $p$ = no. of parameters varied, $w = 4F_o^2/\sigma^2(F_o^2)$).

ligand exchange reactions validates the designation of homoatomic P−P coordinate bonding in these compounds. The quantitative nature of the reactions and the structural simplicity of the cations highlight P−P coordination as a versatile and efficient new synthetic procedure for P−P bond formation.

The bifunctional diphosphosphines 1,2-bis(diphenylphosphino)benzene (dppb) and 1,2-bis(di-*tert*-butylphosphino)benzene (dbpb) react quantitatively (as shown by $^{31}$P{$^1$H} NMR spectroscopy) with **2a**GaCl$_4$ and **2b**OSO$_2$CF$_3$, respectively. However, salts isolated from these reactions contain cations that are rearrangement products of the predicted diphosphine−phosphenium complexes. The "segregated" diphosphine-phosphonium cation **3** is formed in the reaction of dppb with **2a**GaCl$_4$, while the bicyclic di(phosphino)phosphonium cation **4** is formed in the reaction of dbpb with **2b**OSO$_2$CF$_3$.

Views of the formula units for **2a**GaCl$_4$, **2b**GaCl$_4$, **2b**OSO$_2$CF$_3$, **2c**OSO$_2$CF$_3$, **2d**OSO$_2$CF$_3$, **3**GaCl$_4$, and **4**OSO$_2$CF$_3$ determined by X-ray crystallography (Table 2) are shown in Figures 1−7. P−P internuclear distances and angles at the Lewis acceptor center (phosphenium) are given in Table 3, with comparative data for related compounds **7**−**12**, which includes examples of bis(phosphino)−phosphenium (**7**,[20,24,25] **8**[26,27]), phosphine−diaminophosphenium (**9**),[2] phosphine−phosphaalkenium (**10**),[28] phosphine−phosphadiazonium (**11**),[19] and phosphine−diphosphadiazonium (**12**)[21] cations.

All derivatives of **2** adopt a staggered conformation about the P−P bond in the solid state, with a distorted tetrahedral



**7**



**8**
**a: R = Ph**
**b: R = H**



**9**  Dipp = 2,6-diisopropylphenyl



**10**



**11**



**12**

Mes* = 2,4,6-tri-t-butyphenyl

geometry for the tetracoordinate phosphorus centers and a distinctly pyramidal geometry with standard phosphine-like bond angles (90−105°) for the tricoordinate phosphorus centers. Other than the anomalously long P−P interaction in **11**OSO$_2$CF$_3$, the series of P−P bonded compounds exhibit a striking uniformity of structural features, despite differences in molecular charge, connectivity, or coordination number at either phosphorus center. In this context, any of the electronic features of the homoatomic coordinate P−P bond that may be distinct from P−P covalent bonds in compounds such as Ph$_2$PPPh$_2$[29] do not express themselves in the metrical parameters.

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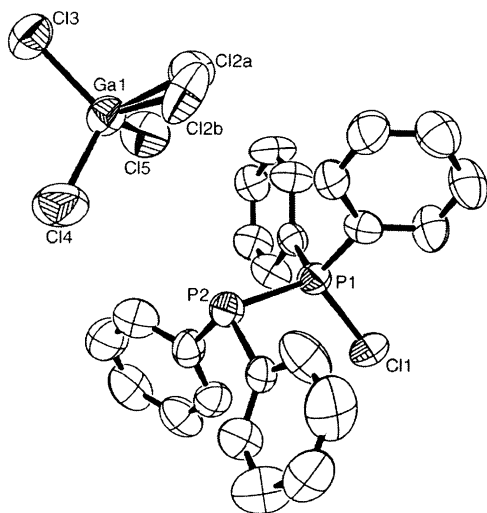(29) Dashti-Mommertz, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1999**, *625*, 954−960.

