

The Quest for Diphosphirenium and Diphosphirenylium Salts, Diheteroatom-Containing Cyclopropenium Analogues

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Introduction

Three-membered rings are not only fascinating species for scientists because of their inherent ring strain but also valuable starting materials for the chemical industry; for example, millions of tons of oxirane (the first heterocycle to be discovered 1859)¹ and aziridine (1888)² are produced each year for the preparation of various polymeric materials (Figure 1).

Historically, all of the isolable carbon and nitrogen three-membered ring systems were obtained before 1960, whereas in the phosphorus-containing series, the story only really started in 1963 with the discovery of phosphiranes **N**³ (Figure 2).

The cyclopropenium salts **C** have attracted considerable attention as prototypes of two- π -electron Hückel aromatic systems.⁷ In contrast, the isoelectronic azirinium **H** and diazirinium salts **M** have yet to be characterized even spectroscopically. The postulated involvement of **M** in the exchange reactions of nucleophiles with halogeno-3*H*-diazirines, a reaction of crucial importance for the synthesis of functionalized diazirines **J** and therefore of carbenes, has recently been refuted.⁵ In fact, very few examples of heteroatom-containing cyclopropenium analogues have been isolated. Among them, only compounds **R**⁸ and **Xa–c**^{9–11} are two- π -electron three-membered Hückel aromatic systems, while derivatives **Q**¹² and **Ya,b**^{13,14} have to be considered as two- π -electron three-membered Hückel-type σ^* -aromatic systems (see below).

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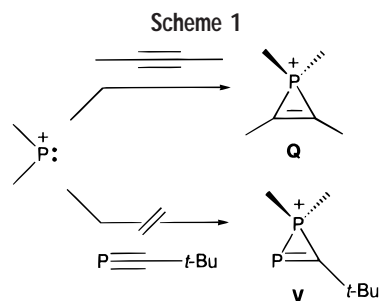
Guy Bertrand was born in Limoges, France, in 1952. He graduated (ingénieur ENSCM) from the University of Montpellier and moved to the University Paul Sabatier as an Attaché de Recherche CNRS in 1975. Since 1988, he has been Directeur de Recherche at the Laboratoire de Chimie de Coordination du CNRS in Toulouse. His research spans a wide range of topics at the border between organic and inorganic chemistry. He serves as an Editorial Board member of *Heteroatom Chem.*, *C. R. Acad. Sci. Fr.*, *Top. Stereochem.*, and *Chem. Rev.* He has received the International Council on Main Group Chemistry Award in 1993 and the Humboldt Award in 1994 and has been elected Membre Correspondant of the French Academy of Sciences in 1996.



FIGURE 1. Oxirane and aziridine.

This Account deals with the synthesis, structure, and reactivity of the diphosphirenium and diphosphirenylium salts **V** and **W**, respectively. Special attention will be given to the differences in bonding and therefore reactivity of these first examples of isolable diheteroatom-containing cyclopropenium analogues.

Synthesis of Diphosphirenium and Diphosphirenylium Salts. By analogy with the synthetic method used to prepare phosphirenium salts **Q**,¹² we initially tried to prepare a diphosphirenium salt of type **V** by [2+1]-cycloaddition reactions of various phosphonium salts to *tert*-butylphosphaalkyne. However, all of our attempts failed (Scheme 1).



As a result, we turned our attention toward a totally different synthetic strategy. Due to their high electrophilicity, dicoordinate^{15a} and, of course monocoordinate^{15b,c} phosphorus cations react with phosphines, giving the corresponding 1,1-adducts. Therefore, a $1\sigma^1,3\sigma^3$ -diphosphaallyl cation, which might conceivably be available through heterolytic cleavage of the P–X bond of a *C*-phosphinophosphaalkene appeared to be a good precursor for the desired diphosphirenium salt **V** (Scheme 2). Since both amino and bulky substituents are known to stabilize cyclopropenium salts,¹⁶ we decided to investigate the Lewis-acid-induced P–N bond cleavage of the phosphoalkene **2**, which is readily synthesized from the corresponding bis(phosphino)diazomethane **1**.¹⁷ Indeed, treatment of **2** with 2 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{NH}$ complex at room temperature afforded diphosphirenium salt **V1** as non-air-sensitive pale-yellow crystals (mp 118 °C) in 60% yield^{18a} (Scheme 2).

Subsequently, we found that using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in the place of $\text{BF}_3 \cdot \text{Et}_2\text{NH}$ brought about the formation of the four-membered heterocycle **3** (60% yield) rather than **V1**.^{18b} We quickly realized that the different outcome of this reaction could be attributed to the lack of the base, which had served to induce the transformation of **3** into **V1** (Scheme 3).

