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Acyclic *catena*-Diphosphinodiphosphonium Dications $[R_3P\text{-}PR'\text{-}PR'\text{-}PR_3]^{2+}$ or Bisphosphine−Diphosphenium Complexes $[R_3P{\rightarrow}PR'\text{-}PR'{\leftarrow}PR_3]^{2+}$: Synthesis by Reductive P−P Coupling of $[R_3P\text{-}PR'Cl]^+$ and Phosphine Ligand Exchange

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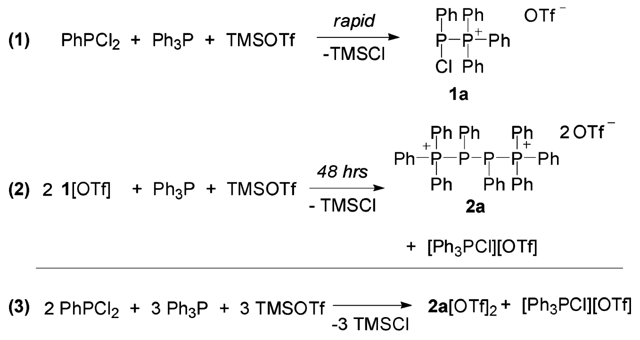
Catenation is the property of carbon that is principally responsible for the extent of organic chemistry. The established series of *catena*-phosphines[1−4] and *catena*-phosphorus anions[1−3;5] highlight an analogous prominence for homoatomic bonding in phosphorus chemistry. We have been systematically developing *catena*-phosphorus cations, composed of the familiar phosphine and phosphonium units,[6−9] as compounds that define a potentially extensive and diverse new direction in fundamental phosphorus chemistry. Here we report the synthesis, characterization, and ligand exchange reactivity of the first acyclic tetraphosphorus dications.

^{31}P NMR spectra of reaction mixtures containing $PhPCl_2$, Ph_3P, and TMSOTf (1:1:1 molar ratio) in CH_2Cl_2 show rapid and quantitative formation of the chlorophosphinophosphonium salt **1a**[OTf] (eq 1). Sharp singlets (22 and 55 ppm) observed at room temperature resolve into the expected doublets ($^1J_{PP} = 333$ Hz) at −60 °C. The solid-state structure of the cation is shown in Figure 1.



$$\mathrm{(1)\quad PhPCl_2 + Ph_3P + TMSOTf \xrightarrow[-TMSCl]{\textit{rapid}} Ph(Cl)P\text{-}\overset{+}{P}Ph_3\ \ OTf^-}$$

1a

$$\mathrm{(2)\quad 2\ \mathbf{1}[OTf] + Ph_3P + TMSOTf \xrightarrow[-\ TMSCl]{\textit{48 hrs}} Ph_3\overset{+}{P}\text{-}PPh\text{-}PPh\text{-}\overset{+}{P}Ph_3\ \ 2\,OTf^- + [Ph_3PCl][OTf]}$$

2a

$$\mathrm{(3)\quad 2\ PhPCl_2 + 3\ Ph_3P + 3\ TMSOTf \xrightarrow[-3\ TMSCl]{} \mathbf{2a}[OTf]_2 + [Ph_3PCl][OTf]}$$

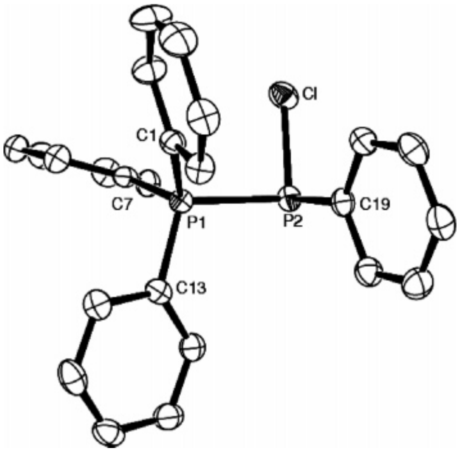


Figure 1. Solid-state structure of one enantiomer of the cation in racemic **1a**[OTf]: P1−P2 = 2.2471(8) Å, P2−Cl = 2.0595(9) Å.