**Figure 1.** View of the solid-state structure of **2a**GaCl$_4$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.
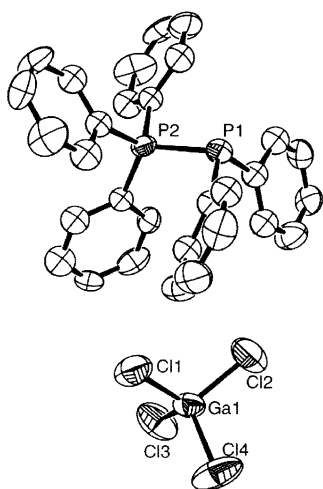


**Figure 2.** View of the solid-state structure of **2b**GaCl$_4$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.

NMR spectroscopic data for derivatives of **2** are listed in Table 1 and are compared with established data for Ph$_3$P, Ph$_2$-PPPh$_2$, and Ph$_4$P$^+$. Resolvated pure salts of **2a** and **2b** give broad $^{31}$P{$^1$H} NMR signals at room temperature in contrast to the reaction mixture for **2b**GaCl$_4$, which shows a poorly resolved AB pattern. An AB pattern is observed for **2b**OSO$_2$CF$_3$ at 193 K with a typical $^1J_{PP}$ value. Solid state $^{31}$P{$^1$H} CP-MAS NMR data for **2b**OSO$_2$CF$_3$, **2c**OSO$_2$CF$_3$, and **2d**OSO$_2$CF$_3$ are consistent with the data obtained for solutions.

An ABX pattern is observed for **3**GaCl$_4$ in the $^{31}$P{$^1$H} solution NMR spectrum with normal $^1J_{PP}$ and $^3J_{PP}$ values. The $^{31}$P{$^1$H} A$_2$B spin system for **4**OSO$_2$CF$_3$ is second order at three fields (250, 400, 500 MHz) and has been favorably simulated, as illustrated in Figure 8. Consistent with the spectroscopic and structural data above, the $^{31}$P {$^1$H coupled} NMR spectrum of **4**OSO$_2$CF$_3$ shows no evidence of $^1J_{PH}$, indicating that both $^t$Bu-phosphino centers of the starting diphosphine have been dehydrogenated as a result of reaction with **2b**OSO$_2$CF$_3$. The
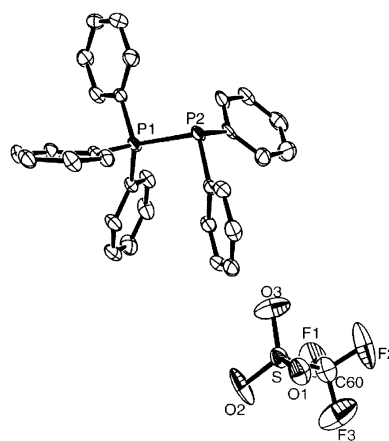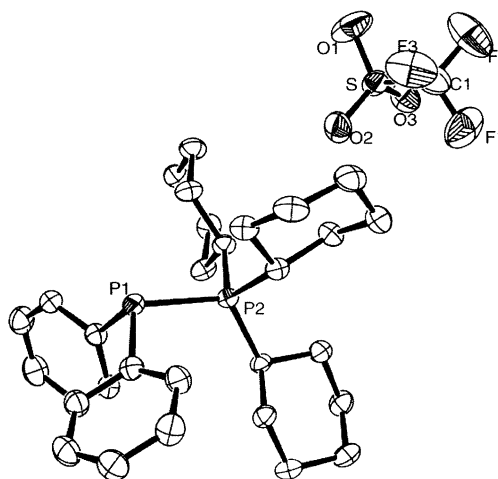
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**Figure 3.** View of the solid-state structure of **2b**OSO$_2$CF$_3$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.



**Figure 4.** View of the solid-state structure of **2c**OSO$_2$CF$_3$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.
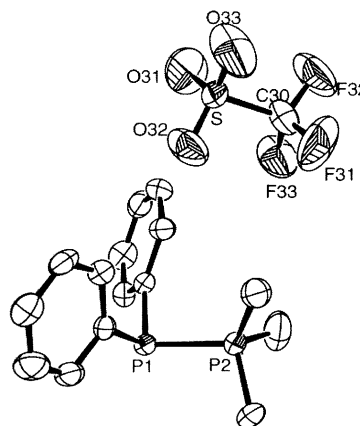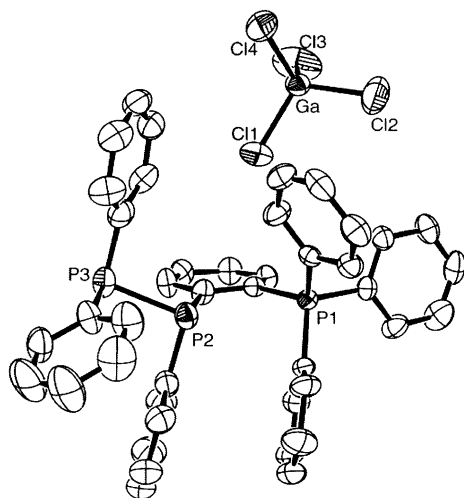