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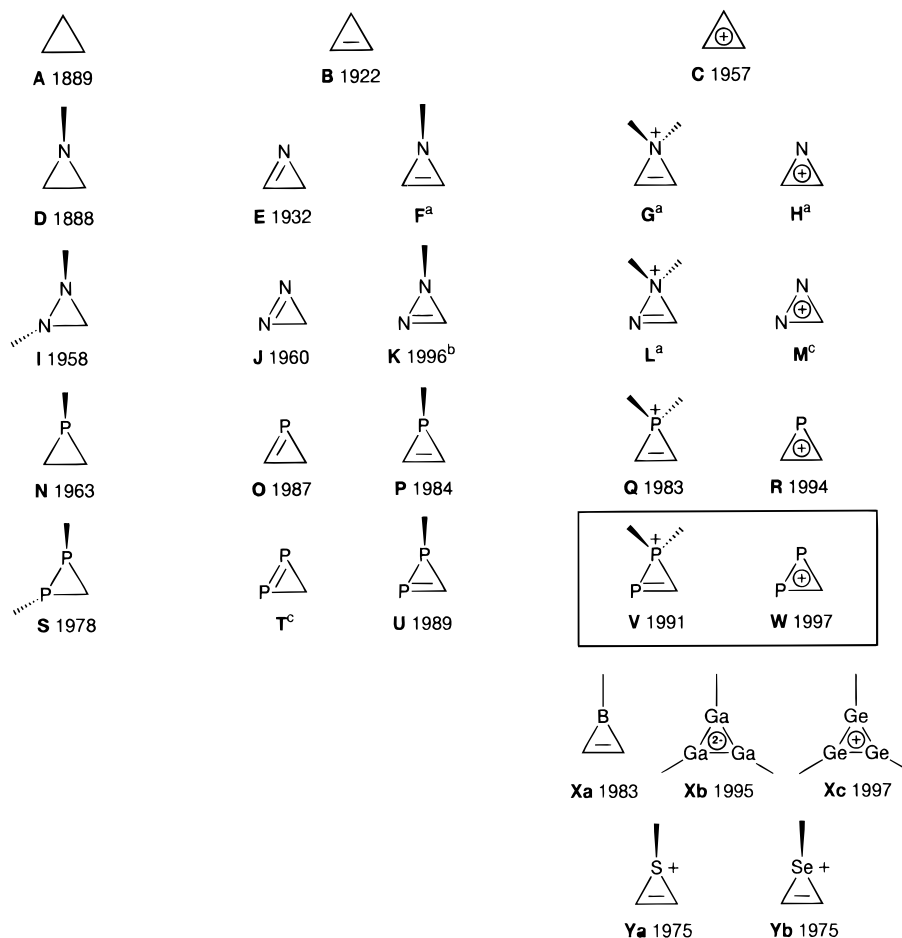
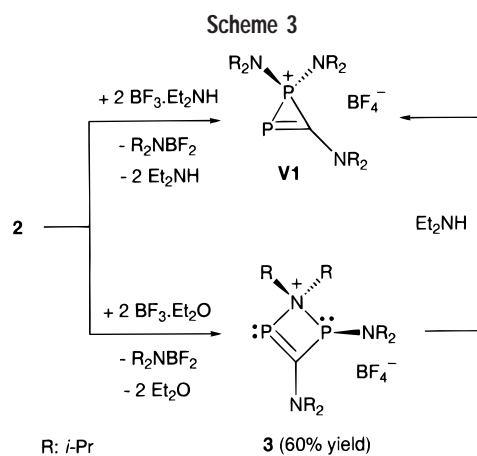
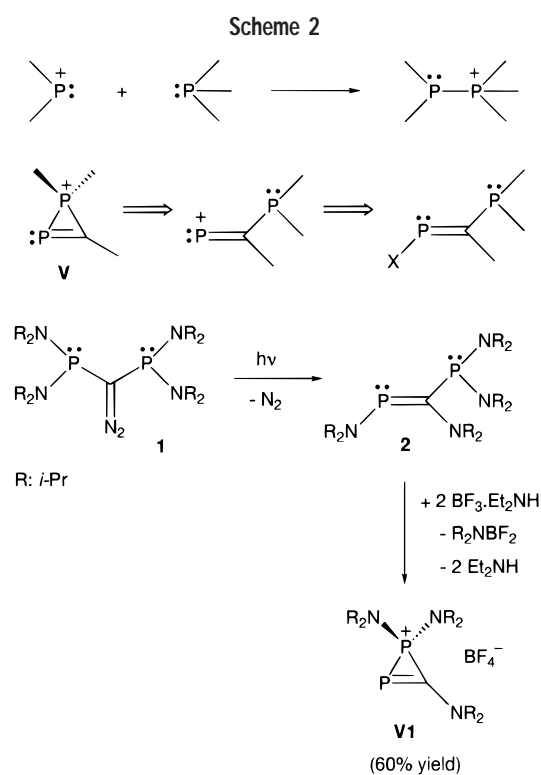
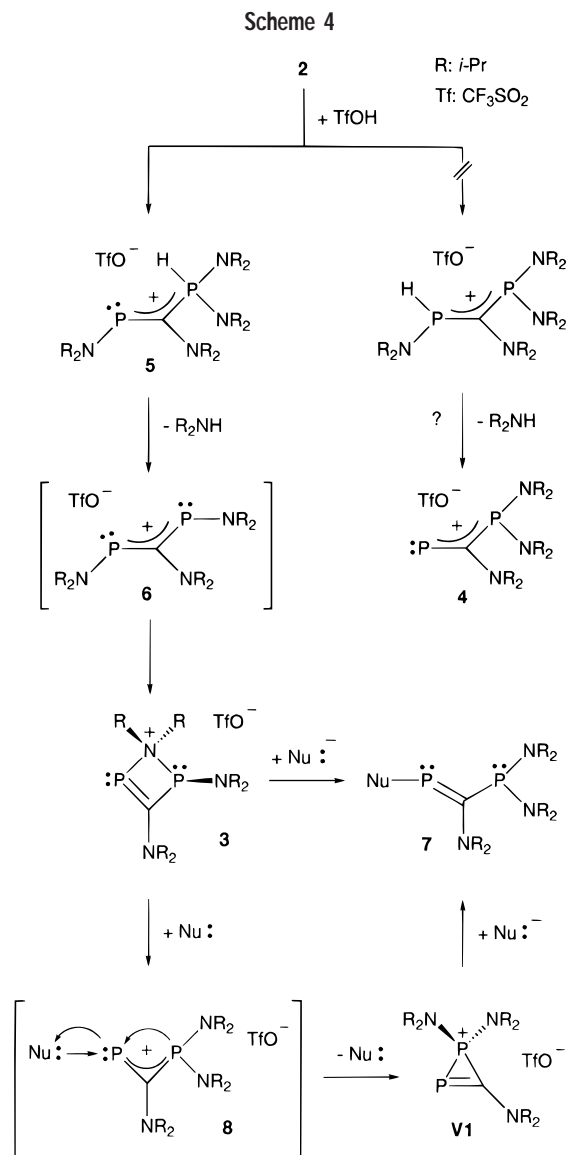


