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Acyclic catena-Diphosphinodiphosphonium Dications [R₃P-PR'-PR₃]²⁺ or $Bisphosphine-Diphosphenium\ Complexes\ [R_3P\rightarrow PR'-PR' \leftarrow PR_3]^{2+}:\ Synthesis$ by Reductive P–P Coupling of [R₃P-PR'CI]⁺ 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 catenaphosphines¹⁻⁴ and *catena*-phosphorus anions^{1-3,5} highlight an analogous prominence for homoatomic bonding in phosphorus chemistry. We have been systematically developing catenaphosphorus 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.

³¹P NMR spectra of reaction mixtures containing PhPCl₂, Ph₃P, and TMSOTf (1:1:1 molar ratio) in CH2Cl2 show rapid and quantitative formation of the chlorophosphinophosphonium salt 1a[OTf] (eq 1). Sharp singlets (22 and 55 ppm) observed at room

(3) 2 PhPCl₂ + 3 Ph₃P + 3 TMSOTf → -3 TMSCI 2a[OTf]2+ [Ph3PCI][OTf]

temperature resolve into the expected doublets (${}^{1}J_{PP} = 333$ Hz) at -60 °C. The solid-state structure of the cation is shown in Figure 1.

After 2 days, reactions containing excess Ph₃P and TMSOTf give $[Ph_3PC1][OTf]$ (³¹P: = 66 ppm),^{10,11} and a new salt has been isolated and characterized as 2a[OTf]2. We conclude that Ph3P 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 PhPCl₂, Ph₃P, and AlCl₃ that gives [Ph₃P-PPh-PPh₃][AlCl₄]₂.¹²

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 (³¹P) and of dissolved crystalline material (³¹P and ¹H) consistently show the



Figure 1. Solid-state structure of one enantiomer of the cation in racemic **1a**[OTf]: P1-P2 = 2.2471(8) Å, P2-C1 = 2.0595(9) Å.



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.

presence of two diastereomers (de = 62%, by ¹H NMR) in solution, indicating that solutions of 2a[OTf]2 contain all three stereoisomers. All three isomers of the "naked" anion [PhP-PPh-PPh-PPh]²⁻ exist in the solid state.5 The 31P 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. ³¹P{¹H} 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 cations⁷ 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'.

The validity of this model is exemplified in the exchange of both Ph₃P groups of **2a** by PMe₃. A white precipitate from the CH₂Cl₂ reaction mixture dissolves in CD₃CN, and a new AA'BB' spin system ($\delta = -52, 25$ ppm), tentatively assigned to *meso-2b*[OTf]₂, is observed by ³¹P NMR spectroscopy as the major product. As for $2a[OTf]_2$, 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 PMe₃ give a 1:1 mixture of 2aand 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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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.

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