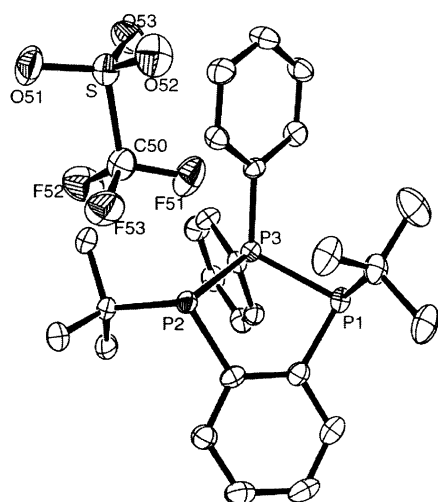**Figure 5.** View of the solid-state structure of **2d**OSO$_2$CF$_3$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.

$^1J_{PP}$ and $^3J_{PP}$ coupling is not resolved in the solid state spectra due to the inherently broad signals.

Cation **3** is composed of a tetraarylphosphonium center and a tetraryldiphosphine "segregated" by a bridging benzo unit. We envision the production of **3** to first involve displacement of Ph$_2$PCl from **2a** by one phosphine site of dppb to give **13**, followed by intramolecular phenyl transfer from the resulting tetracoordinate phosphonium to the second phosphine via a

**Figure 6.** View of the solid-state structure of **3**GaCl$_4$. Ellipsoids are 50% probability, hydrogen atoms have been omitted for clarity.



**Figure 7.** View of the solid-state structure of **4**OSO$_2$CF$_3$. Ellipsoids are 50% probability; hydrogen atoms have been omitted for clarity.

***Table 3.*** P–P Distances (Å) and Sum of the Bond Angles (deg) at the Lewis Acceptor Phosphorus Center

| | P–P (Å) | ∠'s at Lewis acceptor | reference |
|---|---|---|---|
| **2a**GaCl$_4$ | 2.205(4) | 311.7 | this work[10] |
| **2b**OSO$_2$CF$_3$ | 2.230(1) | 305.3 | this work[10] |
| **2b**GaCl$_4$ | 2.220(6) | 311.7 | this work[10] |
| **2c**OSO$_2$CF$_3$ | 2.220(1) | 305.5 | this work |
| **2d**OSO$_2$CF$_3$ | 2.187(2) | 310.1 | this work |
| **3**GaCl$_4$ | 2.243(2) | | this work |
| **4**OSO$_2$CF$_3$ | 2.199(1) | | this work |
| | 2.193(1) | | |
| **7**AlCl$_4$ | 2.137(6) | | 20 |
| **8b**AlCl$_4$ | 2.133(6) | 291.2 | 26 |
| **9**OSO$_2$CF$_3$ | 2.3065(9) | 301.2 | 2 |
| **10**AlCl$_4$ | 2.267(2) | | 28 |
| **11**OSO$_2$CF$_3$ | 2.625(2) | | 19 |
| **12**BPh$_4$ | 2.206(1) | | 21 |
| Ph$_2$PPPh$_2$ | 2.217(1) | | 29 |

bridging Wheland intermediate **14** (Scheme 1). Such facile isomerism of the phosphine–phosphenium **13** (a derivative of **2**) to the "segregated" diphosphine–phosphonium **3** demonstrates the relative thermodynamic instability of the P–P bonded phosphine–phosphenium–phosphine **13** given a route to a more

favorable bonding alternative. Although the isolated P–P bonded phosphine–phosphenium derivatives (**2**) are perhaps only kinetically stable, thermodynamically favored alternative structures are not apparent.