FIGURE 2. Cyclopropanes, cyclopropenes, cyclopropenium salts, and their nitrogen- and phosphorus-containing analogues. The substituents have been omitted on carbon atoms but are represented by an external line on all the heteroatoms. ^aNever, even spectroscopically, characterized. ^bOne 1*H*-diazirine has been spectroscopically characterized. ^cDiazirinium salts **M**⁵ and 3*H*-diphosphirenes **T**⁶ have been postulated as transient intermediates.



Then, we demonstrated the complete mechanism for the reaction leading to the diphosphirenium salt **V1** from phosphalkene **2**. Treating **2** with trifluoromethanesulfonic acid allowed us to spectroscopically characterize the 1 σ^2 ,3 σ^4 -diphosphallyl cation **5**, which clearly demonstrated that the acid reacted at the σ^3 -phosphorus atom of **2**.^{18b} By varying the nature of the amino groups, we then proved that a 1,1-elimination occurred at the σ^4 -phosphorus atom leading to the transient 1 σ^2 ,3 σ^2 -diphosphallyl cation **6**, which was isolated as the donor–



acceptor complex **3**. In other words, in contrast to our intended synthetic strategy, the reaction does not proceed through the $1\sigma^1,3\sigma^3$ -diphosphaallyl cation **4**! Subsequently, we showed that anionic nucleophiles reacted at the σ^2 -phosphorus of **3** or **V1** to afford the corresponding *C*-phosphinophosphaalkenes **7**. In the presence of neutral nucleophiles such as diethylamine, **3** gives the diphosphirenium salt **V1** probably via the transient intermolecular donor–acceptor complexes **8** of the desired $1\sigma^1,3\sigma^3$ -diphosphaallyl cation **4** (Scheme 4). Although our retrosynthetic strategy was not perfect, the desired diphosphirenium salt **V1** was obtained!

Having in hand the diphosphirenium salt **V1**, we were prompted to investigate the possibility of synthesizing a diphosphirenylium salt of type **W**. However, we had to keep in mind that in contrast to the phosphirenium salts **Q**, which are known to be stable, the phosphirenylium salts **R** have only been observed spectroscopically in SO₂ solutions at -78°C ,^{8a} or when complexed in an η^3 -fashion to an electron-rich Ni⁰ center.^{8b} The difficulty in isolating species such as **R** is essentially due to the very high electrophilicity of the phosphorus atom. In addition, the

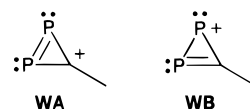
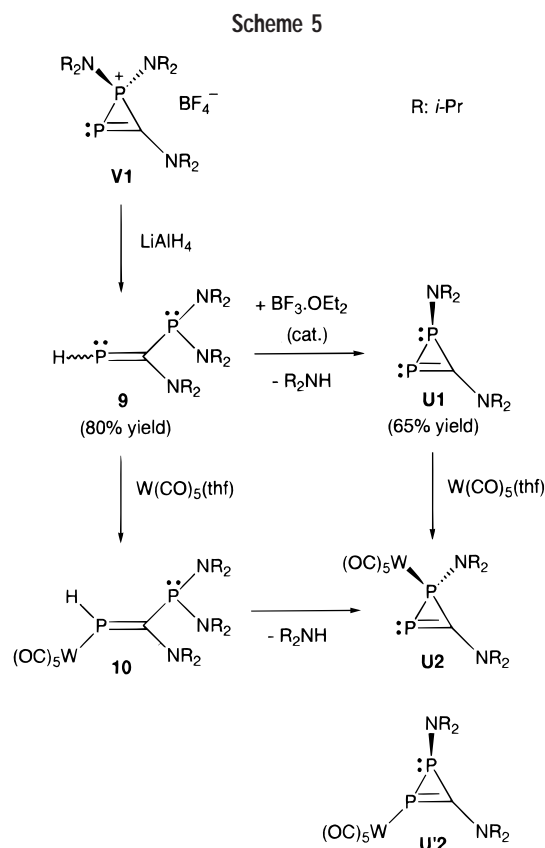


FIGURE 3. Resonance forms of the diphosphirenylium salt **W**.

desired diphosphirenylium **W** would suffer from the presence of either a weak P=P (resonance form **WA**) or P=C double bond¹⁹ (resonance form **WB**) (Figure 3).