After 2 days, reactions containing excess Ph_3P and TMSOTf give $[Ph_3PCl][OTf]$ (^{31}P: = 66 ppm),[10,11] and a new salt has been isolated and characterized as **2a**$[OTf]_2$. We conclude that Ph_3P effects the reductive coupling of two **1a** cations according to eq 2. The overall process is summarized in eq 3 and is distinct from the previously reported reaction of $PhPCl_2$, Ph_3P, and $AlCl_3$ that gives $[Ph_3P\text{-}PPh\text{-}PPh_3][AlCl_4]_2$.[12]

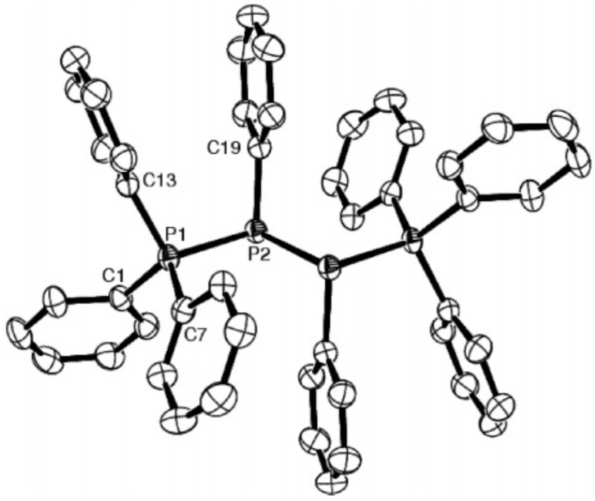


Figure 2. Solid-state structure of the dication in *meso*-**2a**$[OTf]_2$: P1−P2 = 2.2583(10) Å, P2−P2′ = 2.2214(13) Å.

Single crystals of **2a**$[OTf]_2$ reveal the *meso*-(*S*,*R*) configuration of the dication in the solid state (Figure 2), which is consistent with the analogous neutral 2,3-diphosphino-1,4-diphosphorane.[13] Solid samples of **2a**$[OTf]_2$ exhibit reproducible FT-IR data; however, NMR spectra (Figure 3) of the reaction mixture (^{31}P) and of dissolved crystalline material (^{31}P and ^{1}H) consistently show the presence of two diastereomers (de = 62%, by ^{1}H NMR) in solution, indicating that solutions of **2a**$[OTf]_2$ contain all three stereoisomers. All three isomers of the “naked” anion $[PhP\text{-}PPh\text{-}PPh\text{-}PPh]^{2-}$ exist in the solid state.[5] The ^{31}P NMR spectrum for the major isomer of **2a** has been simulated as an AA′BB′ spin system and is tentatively assigned to the *meso*-(*S*,*R*) isomer based on the steric preference

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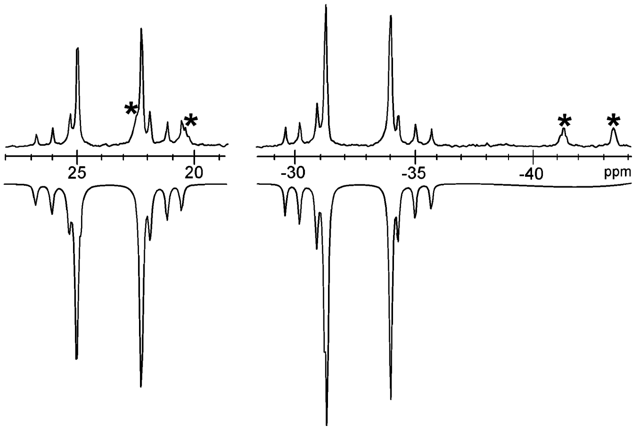


Figure 3. $^{31}P\{^{1}H\}$ NMR spectrum (101.3 MHz) for **2a**[OTf]$_2$ with the simulated (inverted) AA′BB′ spectrum for the *meso*-(*S*,*R*) isomer ($\delta = -33$, 24 ppm); * refers to peaks for the minor isomers (*R*,*R* and *S*,*S*) ($\delta = -42$, 22 ppm).

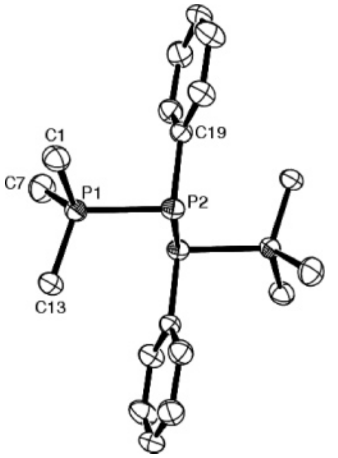
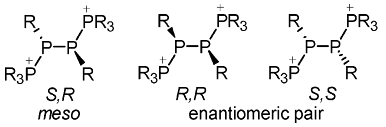
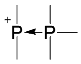


Figure 4. Solid-state structure of the dication in *meso*-**2b**[OTf]$_2$: P1−P2 = 2.2041(9) Å, P2−P2′ = 2.2317(12) Å.

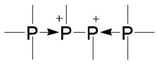
over the *R*,*R* and *S*,*S* enantiomeric pair, which are assigned as the minor component.



