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Diverse Reactivity of the *cyclo*-Diphosphinophosphonium Cation $[(PtBu)_3Me]^+$: Parallels with Epoxides and New *catena*-Phosphorus Frameworks

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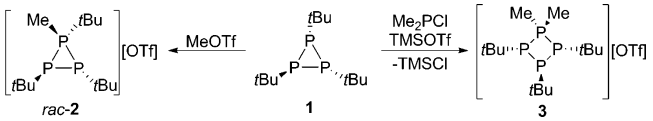
Supporting Information

ABSTRACT: The *cyclo*-diphosphinophosphonium salt $[(PtBu)_3Me][OTf]$ (**2**) has been shown to be highly reactive toward Lewis bases, exhibiting diverse reactivity with phosphines, 4-(dimethylamino)pyridine (dmap) and chlorophosphines, providing approaches to new open-chain and cyclic *catena*-phosphorus frameworks. Reaction of **2** with R_3P (R = Me or *n*Pr) or dmap led to the ring-opened adducts $[R_3P{-}PtBu{-}PtBu{-}P(Me)tBu][OTf]$ (R = Me (**4a**), *n*Pr (**4b**)) and $[(dmap)\text{-}PtBu{-}PtBu{-}P(Me)tBu][OTf]$ (**6**), respectively. The complicated $^{31}P\{^1H\}$ NMR spectra of the three compounds were simulated, evidencing the presence of two diastereomeric forms of **4a**, and single diastereomers of **4b** and **6**. This ring-opening reactivity of the cation in **2** parallels the reactivity of isolobal epoxides with nucleophiles under acidic conditions. Compound **2** was also shown to react with a 2:1 mixture of Me_2PCl and TMSOTf to form the unexpected *cyclo*-diphosphino-1,2-diphosphonium salt $[(Me_2P)_2(PtBu)_2][OTf]_2$ (**8**), which is postulated to result from two consecutive ring-opening and ring-closing steps. In contrast, reaction with $MePCl_2$ furnished $[(MeP)(PtBu)_2(P(Me)tBu)][OTf]$ (**9**), consistent with insertion of a "MeP" moiety into the cationic phosphorus framework of **2**. The importance of ring strain on the reactivity of the cation in **2** was illustrated by comparative studies of the corresponding *cyclo*-tetraphosphorus cation in $[(PtBu)_4Me][OTf]$ (**10**), which exhibits no reactivity under analogous conditions.

INTRODUCTION

The propensity to form catenated frameworks is primarily responsible for the extent and diversity of the chemistry of carbon, representing the basis for modern organic chemistry. In comparison, the chemistry of catenated frameworks of other *p*-block elements is underdeveloped, and is an area of significant current interest.[1] In this context, the often cited "diagonal relationship" between carbon and phosphorus[2] has prompted the development of an array of *catena*-phosphorus compounds. The scope of such compounds has been broadened by the introduction of a cationic charge at phosphorus, which provides for stronger P–P bonds and imparts an enhanced Lewis acidity at a phosphorus center, facilitating the formation of donor–acceptor complexes.[3−5] In this context, the prototypical *cyclo*-triphosphine $(PtBu)_3$ (**1**),[6,7] a foundational framework in *catena*-phosphorus chemistry, can be quaternized with MeOTf (OTf = trifluoromethanesulfonate) to give the *cyclo*-diphosphinophosphonium salt $[(PtBu)_3Me][OTf]$ (**2**) (Scheme 1), and undergoes ring expansion via phosphenium insertion upon reaction with Me_2PCl/TMSOTf to furnish the *cyclo*-triphosphinophosphonium salt $[(PtBu)_3(PMe_2)][OTf]$ (**3**).[8,9]

Scheme 1. Reactions of *cyclo*-$(PtBu)_3$ (1) to form Cationic Phosphorus Frameworks[8,9]



rac-**2** **1** **3**

The cation in **2** provides an interesting origin for systematic reactivity studies, as the P_3 core is both isoelectronic (14 valence electrons) and isolobal with the C_2O core of an epoxide (Figure 1a). The ring strain present in epoxides significantly enhances their reactivity, and these compounds undergo archetypal examples of nucleophilic ring opening reactions (Figure 1b/c), and represent synthetic sources of two carbon units.[10,11] We have now examined the reactivity of **2** with Lewis

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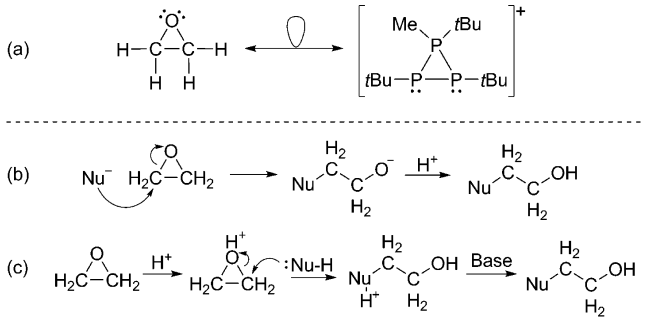


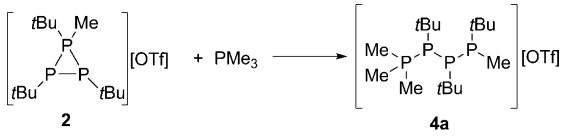
Figure 1. (a) Isolobal and isoelectronic relationship between ethylene oxide and $[(PtBu)_3Me]^+$, and classical reactivity of ethylene oxide with (b) anionic and (c) neutral, protic nucleophiles.

bases and report here the resultant discovery of a variety of routes to new *catena*-phosphorus compounds. In some cases, the reactivity of **2** parallels that of epoxides, and in others it is uniquely divergent.

RESULTS AND DISCUSSION

The reactivity of the prototypical *cyclo*-triphosphine $(PtBu)_3$ (**1**) has not been extensively investigated, despite the significant ring strain (average P−P−P = 60°) in this foundational molecule.[6,7,12] A mixture of **1** and Me_3P in CH_2Cl_2 was, therefore, studied by ^{31}P NMR spectroscopy, with no evidence of reaction apparent over 18 h at ambient temperature in CH_2Cl_2. The treatment, however, of the *cyclo*-diphosphinophosphonium salt $[(PtBu)_3Me][OTf]$ (**2**), itself prepared via methylation of **1** with MeOTf, with 1 equiv of Me_3P in CH_2Cl_2 at ambient temperature results in quantitative consumption of

Scheme 2. Reaction of 2 with Me_3P to Yield 4a



both reactants within 5 min (Scheme 2), as shown in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. Over this period, the resonances associated with **2** (δ_P −23, −49, and −111 ppm) and Me_3P (δ_P −60 ppm) are replaced by a series of broad signals between 20 and −35 ppm (see Supporting Information Figure SI-1), which resolve to a number of overlapping, complicated, closely related multiplets (Figure 2a) upon cooling to −80 °C. A crystalline material was reproducibly obtained from CH_2Cl_2/Et_2O at −30 °C, and was characterized by X-ray crystallography as $[Me_3P{-}PtBu{-}PtBu{-}P(Me)tBu][OTf]$ (**4a**) (see Figure SI-2; the data confirms atomic connectivity only).[13] In this context, the experimental $^{31}P\{^1H\}$ NMR data have been simulated with gNMR (see the Supporting Information) based on two AMNX spin systems (Figure 2c and d), by representing two diastereomeric forms of the cation in **4a**. For each diastereomer, the four distinct phosphorus resonances are interpreted as four discrete phosphorus chemical environments, with the six coupling constants consistent with three ^1J P−P interactions, that is, $250 < J < 400$ Hz,[14−16] and three longer range ($2 \times {}^2J$ and $1 \times {}^3J$) P−P interactions. Analysis of the $^{31}P\{^1H\}$ NMR spectrum at −80 °C also suggests that the two diastereomers are present in a ca. 1:1 ratio. At −80 °C, the ^1H NMR spectrum is also consistent with the presence of two diastereomers, with two distinct sets of resonances corresponding to three distinct "P*t*Bu" groups, and single "PMe" and "Me_3P" moieties. At 25 °C, however, a single set of resonances is observed, with integrals as expected for "P*t*Bu", "PMe", and "Me_3P". The temperature dependence of this spectrum suggests that a ligand exchange process is in operation at 25 °C, consistent with the broad, ill-defined peaks observed in the $^{31}P\{^1H\}$ NMR spectrum at this temperature.