Since the obtention of a stable free diphosphirenylium salt **W** was quite unlikely, we chose to prepare this type of compound in the coordination sphere of a transition metal. Again, the ability of Lewis acids to induce P–N bond cleavage was envisaged, making the 1,3-diamino-diphosphirene complex **U2** the ideal precursor (Scheme 5). However, before our work, only one example of free

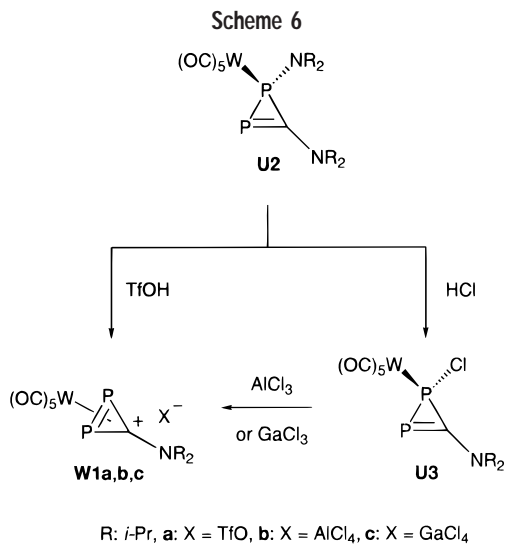


1*H*-diphosphirene **U**^{20a} and two complexes^{20b,c} featuring heterocycle **U** as an η^1 -ligand were known. All of these have been obtained by the addition of scarce transient free or coordinated phosphinidenes to phosphoalkynes. Thus, we first sought a simple synthetic route to free or coordinated 1*H*-diphosphirene **U**, which could be used on multigram scales.

We have already shown that ring-opening reactions occur when the diphosphirenium salt **V1** was treated with nucleophiles.^{18b,21} In a similar way, addition of 1 equiv of lithium aluminum hydride to a THF solution of **V1** afforded the corresponding *P*-hydrogenophosphaalkene **9** as a 50/50 mixture of *Z* and *E* isomers in 80% total yield.²² Then, to induce the necessary 1,3-elimination reaction, a THF solution of **9** was treated at room

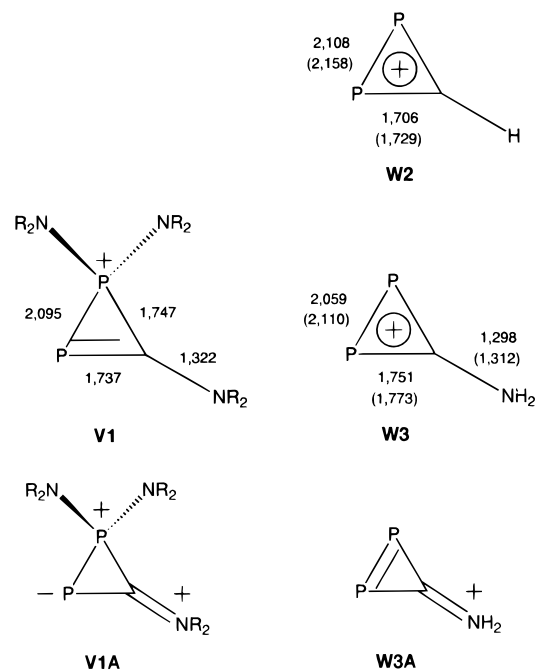
temperature with a catalytic amount (5%) of $\text{BF}_3 \cdot \text{OEt}_2$. After workup, the 1*H*-diphosphirene **U1** was obtained as a light yellow oil in 65% yield. The corresponding coordinated 1*H*-diphosphirene **U2** can be obtained by treatment of **U1** with $\text{W}(\text{CO})_5(\text{THF})$ (42% yield from **9**) or alternatively by addition of 1 equiv of $\text{W}(\text{CO})_5(\text{THF})$ to phosphalkene **9** (80% yield). Monitoring the latter reaction by ^{31}P NMR spectroscopy at 0 °C showed the primary formation of complex **10** as a single isomer in an *E* configuration, where the metal is η^1 -bonded to the σ^2 -phosphorus atom. The transformation of **10** into **U2** involved both the 1,3-elimination of diisopropylamine and the migration of the metal fragment. The former process is probably induced by a catalytic amount of $\text{W}(\text{CO})_5(\text{THF})$, which acts as a Lewis acid; the metal shift is governed by the higher thermodynamic stability of **U2** compared to the isomeric complex **U'2** featuring the metal fragment at the σ^2 -phosphorus atom²³ (Scheme 5).