The structure of **4** is reminiscent of the proposed cyclic intermediate **14** in the formation of **3** but is the result of an elaborate rearrangement from the combination of Ph$_2$P$^+$ and dbpb that is the equivalent of a dehydrogenation. Quantitative [shown in the $^{31}$P{$^1$H} NMR spectrum of the reaction mixture] coincidental formation of Ph$_3$P ($\delta = -5$ ppm), Ph$_2$PH ($\delta = -40$ ppm), and [Ph$_3$PH]$^+$ ($\delta = 2$ ppm) is rationalized in the proposed mechanism presented in Scheme 2. Hydride abstraction from dbpb is envisaged to effect release of Ph$_3$P to give Ph$_2$PH and a phosphenium cation **15** that is stabilized by conjugation onto the phosphinobenzene moiety. Subsequent formation of a phosphine–phosphenium complex **16** involving Ph$_2$PH as a ligand gives access to an *ortho*-diphosphinophosphinobenzene **17**, through deprotonation by Ph$_3$P. Reaction of **17** with a second equivalent of phosphine–phosphenium **2b** removes the second hydride to enable cyclization of the diphosphine–phosphenium to give **4**, through intramolecular P–P coordination.

## Conclusions

A series of phosphine–phosphenium cations have been synthesized by a versatile ligand displacement reaction at Ph$_2$P$^+$, which behaves as a Lewis acceptor despite the presence of a lone pair of electrons at the phosphorus center. Homoatomic P–P coordination is demonstrated as an efficient new synthetic method for P–P bond formation. Complexes of ortho-substituted di(phosphino)benzenes on Ph$_2$P$^+$ undergo rapid rearrangement to give the "segregated" diphosphine–phosphonium cation **3** and the cyclic di(phosphino)phosphonium cation **4**.

## Experimental Section

**General.** All manipulations were carried out in an N$_2$ filled Innovative Technologies drybox. All solvents were distilled prior to use and dispensed in the drybox. CH$_2$Cl$_2$ was dried at reflux over CaH$_2$, P$_2$O$_5$, and again over CaH$_2$. Hexane was dried at reflux over K, and Et$_2$O was dried at reflux over Na/benzophenone. Ph$_3$P, Ph$_2$PCl, GaCl$_3$, Me$_3$SiOSO$_2$CF$_3$, and Me$_3$P (1.0 M in hexane) were purchased from Aldrich Chemical Co., 1,2-bis(*tert*-butylphosphino)benzene was purchased from Quantum Design, and Cy$_3$P was purchased from Strem. All reagents were used as received without further purification. IR spectra were collected on a Bruker VECTOR 22 FT-IR using Nujol mulls and are reported with ranked intensities in parentheses. Solution NMR data were collected on a Bruker AC-250 NMR spectrometer at room temperature unless otherwise indicated. Chemical shifts are reported in ppm relative to a reference standard [85% H$_3$PO$_4$ ($^{31}$P)]. Simulation of the $^{31}$P NMR spectrum of the second-order A$_2$B spin system was done using g-NMR Version 4.0 by Cherwell Scientific. Crystals were mounted inside glass capillaries (<1.0 mm od) and flame sealed or mounted under oil (Paratone) and placed in a cold stream of N$_2$. X-ray diffraction data (Table 2) were collected on a Rigaku AFC5R diffractometer equipped with a rotating anode source using graphite-monochromated Cu Kα ($\lambda = 1.5478$ Å) radiation (**2a**GaCl$_4$, **2b**GaCl$_4$) or on a Bruker PLATFORM diffractometer with a sealed tube generator and a SMART 1000 CCD detector (**2b**OSO$_2$CF$_3$, **2b**OSO$_2$CF$_3$, **3**GaCl$_4$·0.5CH$_2$Cl$_2$, **4**OSO$_2$CF$_3$) using graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation.