While the presence of three stereogenic phosphorus centers in the cation of **4a** dictates that eight stereoisomers are possible (two enantiomers for each of four diastereomers), only two diastereomers are observed experimentally in the $^{31}P\{^1H\}$ and ^1H NMR spectra of **4a** at −80 °C. If the reaction of **2** with Me_3P occurs via attack of Me_3P as a nucleophile at either of the phosphinic centers of **2** (P_A or P_B in Figure 3), representing a classical S_N2 ring opening with the nucleophile approaching *trans* to the $P_A{-}P_C$ or $P_B{-}P_C$ bonds, two diastereomers (*i* and *ii*, respectively, in Figure 3) of the cation in **4a** are expected. In addition, the coordinate nature of the "$Me_3P{-}PtBu$" bond provides an avenue for the access to the two other diastereomers (*iii* and *iv*, Figure 3b) via dissociation of Me_3P from *i* and *ii*, respectively, and reassociation with the resulting prochiral, planar phosphenium cation (Fisher projections of all eight possible isomers are presented in Figure SI-3). Separation and structural elucidation of the two diastereomers observed in solution at −80 °C was not possible, precluding identification of the specific diastereomers present. The observed solid-state structure of **4a** (Figure SI-2), however, illustrates a *threo*, *erythro* configuration (*iii* in Figure 3), implicating a ligand exchange process based on the above arguments, which we note is in-line with the observed temperature dependence of both the ^1H and $^{31}P\{^1H\}$ NMR spectra of the compound.

The potential to form a thermodynamically favored isomer of the cation in **4a** via a ligand-exchange mechanism was explored via thermolysis of a solution of **4a** in chlorobenzene at 100 °C over 18 h. However, analysis of the resulting mixture by $^{31}P\{^1H\}$ NMR spectroscopy showed quantitative consumption of **4a** and a mixture of products dominated by a pair of mutually coupled doublet resonances (δ_P 13.5 and −12.3 ppm) assigned to the novel phosphinophosphonium salt $[Me_3P{-}P(Me)tBu][OTf]$ (**5**) (Scheme 3a), which was isolated and characterized by multinuclear NMR spectroscopy.[14] We interpret the observation in terms of initial cleavage of the coordinate $Me_3P{-}PtBu$ bond in **4a** enabling recyclization to **2**. At this temperature, an alternate reaction between Me_3P and **2** is feasible, in which Me_3P attacks the phosphonium center of the cationic ring, effecting abstraction of "P(Me)*t*Bu" to furnish **5**. Such an abstraction is envisaged to lead to the concomitant formation of *t*BuP═P*t*Bu, with this intermediate diphosphene expected to oligomerize to $(PtBu)_4$. There is, however, no evidence for this species in solution, nor *cyclo*-triphosphine **1**. However, the previously reported,[9] and closely related, triphosphinophosphonium salt $[(PtBu)_3(PMe_2)][OTf]$ (**3**) was shown to react with Me_3P at ambient temperature to yield the known phosphinophosphonium salt $[Me_3P{-}PMe_2][OTf]$ and $(PtBu)_3$ (Scheme 3b, and Supporting Information), in line with the proposed reactivity of **4a** under thermolysis.

Further to the reaction of **2** with the prototypical phosphine Me_3P, the reaction of **2** with nPr_3P in CH_2Cl_2 was also explored, again indicating quantitative consumption of reagents

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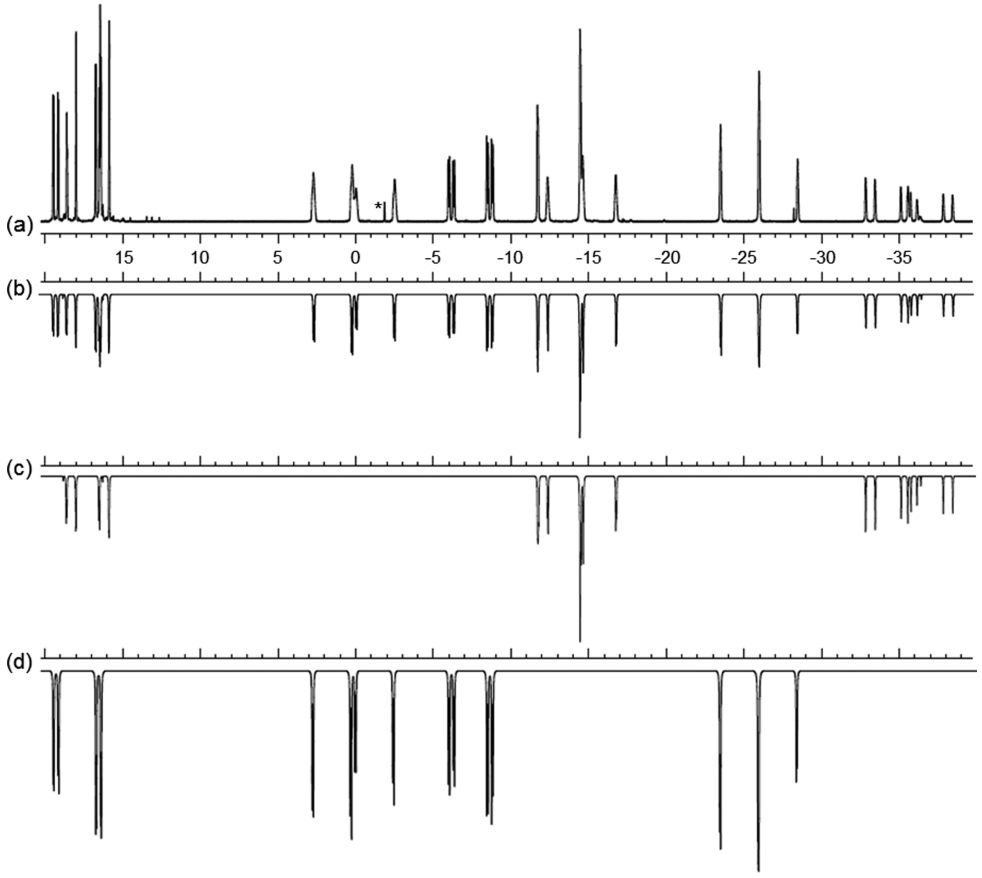
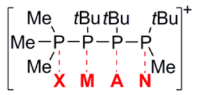
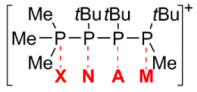


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra of **4a**: (a) experimental (−80 °C, CD_2Cl_2) and (b) simulated. Spectra (c) and (d) represent simulated spectra of the two component isomers (**4a**′ and **4a**″, respectively) present in (b). *Assigned as $[HPMe_3]^+$.