Treatment of **U2** at -78 °C with 2 equiv of trifluoromethanesulfonic acid gave the desired diphosphirenylium salt **W1a** as a highly air and water sensitive red oil, stable for days in solution at room temperature.²⁴ The ionic nature of the complex **W1a** was demonstrated by the preparation of the corresponding tetrachloroaluminate and gallate salts **W1b,c**, which present identical ^{31}P , ^1H , and ^{13}C NMR data. Salts **W1b,c** were obtained in two steps from **U2** by treatment with 2 equiv of hydrogen chloride in pentane, which gives the 1-chloro-1*H*-phosphirene **U3**, followed by addition of a slight excess of aluminum or gallium trichloride (Scheme 6). The η^2 -coordination mode



of the heterocycle in **W1** (via the P=P bond) was deduced from the spectroscopic data: the ^{31}P NMR spectrum showed only one singlet at -157.4 ppm in the range expected for a three-membered phosphorus heterocycle,²⁵ with the axial and equatorial carbonyl groups appearing as two triplets in the ^{13}C NMR spectrum.

Structure of Diphosphirenium and Diphosphirenylium Salts. Cyclopropenium salts **C** are the prototype of 2- π -electron Hückel aromatic systems. Due to the higher electronegativity of nitrogen compared to carbon, the π -



		Mulliken charges	" π " charges
W2	q_{P}	0,50 (0,50)	0,38 (0,38)
	q_{C}	0 (0)	0,24 (0,24)
W3	q_{P}	0,38 (0,37)	0,20 (0,20)
	q_{C}	0,03 (-0,08)	0,24 (0,15)
	q_{N}	0,21 (0,34)	0,36 (0,45)

FIGURE 4. Experimental bond lengths for the diphosphirenium salt **V1**. Calculated bond lengths and atomic charges for the diphosphirenylium salts **W2** and **W3** at the RHF/DZP level (data in parentheses have been obtained at the B3LYP/DZP level). Resonance forms **V1A** and **W3A** are the best representation of the *C*-amino-substituted diphosphirenium **V1** and diphosphirenylium **W3**.

systems of (di)azirinium salts **H** and **M** are strongly polarized toward nitrogen and therefore these compounds are calculated to be less aromatic than the corresponding cyclopropenium salts;²⁶ no study is available on the corresponding tetracoordinate nitrogen containing salts **G** and **L**.

Taking into account the bonding parameters (bond lengths, electron distribution) as well as energetic criteria (resonance energies estimated by homodesmotic reactions), a theoretical investigation^{27a} has recently established that phosphirenylium salts **R** benefit from significant stabilization, even though the electron delocalization is estimated to be only 70% to that of the cyclopropenium salts **C**. According to calculations,^{27b,c} the PP and PC bond distances in the parent diphosphirenylium salt **W2** are halfway between those of single and double bonds, but the positive charge is essentially distributed over the two phosphorus centers (Figure 4). In other words, although the electronegativity of phosphorus is very close to that of carbon, the electronic delocalization becomes less with

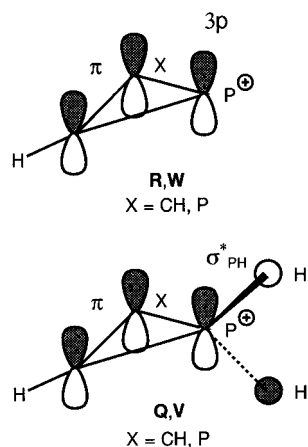


FIGURE 5. Molecular orbitals involved in the aromaticity of the (di)phosphirenylium and (di)phosphirenium salts **Q**, **R**, **V**, and **W**.

increasing phosphorus substitution in the ring system because the P(3p)–C(2p) and P(3p)–P(3p) interactions are usually weak (π -bond strengths: C=C, 70 kcal·mol⁻¹; P=C, 48 kcal·mol⁻¹; P=P, 34 kcal·mol⁻¹).¹⁹

Energies and structural data available from experimental^{12b,18a} as well as theoretical²⁸ studies demonstrate that (di)phosphirenium salts **Q** and **V** also benefit from a certain amount of aromatic stabilization. However, the resonance energies of phosphirenium salts **Q** have been calculated to be half those of the corresponding phosphirenylium salts **R**.