Ligand exchange reactions previously described for phosphinophosphonium cations[7] such as **1a** implicate the coordination complex **1′**. Application of this model to **2a** defines the first example of a bisphosphine *catena*-diphosphenium complex, represented by **2′**.



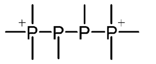
1'



2'

The validity of this model is exemplified in the exchange of both Ph_3P groups of **2a** by PMe_3. A white precipitate from the CH_2Cl_2 reaction mixture dissolves in CD_3CN, and a new AA′BB′ spin system ($\delta = -52$, 25 ppm), tentatively assigned to *meso*-**2b**[OTf]$_2$, is observed by ^{31}P NMR spectroscopy as the major product. As for **2**a[OTf]$_2$, the *R*,*R* and *S*,*S* isomers of **2b**[OTf]$_2$ ($\delta = -56$, 23 ppm) are present in solution (de = 72%), and single crystals of *meso*-**2b**[OTf]$_2$ (Figure 4) have been characterized. Reactions of **2a**[OTf]$_2$ with one equivalent of PMe_3 give a 1:1 mixture of **2a** and **2b**.

Cations **2a** and **2b** represent the first derivatives of acyclic *catena*-tetraphosphorus dications and are new members of a scarcely explored family of *catena*-phosphorus dications with topologies **3**,[14] **4**,[15] **5**,[16] **6**,[12] and **7**.[17−22] The reductive coupling of **1a** represents a rational and potentially versatile, synthetic method to diversify and extend *catena*-phosphorus chemistry. In addition, the recognition of **2** as a bisphosphine complex of a *catena*-diphosphenium dication (**2′**) is expected to provide a synthon to a vast array of new polyphosphorus coordination complexes by the introduction of an appropriate Lewis base.



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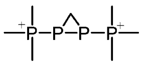

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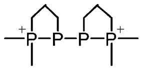

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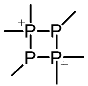

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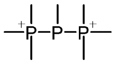

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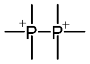

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Supporting Information Available: Experimental details, characterization data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492−512.
(2) Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 419−441.
(3) Baudler, M.; Glinka, K. *Chem. Rev.* **1993**, *93*, 1623−1667.
(4) Baudler, M.; Glinka, K. *Chem. Rev.* **1994**, *94*, 1273−1297.
(5) Geier, J.; Harmer, J.; Grutzmacher, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 4093−4097.
(6) Burford, N.; Cameron, T. S.; Ragogna, P. J.; Ocando-Mavarez, E.; Gee, M.; McDonald, R.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 7947−7948.
(7) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. *J. Am. Chem. Soc.* **2003**, *125*, 14404−14410.
(8) Burford, N.; Dyker, C. A.; Decken, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2364−2367.
(9) Burford, N.; Dyker, C. A.; Lumsden, M. D.; Decken, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6196−6199.
(10) This shift is consistent with related chlorotriphenylphosphonium salts (see ref 11 and references therein). Presence of the triflate counterion is supported by ^{19}F NMR. Three equivalents of TMSOTf are necessary to facilitate the reductive coupling.
(11) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M.; Thompson, G. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4823−4827.
(12) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff, K.; Sheldrick, W. S. *Chem. Commun.* **1985**, 1447−1448.
(13) Karsch, H. H.; Witt, E. *J. Organomet. Chem.* **1997**, *529*, 151−169.
(14) Lochschmidt, S.; Muller, G.; Huber, B.; Schmidpeter, A. *Z. Naturforsch.* **1986**, *41b*, 444−454.
(15) Kilian, P.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2006**, 2175−2183.
(16) Heuer, L.; Ernst, L.; Schmutzler, R.; Schomburg, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1507−1509.
(17) Alder, R. W.; Ganter, C.; Harris, C. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1170−1172.
(18) Alder, R. W.; Ganter, C.; Harris, C. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1172−1174.
(19) Alder, R. W.; Ellis, D. D.; Gleiter, R.; Harris, C. J.; Lange, H.; Orpen, A. G.; Read, D.; Taylor, P. N. *J. Chem. Soc., Perkin. Trans. 1* **1998**, 1657−1668.
(20) Schomburg, D.; Bettermann, G.; Ernst, L.; Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 975−976.
(21) Romakhin, A. S.; Palyutin, F. M.; Ignat'ev, Yu. A.; Nikitin, E. V.; Kargin, Yu. M.; Litvinov, I. A.; Naumov, V. A. *Izv. Akad. Nauk, Ser. Khim.* **1990**, *3*, 664−669.
(22) Nikitin, E. V.; Romakhin, A. S.; Zagumennov, V. A.; Babkin, Yu. A. *Electrochim. Acta* **1997**, *42*, 2217−2224.

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