Table 1. Simulated ^{31}P NMR Parameters for the Observed Diastereomers of 4a

Isomer	Spin System	^{31}P Chemical Shift (ppm)				Coupling Constant (Hz)					
		A	M	N	X	J_{AM}	J_{AN}	J_{AX}	J_{MN}	J_{MX}	J_{NX}
4a'		-35.5	-14.6	-13.2	17.2	-334	-397	92	-5	-312	-4
4a''		-25.8	-7.5	0.1	17.8	-362	-361	-5	10	46	-400

within minutes by ^{31}P NMR spectroscopy. In this case, the product was isolated as a colorless oil, illustrating only broad, ill-defined resonances in the $^{31}P\{^{1}H\}$ NMR spectrum at 25 °C, and four distinct multiplet resonances at −80 °C (Figure 4a). The spectrum is simplified relative to that for **4a** under the same conditions, and simulation using gNMR (Figure 4b and Table 2) suggested a single AMNX spin system, consistent with the open-chain cation in $[n\mathrm{Pr}_3\mathrm{P}-\mathrm{P}t\mathrm{Bu}-\mathrm{P}t\mathrm{Bu}-\mathrm{P}(\mathrm{Me})t\mathrm{Bu}]$-[OTf] (**4b**). An additional series of low intensity resonances, apparent at −80 °C, are assigned to a second minor diastereomer of **4b**, in contrast to **4a**, for which two isomers appear in a ca. 1:1 ratio. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of the isolated product are also consistent with the assigned structure for **4b**, illustrating the presence of chemically equivalent *n*Pr groups and a triflate anion, respectively. The isolation of **4b** as an oil precluded analysis of the solid-state structure of this compound by X-ray diffraction.

The differing isomeric distributions in the formation of **4a** and **4b**, apparent by ^{31}P NMR spectroscopy at −80 °C, imply that the phosphine cone angle defines the observed distribution (cf. cone angle Me_3P = 118° and $n\mathrm{Pr}_3\mathrm{P}$ = 132°),[17] given that the relative basicities of Me_3P and $n\mathrm{Pr}_3\mathrm{P}$ are essentially comparable.[18] The differing steric encumbrance of the two phosphine donors may lead to a preferred attack at either of the phosphinic centers of the cation in **2** (P_A and P_B in Figure 3), or to differing thermodynamic stabilities of the various possible configurations of the open-chain cation. The former possibility, however, is supported by the observation that mixtures of **2** with Ph_3P and $t\mathrm{Bu}_3\mathrm{P}$ (cone angles 145° and 182°, respectively)[17] show no evidence of reaction by ^{31}P NMR spectroscopy over 20 h at ambient temperature, suggesting that steric encumbrance at the donor is particularly important with respect to the initial ring-opening process.

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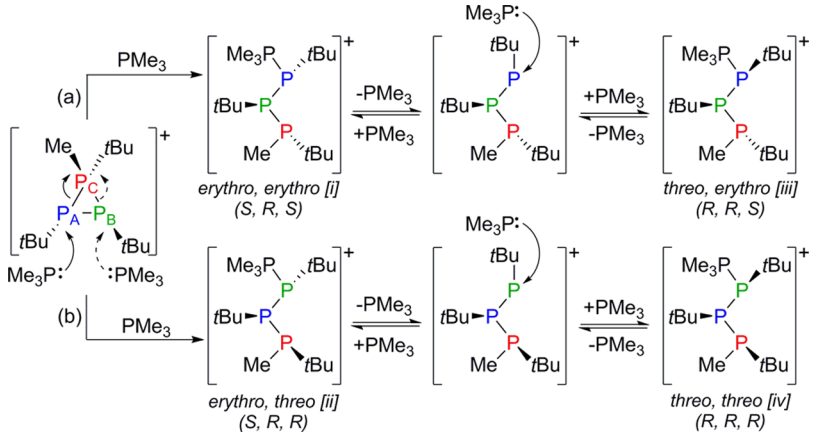
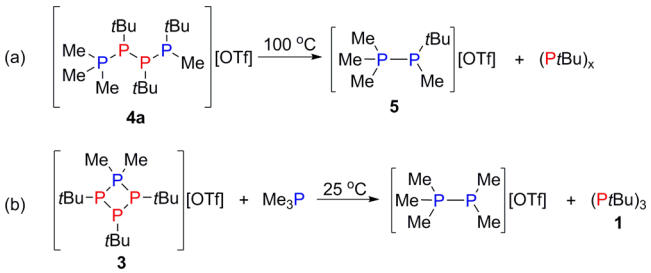


Figure 3. Proposed routes to the four possible diastereomers of the cation in **4a** derived from the *S, S* enantiomer of the cation in racemic **2**. Pathway (a) represents derivatives of nucleophilic attack at P_A, and (b) those of attack at P_B.

Scheme 3. Phosphenium Abstraction by Me_3P Resulting from (a) Thermolysis of 4a and (b) Treatment of 3 with Me_3P



Irrespective of the mechanistic aspects, quantitative formation of **4a/b** via the reactions of **2** with trialkylphosphines represent, to our knowledge, the first examples of nucleophilic ring-opening of a phosphorus homocycle. In addition, we note that compounds **4a/b** are isolobal inorganic models for the protonated intermediates invoked in acid-catalyzed ring-opening of epoxides (Figure 5), illustrating the parallel reactivity of the cation in **2** and epoxides toward nucleophilic attack.

While mixtures of triphosphine **1** with 1 equiv of dmap in CH_2Cl_2 over 18 h at ambient temperature show no evidence of reaction in the ^1H or ^{31}P NMR spectra, reaction of **2** with dmap over 1 h at ambient temperature in CH_2Cl_2 results in quantitative conversion to [(dmap)−P*t*Bu−P*t*Bu−P(Me)*t*Bu]-[OTf] (**6**) (Scheme 4), which has been characterized by multinuclear NMR spectroscopy, elemental microanalysis, and single crystal X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectrum of **6** at 25 °C is less complicated than those for derivatives of **4**, showing three distinct, well-resolved resonances [δ_P = 129.9 (d), −12.9 (d), −31.7 (t)]. The observed P−P coupling pattern is consistent with an AMX spin system, in which $^1J_{AM} \approx {}^1J_{AX}$, giving rise to an apparent triplet for the resonance of A, and for which the $^2J_{MX}$ coupling is not resolved, as simulated using gNMR (see Figure 6b and Table 3). Although both ^1H and ^{13}C NMR spectra at 25 °C were consistent with the formation of a single isomer of **6**, an additional low intensity broad singlet at −23 ppm is apparent in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature. The peak resolves to two singlets at −80 °C (Figure 6a), and a third resonance becomes apparent as a shoulder on the larger peak at 136 ppm. This minor product could not be isolated, and the favorable microanalysis of **6** is consistent with this species being a minor diastereomeric form.