**2a**GaCl$_4$. GaCl$_3$ (0.9 g, 5.2 mmol) in CH$_2$Cl$_2$ (10 mL) was added to Ph$_2$PCl (2.3 g, 10 mmol) and stirred for 1 h at rt. Removal of solvent in vacuo gave a white solid, which was washed with C$_6$H$_6$. Anal. Calcd
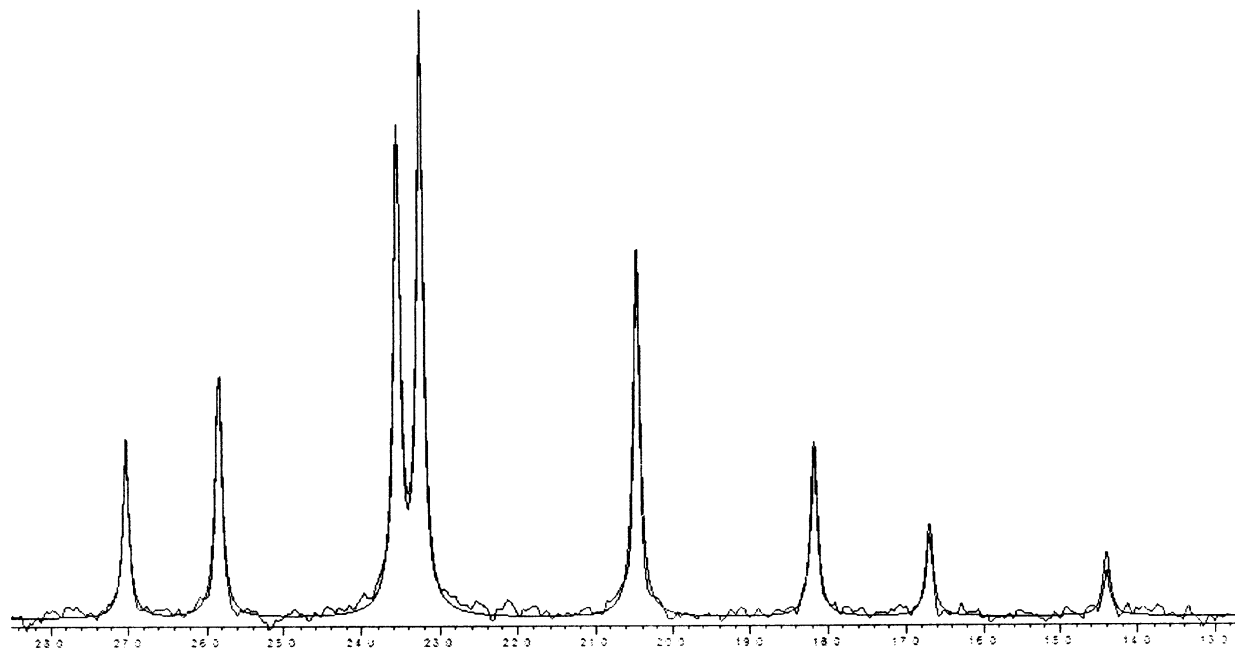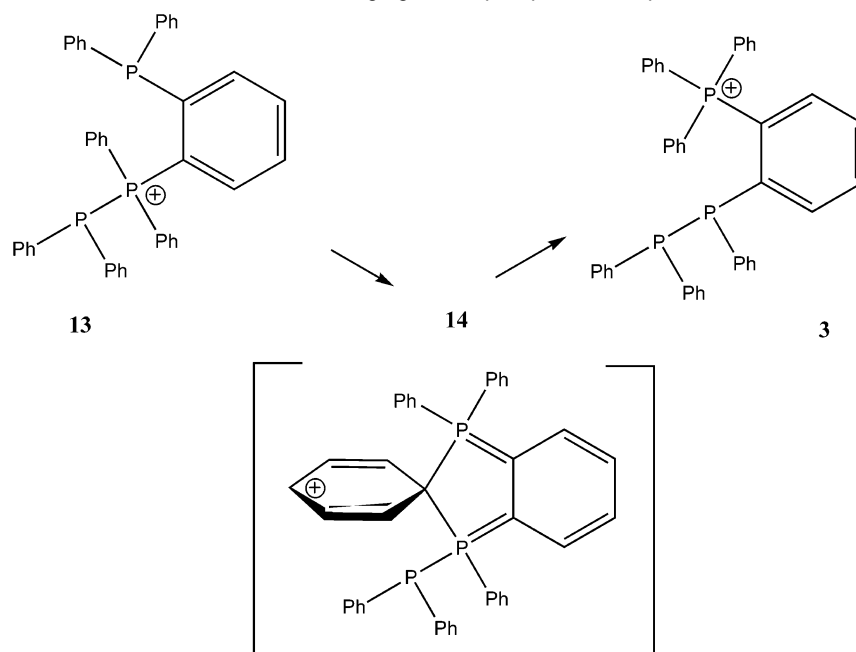
**Figure 8.** Experimental and simulated $^{31}P$ NMR spectra of **4**OSO$_2$CF$_3$ in solution.