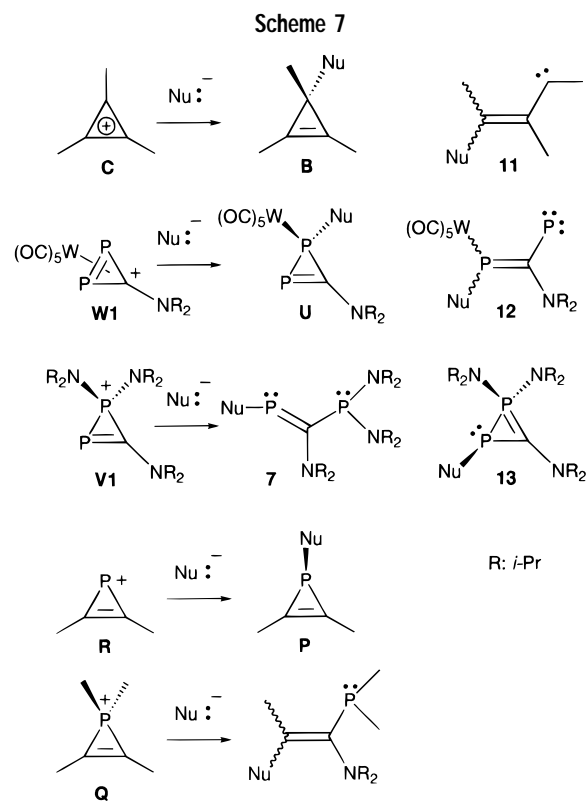
This striking difference between the σ^2 - and σ^4 -phosphorus-containing systems can be explained by considering the nature of the empty *p*-type orbital which is involved in the delocalization of the two- π -electrons over the ring. In (di)phosphirenylium salts **R** and **W** (which feature dicoordinate phosphorus centers), it is a 3p non-bonding orbital, while it is a σ^*_{PX} -type antibonding orbital for (di)phosphirenium salts **Q** and **V** (which feature tetra-coordinate phosphorus centers) (Figure 5). It is thus clear that the Hückel-type three-orbital two-electron interaction characteristic of the cyclopropenium cations **C** is more favored in (di)phosphirenylium salts **R** and **W** than in the corresponding (di)phosphirenium salts **Q** and **V**.

In the carbon series, it is well-established that the presence of amino substituents increases the stability of the cyclopropenium salts.^{16b} In the phosphorus series,^{27a} a similar effect has been predicted theoretically for phosphirenylium salts **R**, while in the diphosphorus-containing series, a single-crystal X-ray diffraction study of the diphosphirenium salt **V1** and a theoretical investigation of the diphosphirenylium salt **W3** afford some understanding of the influence of the amino substituent. The geometric parameters of the amino-substituted derivatives **V1** and **W3** are very similar (Figure 4). In both cases, there is a planar geometry around the ring carbon and the nitrogen atom, while the CN distances are typical of C=N double bonds and comparable to the value found in the tris(dimethylamino)cyclopropenium salt.^{16b} The PP distances are in the range associated with PP double bonds, and the PC bond lengths refer to single bonds. These data strongly suggest that, in both cases, the positive charge is

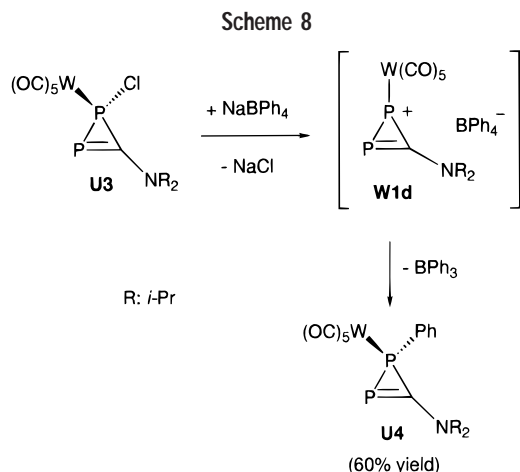
shifted outside of the ring, and therefore resonance structures **V1A** and **W3A** best describe these compounds (Figure 4). The major difference between these two derivatives is the nature of the PP bond, which is a genuine π -bond in **W3**, while compound **V1** exhibits a strong ylidic character comparable to that observed in phosphinylidene- σ^4 -phosphoranes (RP=PR₃).²⁹

Reactivity of Diphosphirenium and Diphosphirenylium Salts. Since both compounds **V1** and **W1** have only been recently discovered, little is known about their reactivity. However, some interesting features are emerging and corroborate the fact that the diphosphirenylium **W1** is more closely related to cyclopropenium salt **C** than the diphosphirenium **V1**.

Nucleophiles react with cyclopropenium **C** and diphosphirenylium salts **W1** affording the corresponding cyclopropenes **B** and 1*H*-diphosphirenes **U**, respectively. As briefly mentioned in the synthetic part of this review, lithium salts also react at the dicoordinate phosphorus atom of the diphosphirenium salt **V1**,^{18b,21} but in this case, ring-opening reactions occur, affording the phosphalkenes **7**. These results, as a whole, are easily explained by considering the much larger thermodynamic stabilities of the cyclopropenes **B**, 1*H*-diphosphirenes **U**, and phosphalkenes **7** compared with those of vinylcarbenes **11**, phosphalkenephosphinidenes **12**, and cyclic 4 π -electron ylides **13**, respectively. These results parallel those obtained with the phosphirenylium **R** and phosphirenium salts **Q** (Scheme 7).^{8,12}

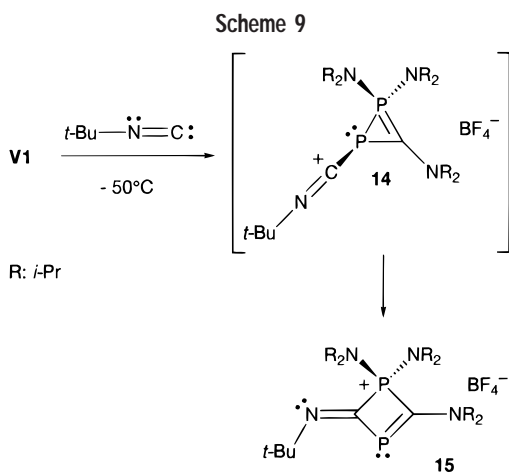


While diphosphirenium **V1** and also cyclopropenium **C** exist as borate salts, attempts to abstract chloride from diphosphirene **U3** with sodium tetraphenylborate led to



the phenyl-substituted 1*H*-diphosphirene **U4** (Scheme 8).²⁴ These results clearly demonstrate that diphosphirenylium **W1** is much more electrophilic than either the diphosphirenium **V1** or the cyclopropenium salts **C**.