Analysis of crystals of **6** by X-ray diffraction following recrystallization from CH_2Cl_2/Et_2O at −30 °C confirmed the expected atomic connectivity (Figure 7). The asymmetric unit of **6** contains two formula units (see also Figure SI-5), illustrating an ionic formulation in which the shortest interion contacts are O---C interactions between the anion and the *meta* position of the dmap ligand which measure 3.318(4) and 3.259(4) Å, respectively, for the two distinct formula units. The N−P bond length averages 1.816(2) Å, which is within the range defined by other examples of N−P bonds within cationic complexes (1.71−2.41 Å),[19−26] and is of similar magnitude to the sum of the covalent radii (Σ_{CR}) of the two elements, 1.82 Å.[27] The three phosphorus centers in each cation exhibit distorted pyramidal geometries, consistent with the presence of a stereochemically active lone pair at each site, and the

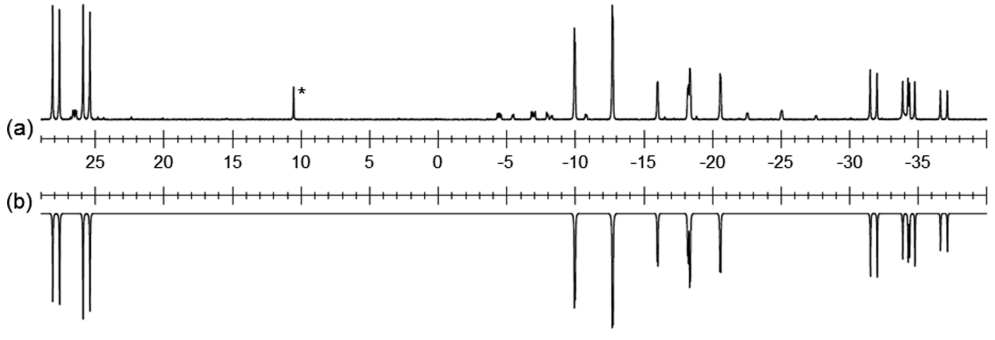


Figure 4. $^{31}P\{^1H\}$ NMR spectra of **4b**: (a) experimental (−80 °C, CD_2Cl_2) and (b) simulated. *Unidentified impurity (~2%).

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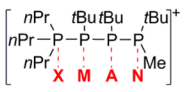
Table 2. Simulated ^{31}P NMR Spectroscopic Parameters for 4b

Spin System	^{31}P Chemical Shift (ppm)				Coupling Constant (Hz)					
	A	M	N	X	J_{AM}	J_{AN}	J_{AX}	J_{MN}	J_{MX}	J_{NX}
	-34.3	-18.3	-11.4	26.7	-346	-404	76	-5	-325	-2

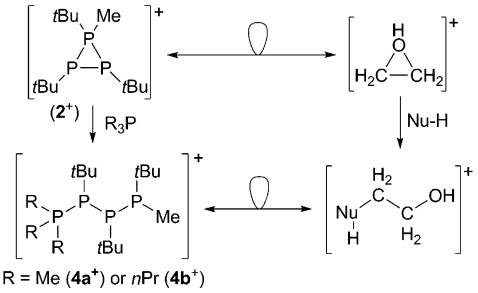
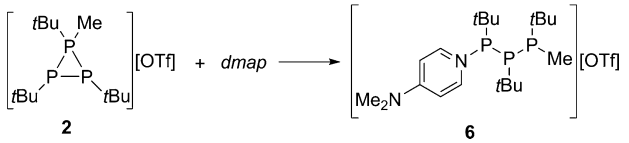


Figure 5. Isolobal relationship between the cations in **2** and **4a**/**b** with the intermediates in the acid-catalyzed ring-opening of epoxides.

Scheme 4. Reaction of 2 with dmap to Yield 6



observed *pseudo*-gauche conformation for the N−P−P−P chain (average torsion angle = 29.07(7)°) likely minimizes steric interactions between the bulky *t*Bu groups. Interestingly, the cation exhibits *threo*, *erythro* stereochemistry as in the case of Me_3P adduct **4a**. This suggests that the mechanism of formation of **6** cannot involve solely an S_N2 ring-opening of the cation in **2** by dmap, and based on the previously introduced mechanistic considerations (see Figure 3) must invoke an initial ring-opening reaction followed by ligand dissociation/reassociation to produce the observed configuration. Furthermore, the observation of a single diastereomer of **6** by NMR spectroscopy from samples of both the crude amorphous reaction products and purified crystalline material imply that the *threo*, *erythro* configuration is in this case thermodynamically favored.

Observation of a single diastereomer of **6** by NMR spectroscopy contrasts the formation of two diastereomers of **4a** in an approximately 1:1 ratio, and prompted the investigation of the reaction of **6** with Me_3P as a potential route to a single diastereomer of **4a**. While the reaction of **6** with 2 equiv of Me_3P over 18 h evidences ligand exchange of dmap for Me_3P in the ^{1}H and ^{31}P{^{1}H} NMR spectra, both previously observed isomers of **4a** are apparent at −80 °C along with other minor products (Figure SI-6), inconsistent with a simple S_N2 ligand exchange process.

Mixtures of **2** with pyridine, NEt_3, 2,2′-bipyridine (2,2′-bipy) or 4,4′-bipyridine (4,4′-bipy) in CH_2Cl_2 showed no evidence of reaction by ^{31}P NMR spectroscopy over 18 h at ambient temperature, which we attribute to the lower basicity of each donor relative to dmap.[28] Moreover, reaction of **2** with the representative NHC 1,3-di-*tert*-butyl-4,5-dihydroimidazol-2-ylidene (*t*BuImz) leads to an intractable mixture containing multiple products, none of which are consistent with the desired [(*t*BuImz)−P*t*Bu−P*t*Bu−P(Me)*t*Bu][OTf].[29] Treatment of **2** with MeLi or [Li][PPh_2] at −78 °C in THF also leads to intractable mixtures, with the oily yellow products inconsistent with the targeted symmetric triphosphine *t*Bu-(Me)P−P*t*Bu-P(Me)*t*Bu[30] and tetraphosphine Ph_2P−P*t*Bu−P*t*Bu−P(Me)*t*Bu,[31] respectively.

The insertion of phosphenium cations into the P−P bonds of neutral three and four membered phosphorus rings is well established,[9,32−34] and we envisaged analogous reactivity for the cation in **2**. To this end, a solution of **2** in CH_2Cl_2 was treated with Me_2PCl/TMSOTf in a 1:1:1 ratio, and the mixture was analyzed by ^{31}P NMR spectroscopy. After 1 h at ambient temperature, approximately 45% consumption of **2** is observed, along with the appearance of a new, closely related AA′B spin system ($\delta A \approx \delta A' = -110.1$, $\delta B = -49.5$, $J_{AB} \approx J_{A'B} = 312$ Hz) assigned to [(*t*BuP)$_2$(PMe_2)][OTf] (**7**), based on the similarity with the chemical shifts and pattern for **2** (AMX spin system: $\delta A = -110.6$, $\delta M = -48.9$, $\delta X = -23.4$, $J_{AM} = 125$ Hz, J_{AX} =

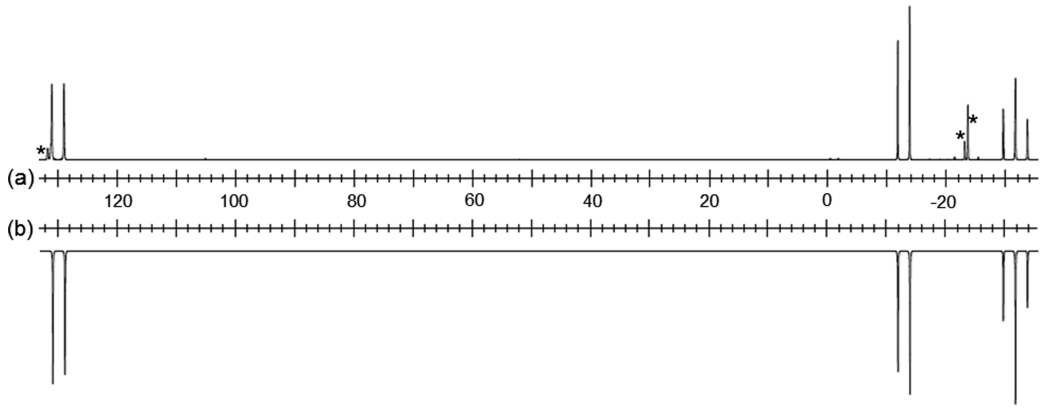


Figure 6. ^{31}P{^{1}H} NMR spectra of **6**: (a) experimental (−80 °C, CD_2Cl_2) and (b) simulated. *Resonances tentatively assigned as a second isomer of **6**.