**Scheme 1.** Proposed Mechanism for the Formation of the "Segregated" Diphosphine−Phosphonium Cation **3**



(Found): C, 46.7 (46.8); H, 3.3 (3.3). Crystals were grown using liquid/liquid diffusion from CH$_2$Cl$_2$/hexane; 2.5 g, 77%; mp 103−105 °C; IR (cm$^{-1}$) 367(4), 381(1), 496(7), 532(9), 681(5), 691(8), 745(3), 752-(6), 1105(10), 1436(2).

**2bOSO$_2$CF$_3$.** Ph$_2$PCl (1.0 g, 4.5 mmol) was added to Me$_3$SiOSO$_2$-CF$_3$ (1.2 g, 5.4 mmol 20% excess) in CH$_2$Cl$_2$ (20 mL). The mixture was stirred for 45 min at rt, added to Ph$_3$P (1.5 g, 5.4 mmol), and stirred for 45 min. Removal of solvent in vacuo gave a white solid, which was redissolved in CH$_2$Cl$_2$, and slow solvent evaporation gave clear, cubelike crystals; 2.14 g, 80%; mp 163−164 °C. Anal. Calcd (Found): C, 62.4 (62.2); H, 4.2 (4.0). IR (cm$^{-1}$) 488(9), 636(2), 693-(5), 741(6), 1029(4), 1124(8), 1150(7), 1222(10), 1260(1), 1439(3).

**2bGaCl$_4$.** Ph$_3$P (0.25 g, 0.97 mmol) in CH$_2$Cl$_2$ (15 mL) was added to a solution of [Ph$_2$PCl−PPh$_2$][GaCl$_4$] (0.60 g, 0.97 mmol) in CH$_2$Cl$_2$ (20 mL) and stirred for 1 h at rt. Removal of solvent in vacuo gave a

white solid; 0.56 g, 87.6%; mp 153−155 °C. Anal. Calcd (Found): C, 54. 7 (54.5); H, 3.8 (3.8). IR (cm$^{-1}$) 374(3), 489(7), 503(6), 550(9), 690(5), 720(4), 746(2), 1101(8), 1439(1); crystals were obtained using liquid/liquid diffusion from CH$_2$Cl$_2$/hexane.

**2cOSO$_2$CF$_3$.** A solution of Cy$_3$P (0.06 g, 0.20 mmol) in CH$_2$Cl$_2$ (1 mL) was added dropwise (5 min) to a solution of [Ph$_3$P−PPh$_2$][OSO$_2$-CF$_3$] (0.12 g, 0.20 mmol) in CH$_2$Cl$_2$ (3 mL). The reaction mixture was stirred for 1 h at rt. The volume was reduced to 2 mL in vacuo, and Et$_2$O was added (5 mL) to give a white precipitate. Crystals were obtained using liquid/liquid diffusion from CH$_2$Cl$_2$/hexane; 0.10 g, 77%; mp 117−118 °C. Anal. Calcd (Found): C, 60.6 (58.0); H, 7.1 (6.5); IR (cm$^{-1}$): 635(6), 722(9), 748(7), 1029(5), 1175(4), 1219(8), 1262-(3), 1301(10), 1377(2), 1458(1).

**2dOSO$_2$CF$_3$.** Me$_3$P (1.0 M in hexanes, 0.10 mL, 0.10 mmol) was added to a stirred solution of [Ph$_3$P−PPh$_2$][OSO$_2$CF$_3$] (0.06 g, 0.10