It is well documented that carbenium ions undergo nucleophilic attack by the carbon atom of isocyanides.³⁰ Significantly, diphosphirenium **V1** reacts at $-50\text{ }^{\circ}\text{C}$ with *tert*-butyl isocyanide in a similar manner to give the transient nitrilium salt **14**, which undergoes a ring expansion reaction affording **15** (Scheme 9).²¹ Note that **15** is



one of the very rare four-membered heterocycles featuring a phosphalkene moieties.³¹

The interaction of transition metal complexes with cyclopropenium cations **C** has been widely studied.^{32–34} Besides the expected η^3 (an example of η^3 ligation has also been observed by Nixon et al. with phosphirenylium **R^{8b}**) and η^1 ligations,^{32,33} the η^2 coordination mode with various extents of intrusion of the metal into the CC bond have also been observed.³⁴ The latter types of complex represent points on the potential energy surface calculated for the conversion of a metalatetrahedrane (η^3 -cyclopropenyl) to a metallacyclobutadiene complex (complete insertion of the metal into the CC bond),³⁵ a process which has been recognized to play an important role in alkyne metathesis.³⁶ The complex **16a**³⁷ obtained by treatment of diphosphirenium **V1** with 1 equiv of palladium tetrakis(triphenylphosphine) at $-40\text{ }^{\circ}\text{C}$ fits into this category

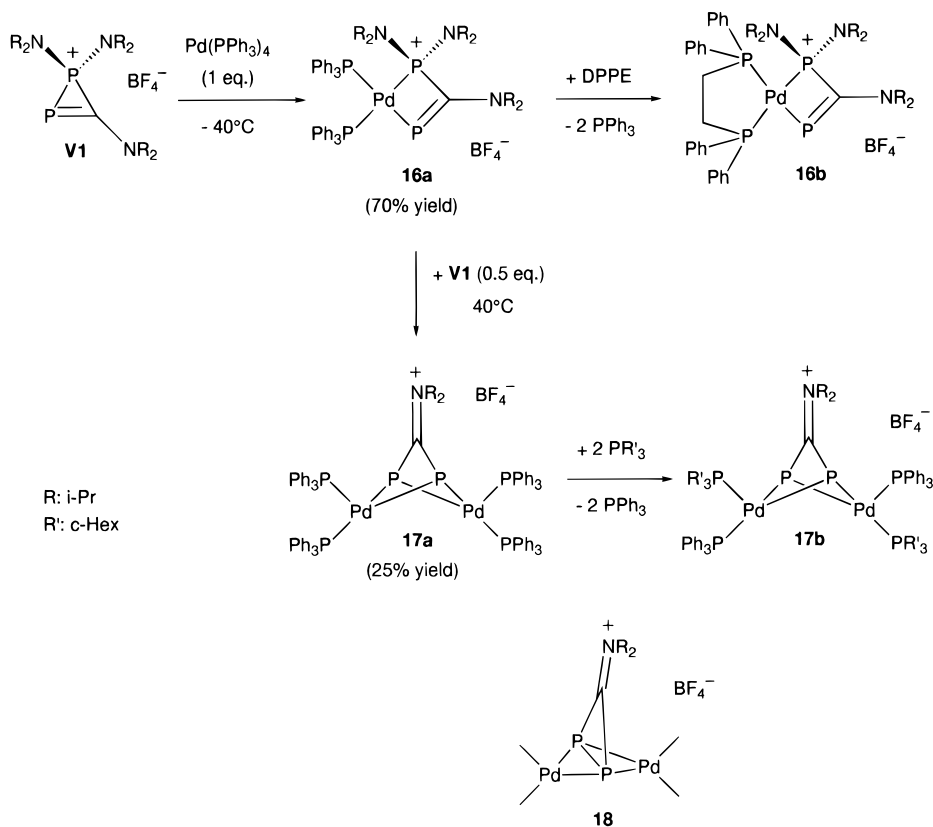
(Scheme 10). The cleavage of the PP bond was suggested by the large deshielding of the σ^2 -P ^{31}P NMR signal compared to that of the diphosphirenium salt **V1** ($\Delta\delta = 195$ ppm) and was confirmed by a single-crystal X-ray diffraction study of the complex **16b**. Indeed, the PP distance of 2.655 Å is longer than a normal P–P single bond, which is about 2.20–2.35 Å,³⁸ and is also longer than that observed in the related 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane (2.34 Å).³⁹ However, the correlation between bond length and bond order is not always simple; yet, as the ring carbon lies only 0.19 Å out of the P–Pd–P plane, a bicyclic structure can be ruled out. The palladium atom has a slightly distorted square-planar geometry, probably due to the strain in the four-membered ring, and can be considered as Pd(II). Since the σ^2 -PC bond length [1.745(3) Å] falls in the range observed for *C*-amino-substituted phosphalkenes,⁴⁰ complexes **16** have to be considered as the first examples of diphosphametallacyclobutene.