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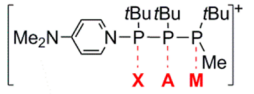
Table 3. Simulated ^{31}P NMR Spectroscopic Parameters for 6

Spin System	^{31}P Chemical Shift (ppm)			Coupling Constant (Hz)		
	A	M	X	J_{AM}	J_{AX}	J_{MX}
	-31.6	-12.9	129.9	-411	-416	8

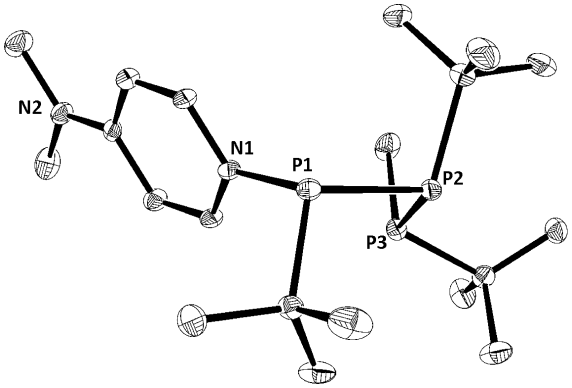
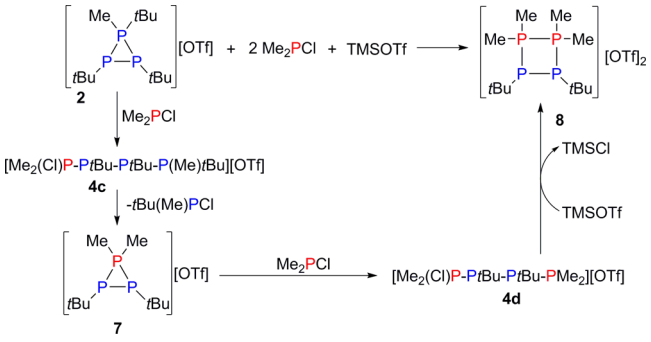


Figure 7. Solid-state structure of one of two structurally similar cations in the asymmetric unit of **6**. All hydrogen atoms are omitted for clarity.

336 Hz, J_{MX} = 316 Hz), and a new singlet (δ_P 119 ppm) assigned to *t*Bu(Me)PCl.[35] We speculate that the formation of **7** occurs via the insertion of a "Me_2P" unit into **2** with elimination of a "*t*Bu(Me)P" moiety (Scheme 5), and consistently the resonances for **7** and *t*Bu(Me)PCl appear in a ca. 1:1 ratio. Despite the incomplete conversion of **2**, the presence of unreacted Me_2PCl (δ_P = 94 ppm) was not evident in the $^{31}P\{^1H\}$ NMR spectrum, and a series of broad ill-resolved resonances observed in the baseline are tentatively assigned to the open-chain species $[Me_2(Cl)P{-}PtBu{-}PtBu{-}PMeR]^+$ [R = *t*Bu (**4c**), Me (**4d**)], resulting from nucleophilic attack of **2** or **7** by Me_2PCl. Attempts to isolate either **7** or **4c** were, however, unsuccessful, with a colorless solid instead isolated following crystallization at −30 °C and characterized by spectroscopic, crystallographic and analytic methods as $[(Me_2P)_2(PtBu)_2][OTf]_2$ (**8**). Based on this observation, the reaction of **2** with two equivalents of Me_2PCl provided an improved crystalline yield of **8** (35%), and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicates an essentially quantitative formation of **8** (Scheme 5). The ^1H NMR spectrum of **8** comprises three resonances with relative integration 1:1:3, which are assigned as two pairs of distinct methyl groups, and two identical or closely related *t*Bu groups. The $^{31}P\{^1H\}$ NMR spectrum contains two complex, second order, multiplet resonances (Figure 8a) and was simulated using gNMR as an AA′BB′ spin system (Figure 8b), which also furnished the P−P coupling constants (Table 4). The $^1J_{PP}$ couplings corresponding to the phosphine−phosphonium (A−B/A′−B′, −282 Hz) bonds and the phosphine−phosphine bond (A−A′, −164 Hz) are consistent with the values in the tetraphosphorus monocation, $[(PtBu)_3(PMe_2)]^+$ (−251 and −143 Hz, respectively),[9] and in other related cations.[14] The calculated phosphonium−phosphonium coupling (B−B′), −37 Hz, is relatively small, but comparable to the values reported for other known 1,2-diphosphonium salts (48−219 Hz).[15,36,37]

Scheme 5. Synthesis and Proposed Mechanism for the Formation of 8



The solid-state structure of **8**, which crystallized in the $P2_1/c$ space group, contains a distinct dication and two triflate anions in the asymmetric unit, with the two shortest P---OTf contacts 3.421(2) and 3.499(2) Å [Σ_{CR} = 1.74 Å],[27] respectively (Figure 9). The dication contains a puckered tetraphosphorus ring [139.4° between the planes defined by P2−P1−P4 and P2−P3−P4, and P−P−P angles averaging 86.3°] with two neighboring tricoordinate "P*t*Bu" centers and two neighboring tetra-coordinate "PMe_2" centers. The angles around the two

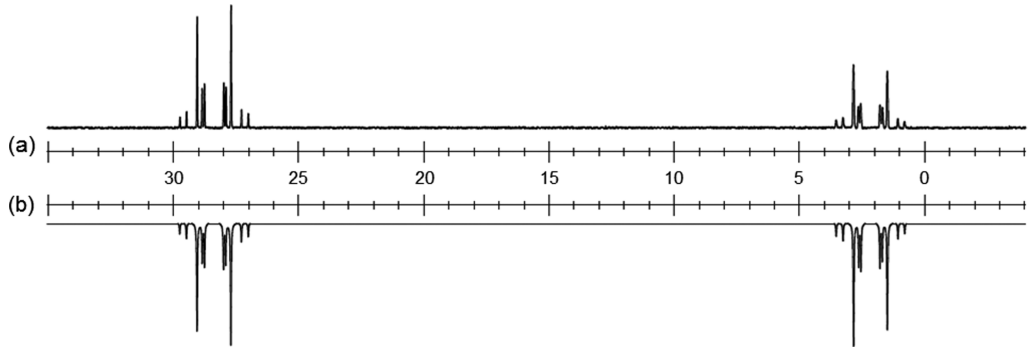


Figure 8. $^{31}P\{^1H\}$ NMR spectra of **8**: (a) experimental (25 °C, d_3-MeCN) and (b) simulated.

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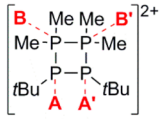
Table 4. Simulated ^{31}P NMR Spectroscopic Parameters for 8

Spin System	^{31}P Chemical Shift (ppm)				Coupling Constant (Hz)					
	A	A'	B	B'	$J_{AA'}$	J_{AB}	$J_{AB'}$	$J_{A'B}$	$J_{A'B'}$	$J_{BB'}$
	2.2	2.2	28.4	28.4	-164	-282	9	9	-282	-37

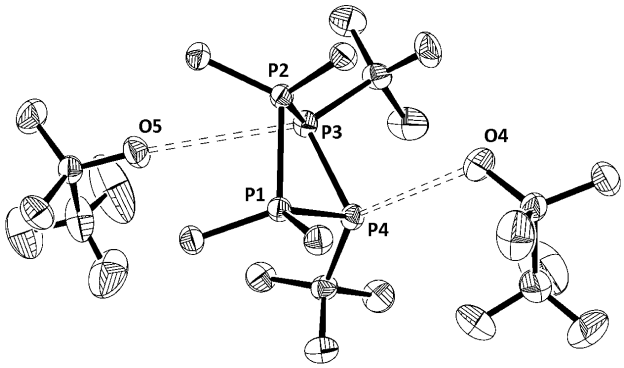


Figure 9. Solid-state structure of 8. All hydrogen atoms omitted for clarity.

tricoordinate centers (average 100.5°) are distinctly narrower than those at the two tetra-coordinate centers (average 109.1°), consistent with the presence of a stereochemically active lone pair at each of the tricoordinate centers. The four P−P bonds range from 2.193(1) [Me_2P−P*t*Bu; (P1−P4)] to 2.256(1) Å [*t*BuP−P*t*Bu; (P3−P4)], with the mean value [2.22 Å] consistent with that reported for P_4,[38] and the longer bonds reflecting the greater steric encumbrance of the *t*Bu groups, which occupy opposite faces of the puckered ring.