**Scheme 2.** Proposed Mechanism for the Formation of **4**
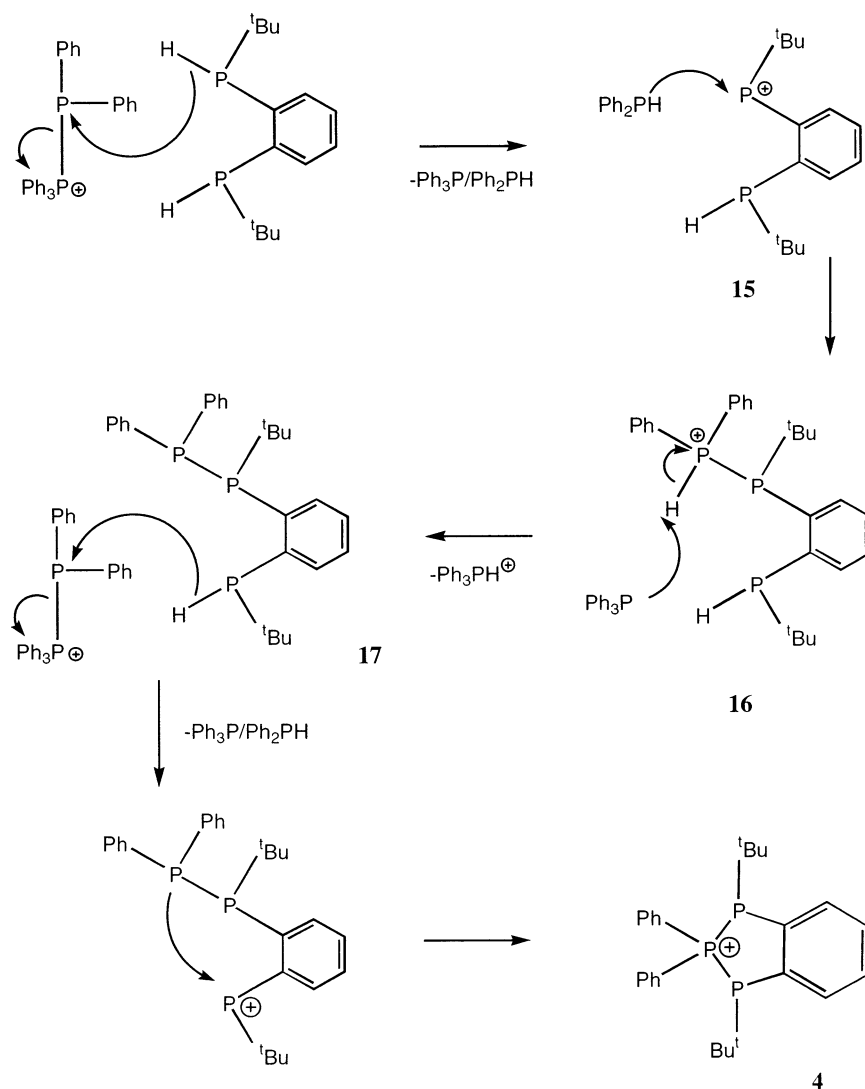


mmol) in CH₂Cl₂ (3 mL) for 1 h at rt. The volume was reduced in vacuo, and the addition of pentane gave a white powder; 0.03 g, 76%; mp 57–58 °C. Anal. Calcd (Found): C, 46.8 (50.6); H, 4.6 (4.7). Crystals were obtained using vapor diffusion (CH₂Cl₂/Et₂O) at −30 °C; IR (cm⁻¹) 741(8), 961(10), 1030(5), 1151(7), 1167(9), 1256(3), 1280(4), 1300(6), 1378(2), 1467(1).

**3GaCl₄.** A solution of bis(1,2-diphenylphosphino)benzene (dpbz) (0.05 g, 0.11 mmol) in CH₂Cl₂ (2 mL) was added to a solution of [Ph₂-PCl−PPh₂][GaCl₄] (0.11 mmol) in CH₂Cl₂ (3 mL), giving a yellow reaction mixture, which was stirred for 12 h at rt. Reduction of solvent volume (0.5 mL) in vacuo and addition of *n*-pentane (5 mL) gave a yellow precipitate; 0.049 g, 55%; mp126–128 °C. Anal. Calcd (Found): C, 59.1 (58.0); H, 4.1 (3.9). Yellow, rectangular prism crystals were obtained using vapor diffusion (CH₂Cl₂/Et₂O); IR (cm⁻¹) 374(7), 534(8), 686(6), 719(3), 732(4), 1107(4), 1177(2), 1506(1), 2341(10), 2360(9).

**4OSO₂CF₃.** 1,2-Bis(*tert*-butylphosphino)benzene (0.025 g, 0.10 mmol) was added to a stirred solution of [Ph₃P−PPh₂][OSO₂CF₃] (0.12 g, 0.20 mmol) in CH₂Cl₂ (3 mL) for 12 h at rt. The volume was reduced in vacuo, and the addition of pentane gave a white powder; 0.07 g, 63%; mp 164–166 °C. Anal. Calcd (Found): C, 55.3 (55.5); H, 5.5 (4.7). Crystals were obtained using vapor diffusion (CH₂Cl₂/Et₂O); IR

(cm⁻¹) 637(8), 751(9), 1032(7), 1149(4), 1222(10), 1250(2), 1280(3), 177(6), 1466(1).

**Supporting Information Available:** Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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