The cation in 8 represents the first example of a cyclic polyphosphorus framework (homocycle) containing adjacent tetra-coordinate phosphorus (phosphonium) centers. While a bond between two formally cationic centers is intuitively disfavored, examples of acyclic 1,2-diphosphonium cations, $[R_3P{-}PR_3][X]_2$, have been structurally characterized,[15,39,40] as well as rare examples of heterocyclic frameworks containing 1,2-diphosphonium connectivity (Figure 10, structures A−C),[36,37,41] with reported P−P bond lengths of the range 2.165(2)−2.277(1) Å (cf. P1−P2 = 2.207(1) Å in 8). The cation in 8 can also be compared with examples of isomeric tetraphosphorus homocycles containing a 1,3-diphosphonium arrangement $[(RR'P)_2(PR)_2][X]_2$ (R, R′ = $C_6H_3(OMe)_2$, X = Me_3SnF_2; R = Cy, R′ = Me, X = OTf) (Figure 10, structure D).[42,43] For R, R′ = $C_6H_3(OMe)_2$, the steric bulk of the substituents imposes a planar tetra-phosphorus ring, with P−P bond lengths of 2.231 and 2.232 Å, and a relative *trans* configuration of the respective phosphine centers. In contrast, for R = Cy, R′ = Me, the tetra-phosphorus ring is highly puckered with the angles between the planes defined by P1−P2−P3 and P1−P4−P3 measuring 148.5° (cf. 139.2° in 8); nevertheless, the four P−P bonds are consistent in length, averaging 2.214(1) Å.

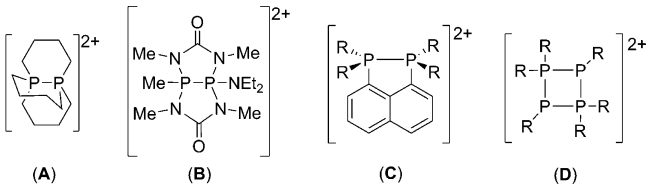
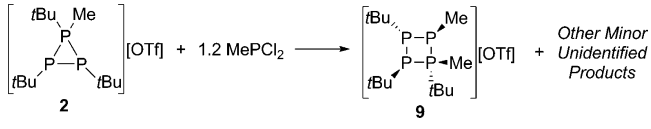


Figure 10. Examples of cyclic 1,2- (structures A−C) and 1,3-diphosphonium (structure D) dications.

We postulate that the formation of 8 involves a series of ring opening/closing and elimination steps (Scheme 5) initiated by nucleophilic attack of a phosphinic center in 2 by Me_2PCl, analogous to the reactivity with R_3P and dmap, which is envisaged to furnish the open-chain tetraphosphorus complex 4c. Subsequent elimination of *t*Bu(Me)PCl, as evidenced in the ^{31}P NMR spectra, enables cyclization to yield the diphosphinophosphonium salt 7, with the conversion of 2 to 7, an effective substitution of *t*Bu for Me at the phosphonium center, presumably driven by a reduction in the steric strain present in the phosphorus framework. Attack of 7 by a second equivalent of Me_2PCl is envisaged to lead to a second intermediate open-chain tetra-phosphorus salt, [Me_2(Cl)P−P*t*Bu-P*t*Bu-PMe_2]-[OTf] (4d), which can undergo cyclization in the presence of TMSOTf to yield 8.[44] Analogous mixtures of 2 with R_2PCl/TMSOTf (R = *t*Bu or Ph) showed no evidence of reactivity by ^{31}P NMR spectroscopy over 18 h at ambient temperature in CH_2Cl_2, presumably reflecting the greater steric bulk of these chlorophosphines, and also reduced basicity in the case of Ph_2PCl.

The reaction of 2 with 1 equiv of $MePCl_2$ in CH_2Cl_2 at ambient temperature results in almost complete conversion of the resonances associated with 2 to a series of new resonances in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture. Quantitative consumption of 2 is achieved by the introduction of a slight excess of $MePCl_2$, leading to a ^{31}P{^{1}H} NMR spectrum dominated by four complex resonances (δ_P 21.5, −26.4, −32.5, −97.4) of similar integrals, all appearing as doublets of doublets of doublets with evidence of second order effects. This new product was isolated (crystalline yield 38%) and spectroscopically characterized as the triphosphinophosphonium salt [(MeP)(P*t*Bu)$_2$(P(Me)*t*Bu)][OTf] (9), representing a product of insertion of "MeP" into the P−P framework of the cation in 2 (Scheme 6) and thus implicating a redox process. The ^{31}P{^{1}H} NMR spectrum of the purified product (Figure 11a) was assigned by simulation with gNMR (Figure 11b and Table 5), and the magnitudes of the six observed P−P coupling constants elucidated and interpreted as four $^1J_{PP}$ and two $^2J_{PP}$ couplings, consistent with a

Scheme 6. Reaction of 2 with $MePCl_2$ to Yield 9 (One of the Two Possible Enantiomers of This Diastereomer of 9 is Represented)



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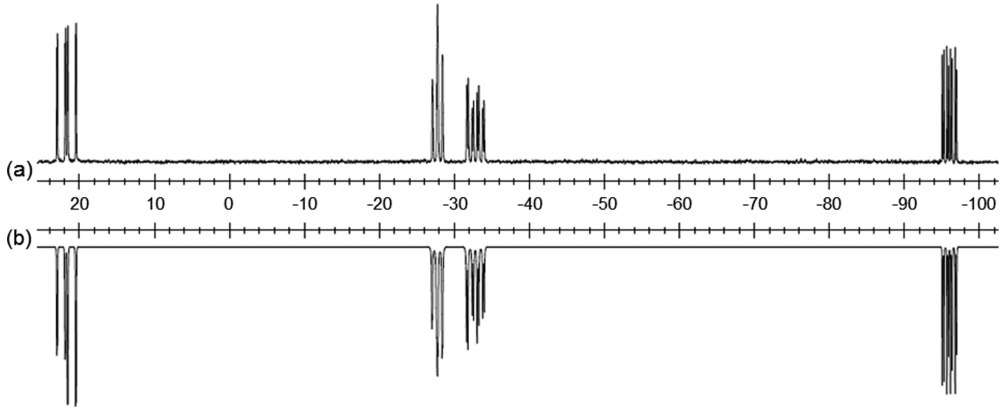
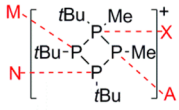


Figure 11. $^{31}P\{^{1}H\}$ NMR spectra of purified **9**: (a) experimental (25 °C, CD_2Cl_2) and (b) simulated.

Table 5. Simulated ^{31}P NMR Spectroscopic Parameters for 9

Spin System	^{31}P Chemical Shift (ppm)				Coupling Constant (Hz)					
	A	M	N	X	J_{AM}	J_{AN}	J_{AX}	J_{MN}	J_{MX}	J_{NX}
	-96.0	-32.8	-27.8	21.7	41	-124	-221	-151	-289	19

tetraphosphorus cycle containing four unique phosphorus centers. Furthermore, the presence of two couplings of >200 Hz are also in line with ^{1}J coupling between a phosphonium center and a phosphine center,[14,45] and those of <200 with adjacent *trans* phosphinic centers,[9] consistent with a tetraphosphorus cycle of three phosphine and one phosphonium center.

The ^{1}H NMR spectrum is also consistent with this assignment, displaying signals attributable to two distinct Me groups and three different *t*Bu groups. The two methyl resonances exhibit significantly differing chemical shifts, δ_P 2.29 and 1.70 ppm, with the former consistent with a phosphonium environment, and the latter a phosphine.[40,45] Consistently, a 2D proton-phosphorus correlation experiment ($^{31}P_{HMBC}$), illustrated coupling between the proposed phosphonium resonance at δ_H 2.29, and three of the four resonances in the ^{31}P NMR spectrum (A, M and X, respectively), and likewise the phosphinic resonance at δ_H 1.70 showed coupling with a different combination of three resonances (A, N and X), corresponding to ^{2}J and ^{3}J couplings, respectively (see Supporting Information, Figures SI-7–SI-10). Unsurprisingly, ^{4}J couplings are not evident, allowing complete assignment of the ^{31}P AMNX spin system as illustrated in Table 5. Similarly, the three *t*Bu resonances each correlate with a single phosphorus resonance (M, N, and X, respectively), again illustrating the absence of $^{4}J_{PH}$ coupling, and allowing the assignment of these resonances within the ^{1}H NMR spectrum.

The ^{1}H NMR resonances of the two P–Me environments also provide further structural insight by virtue of their multiplicities. The phosphonium resonance appears as a broadened doublet consistent with no significant long-range P–H coupling, with the phosphine resonance appearing as a second order eight-line multiplet, consistent with ^{3}J coupling. Based on previously reported correlations between the solid-state structures and NMR spectra of cationic phosphorus frameworks,[9] the latter observation suggests that the phosphinic Me group must be *cis* to the lone pair of at least one adjacent phosphine center. The cation in **9** is, therefore, suggested to comprise a tetraphosphorus ring containing a "P(Me)*t*Bu" phosphonium center, adjacent to "P*t*Bu" and "PMe" moieties, with a second "P*t*Bu" forming the fourth member of the cycle. Although the relative stereochemistry of the other phosphorus centers in **9** cannot be definitively assigned, based on steric arguments the most probable diastereomer would contain *cis*-methyl groups, with vicinal *t*Bu groups in all cases *trans* configured, as illustrated in Scheme 6.

The cation in **9** is a structural isomer of the cation in **3**, the product of the P–P insertion of $[Me_2P]^+$ into **1**,[8,9] and is related to the growing library of *cyclo*-triphosphinophosphonium salts.[9,34,46] While these salts can all be described by the general formula $[(R''R'P)(PR)_3][X]$, with identical substitution at all three phosphine centers, the cation in **9** represents an example of a lower symmetry substitution pattern, highlighting the unique preparation of **9** through P–P insertion of a notional neutral "PMe" moiety into an existing cationic framework. Although at least one redox process must be involved in the formation of **9**, the mechanism of this reaction remains to be elucidated. Analysis of the reaction mixture of $MePCl_2$ and **2** by ^{31}P NMR spectroscopy indicates the formation of **9** as the major product along with a number of minor unidentified products. Significantly, there was no evidence for the formation of the possible oxidation products $MePCl_4$[47] or *t*Bu(Cl)P–P(Me)*t*Bu–P(Cl)*t*Bu, which would be expected to appear in at least a 1:1 ratio with **9** if formed. Nonetheless, based on the reactions of **2** with other phosphines, we tentatively postulate the reaction may involve initial nucleophilic ring-opening of **2** by the chlorophosphine donor.

The reactions of **2** described above demonstrate diversity which is facilitated by the significant ring strain (average P–P–P angle = 60°) in the triphosphorus cation. In contrast, mixtures of the analogous tetra-phosphorus salt $[(PtBu)_4Me][OTf]$ (**10**) with R_3P (R = Me or *n*Pr), $Me_{3-x}PCl_x$ (x = 1 or 2), or dmap show no evidence of reaction under analogous conditions to those successfully employed for **2**. We attribute

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the relative inertness of **3** to the lower ring strain present in the cation (average P−P−P angle = 88°)[9] compared with that of **2**.

SUMMARY

The reactivity of the *cyclo*-diphosphinophosphonium salt $[(PtBu)_3Me][OTf]$ (**2**) with tertiary phosphines, chlorophosphines, and nitrogen donors has been investigated. The inherent ring strain of the cation in **2** promotes rapid reactivity at ambient temperature, which contrasts the inertness of the corresponding *cyclo*-triphosphinophosphonium salt $[(PtBu)_4Me][OTf]$ (**10**) under the same conditions.

Reactions of **2** with R_3P (R = Me or *n*Pr) quantitatively furnish the respective open-chain triphosphinophosphonium salts $[R_3P-PtBu-PtBu-P(Me)tBu][OTf]$ (R = Me (**4a**), *n*Pr (**4b**)). When R = Me, two diastereomeric forms are evidenced in the complicated $^{31}P\{^1H\}$ NMR spectra at −80 °C, but a single diastereomer is observed when R = *n*Pr. This differing reactivity is attributed to the greater steric encumbrance of nPr_3P, consistent with the observations that tBu_3P and Ph_3P do not react with **2** under the same conditions. Reaction of **2** with dmap yields a single diastereomer of an analogous open-chain triphosphinopyridinium salt [(dmap)-P*t*Bu-P*t*Bu-P(Me)*t*Bu]-[OTf] (**6**). The coupling constants in the complicated $^{31}P\{^1H\}$ NMR spectra observed for compounds **4a**/**b** and **6** were elucidated via simulation using gNMR. To our knowledge, these reactions represent not only routes to novel *catena*-phosphorus complexes, but also the first examples of nucleophilic ring-opening reactions of phosphorus homocycles.

Reaction of **2** with a 2:1 mixture of Me_2PCl and TMSOTf gives the unusual *cyclo*-diphosphino-1,2-diphosphonium salt $[(Me_2P)_2(PtBu)_2][OTf]$ (**8**) through two distinct ring opening/cyclization steps, via the diphosphinophosphonium salt $[(Me_2P)(PtBu)_2][OTf]$ (**7**). The cation in **8** represents a rare example of a cyclic 1,2-diphosphonium salt, and the first example of such connectivity within a homocycle. Reaction of $MePCl_2$ with **2** results in insertion of "MeP" into the cationic triphosphorus framework to form the triphosphinophosphonium salt $[(MeP)(PtBu)_2P(Me)tBu][OTf]$ (**9**), the first example of such a route to this class of polyphosphorus cation usually accessed via the insertion of phosphenium centers into neutral polyphosphorus frameworks.

The ring-opening reactivity of **2** parallels to some extent that of isoelectronic/isolobal epoxides, and reveals inorganic analogues of intermediates formed in their acid-catalyzed ring-opening. However, the insertion and ring-expansion observed for **2** upon reaction with chlorophosphines illustrates reactivity that has not been observed in the corresponding organic systems.

ASSOCIATED CONTENT

Supporting Information

Details of all reported experiments along with crystallographic information pertaining to compounds **4a**, **6** and **8** are described, along with relevant spectra, as indicated in the above text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For recent high profile examples, see:. Abersfelder, K.; White, A. J. P.; Rzepa, H. S.; Scheschkewitz, D. *Science* **2010**, *327*, 564−566. Chitnis, S. S.; Carpenter, Y.-Y.; Burford, N.; McDonald, R.; Ferguson, M. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 4863−4866. Al-Rafia, S. M. I.; Momeni, M. R.; McDonald, R.; Ferguson, M. J.; Brown, A.; Rivard, E. *Angew. Chem., Int. Ed.* **2013**, *52*, 6390−6395. Dielmann, F.; Sierka, M.; Virovets, A. V.; Scheer, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6860−6864. Braunschweig, H.; Ye, Q.; Vargas, A.; Dewhurst, R. D.; Radacki, K.; Damme, A. *Nat. Chem.* **2012**, *4*, 563−567.

(2) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*; Wiley: New York, 1998.

(3) Dutton, J. L.; Ragogna, P. J. *Coord. Chem. Rev.* **2011**, *255*, 1414−1425.

(4) Robertson, A. P. M.; Gray, P. A.; Burford, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 6050−6069.

(5) Burford, N.; Ragogna, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4307−4315.

(6) Baudler, M.; Gruner, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1311−1312.

(7) Baudler, M.; Glinka, K. *Inorg. Synth.* **1989**, *25*, 1−5.

(8) Burford, N.; Dyker, C. A.; Lumsden, M.; Decken, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6196−6199.

(9) Dyker, C. A.; Burford, N.; Menard, G.; Lumsden, M. D.; Decken, A. *Inorg. Chem.* **2007**, *46*, 4277−4285.

(10) Padwa, A.; Murphree, S. S. *ARKIVOC* **2006**, *(iii)*, 6−33.

(11) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737−799.

(12) Hahn, J.; Baudler, M.; Krüger, C.; Tsay, Y.-H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 797−805.

(13) Despite extensive attempts to furnish high quality single crystals of **4a**, only low quality crystals could be attained. X-ray diffraction studies on these crystals repeatedly confirmed the atomic connectivity, but were not appropriate for the determination of detailed metrical parameters. The best of these "connectivity only" structures is illustrated in Figure SI-2, and has an *R*-factor of 14.37%. We attribute the difficulties in attaining well-formed crystals of **4a** to the conformational nonrigidity of the complex and the presence of two diastereomers in solution.

(14) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404−14410.

(15) Weigand, J. J.; Riegel, S. D.; Burford, N.; Decken, A. *J. Am. Chem. Soc.* **2007**, *129*, 7969−7976.

(16) Ali, A. A. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1988**, 2775−2780.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(18) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791−5794.

(19) Reed, R.; Réau, R.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed.* **1993**, *32*, 399−401.

(20) Burford, N.; Spinney, H. A.; Ferguson, M. J.; McDonald, R. *Chem. Commun.* **2004**, 2696−2697.

(21) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087−1091.

(22) Burford, N.; Phillips, A. D.; Spinney, H. A.; Lumsden, M.; Werner-Zwanziger, U.; Ferguson, M. J.; McDonald, R. *J. Am. Chem. Soc.* **2005**, *127*, 3921−3927.

(23) Blättner, M.; Nieger, M.; Ruban, A.; Schoeller, W. W.; Niecke, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2768−2771.

(24) Meisel, M.; Lönnecke, P.; Grimmer, A.-R.; Wulff-Molder, D. *Angew. Chem., Int. Ed.* **1997**, *36*, 1869−1870.
(25) Huynh, K.; Chun, C. P.; Lough, A. J.; Manners, I. *Dalton Trans.* **2011**, *40*, 10576−10584.
(26) Boomishankar, R.; Ledger, J.; Guilbaud, J.-B.; Campbell, N. L.; Bacsa, J.; Bonar-Law, R.; Khimyak, Y. Z.; Steiner, A. *Chem. Commun.* **2007**, 5152−5154.
(27) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 186−197.
(28) As Lewis acid/base adducts, stable ring-opened complexes of **2**, e.g., **4a**, **4b**, and **6**, are likely to be in equilibrium with **2** and free ligand, albeit in favor of the products. As such, we note that apparently unreactive donors may react with **2**, but with equilibria strongly favoring **2** and the free ligand.
(29) At the suggestion of a reviewer, we preliminarily explored the reaction of **2** with cyclohexyl isocyanide under similar conditions. The reaction yielded a yellow oil which was characterized by $^{31}P\{^{1}H\}$ NMR spectroscopy at 25 °C, indicating the formation of a mixture dominated by a new AMX spin system (see Supporting Information), consistent with a new ring-opened product.
(30) Armstrong, D. R.; Feeder, N.; Hopkins, A. D.; Mays, M. J.; Moncrieff, D.; Wood, J. A.; Woods, A. D.; Wright, D. S. *Chem. Commun.* **2000**, 2483−2484.
(31) Two sets of resonances (δ_P −56 and −94 ppm) corresponding to $(PtBu)_3$ (**1**) were observed, suggesting that $Li[PPh_2]$ may effect abstraction of MeOTf from **2**, although Ph_2PMe was not observed in the ^{31}P NMR spectrum.
(32) Burford, N.; Dyker, C. A.; Decken, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2364−2367.
(33) Weigand, J. J.; Holthausen, M.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 295−298.
(34) Holthausen, M. H.; Knackstedt, D.; Burford, N.; Weigand, J. J. *Aust. J. Chem.* **2013**, *66*, 1155−1162.
(35) Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth, R.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2009**, *28*, 5432−5444.
(36) Schomburg, D.; Bettermann, G.; Ernst, L.; Schmutzler, R. *Angew. Chem., Int. Ed.* **1985**, *24*, 975−976.
(37) Alder, R. W.; Ganter, C.; Harris, C. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1172−1174.
(38) Cossairt, B. M.; Cummins, C. C.; Head, A. R.; Lichtenberger, D. L.; Berger, R. J. F.; Hayes, S. A.; Mitzel, N. W.; Wu, G. *J. Am. Chem. Soc.* **2010**, *132*, 8459−8465.
(39) Romakhin, A. S.; Palyutin, F. M.; Ignat'ev, Y. A.; Nikitin, E. V.; Kargin, Y. M.; Litvinov, I. A.; Naumov, V. A. *Russ. Chem. Bull.* **1990**, *39*, 585−589.
(40) Weigand, J. J.; Burford, N.; Decken, A.; Schulz, A. *Eur. J. Inorg. Chem.* **2007**, 4868−4872.
(41) Somisara, D. M. U. K.; Bühl, M.; Lebl, T.; Richardson, N. V.; Slawin, A. M. Z.; Woollins, J. D.; Kilian, P. *Chem.—Eur. J.* **2011**, *17*, 2666−2677.
(42) Heuer, L.; Ernst, L.; Schmutzler, R.; Schomburg, D. *Angew. Chem., Int. Ed.* **1989**, *28*, 1507−1509.
(43) Riegel, S. D.; Burford, N.; Lumsden, M. D.; Decken, A. *Chem. Commun.* **2007**, 4668−4670.
(44) Given the preferred formation of **8** upon addition of either 1 or 2 equiv of Me_2PCl to **2**, the initial ring opening of **2** with Me_2PCl may be either rate limiting or an equilibrium process, such that in the presence of a single equivalent of Me_2PCl compound **8** continues to be feasible.
(45) Carpenter, Y.-Y.; Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2008**, *130*, 15732−15741.
(46) Weigand, J. J.; Burford, N.; Davidson, R. J.; Cameron, T. S.; Seelheim, P. *J. Am. Chem. Soc.* **2009**, *131*, 17943−17953.
(47) Deng, R. M. K.; Dillon, K. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1911−1916.