Very surprisingly, when a dichloromethane solution of the complex **16a** was refluxed overnight in the presence of the three-membered heterocycle **V1** (0.5 equivalent), a new complex **17a** was obtained in 25% yield (Scheme 10).⁴¹ A single-crystal X-ray diffraction study of derivative **17b** revealed that the CN bond length [1.325(10) Å] is in the range expected for a double bond, which implies that the positive charge is more or less localized at nitrogen. The palladium atoms have a slightly distorted square-planar geometry and can be considered as Pd(II). At first glance, these compounds can be regarded either as [1.1.1]-propellanes **18**,⁴² which possess bridgehead phosphorus atoms having an inverted tetrahedral geometry or, alternatively, as tricyclo[1.1.1]pentanes (asteranes) **17**, in which the P–P bond is broken. The σ^3 -P $\cdots\sigma^3$ -P distance [2.681(3) Å] in **17b** is much shorter than that observed in the 1,3-diphospha-2,4-disila-5-platinabicyclo[1.1.1]pentane (3.063 Å)³⁹ and related P_2B_3 , $\text{P}_2\text{B}_2\text{Si}$, and $\text{P}_2\text{B}_2\text{Ge}$ derivatives (2.86–3.07 Å)⁴³ but longer than normal P–P single bond lengths.³⁸ The P–C–P bond angle [96.4(4) $^{\circ}$] is quite comparable to that observed in the four-membered ring **16b** (96.2 $^{\circ}$) but much larger than in the three-membered ring **V1** (73.9 $^{\circ}$). Therefore, complexes **17** can be regarded as having an asterane structure with two strongly pyramidalized bridgehead phosphorus atoms (Σ angles = 254.0 and 251.7 $^{\circ}$). Although the stoichiometry of the reaction, the cleavage of the diisopropylamino groups, and the mechanism as a whole for the reaction leading to **17a** are still obscure, this type of complex is unique in several respects. Of particular interest, it features two pyramidalized μ^2 -phosphinidene units⁴⁴ (unknown before this work) and is the first asterane possessing a trigonal carbon atom.

Note that complex **16a** results from the insertion of one Pd(PPh₃)₂ fragment into the PP bond of the diphosphirenium salt **V1**,⁴⁵ while derivative **17a** formally results from the insertion of two Pd(PPh₃)₂ fragments into the PP bond of a diphosphirenylium salt **W**.

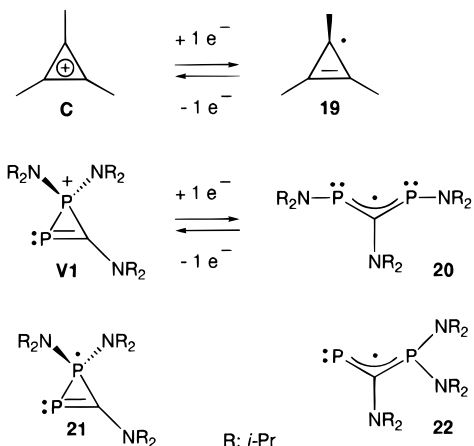
Reduction of cyclopropenium salts **C** leads to the corresponding cyclopropenyl radicals **19**,⁴⁶ while under the same conditions, the diphosphirenium salt **V1** undergoes a ring-opening reaction.⁴⁷ After migration of an

Scheme 10



amino group, a surprisingly⁴⁸ stable $1\sigma^2,3\sigma^2$ -diphosphallyl radical **20** was obtained in 60% yield (mp 95–96 °C). The mass spectrum of **20** revealed that no fragmentation reaction occurred during the reduction of **V1**, while the splitting pattern of the ESR signal demonstrated the symmetrical structure of the radical obtained. According to calculations for the parent compounds (R=H), the cyclic radical **21** is not an energy minimum, while the unsymmetrical allyl radical **22** is 6.2 kcal/mol higher in energy than the symmetrical allyl radical **20**. Interestingly, oxidation of both radicals **19** and **20** regenerates the starting cations **C** and **V1** (Scheme 11).

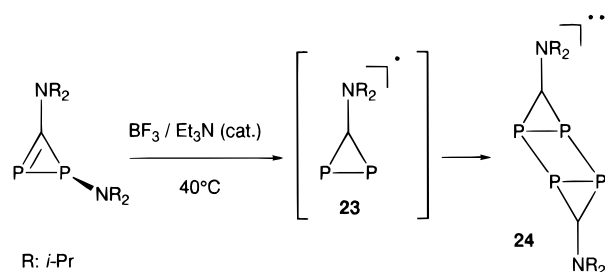
Scheme 11



So far, no free diphosphirenylium salt **W** is available, but one can easily predict that a reduction should lead to

a diphosphirenyl radical.⁴⁹ In fact, such a radical **23** has recently been postulated as an intermediate in the preparation of the singlet biradical **24**, a new type of benzene valence isomer (Scheme 12).⁵⁰

Scheme 12



Conclusion and Perspectives

Both the diphosphirenium **V** and the diphosphirenylium salts **W** are two- π -electron systems which benefit from a certain amount of aromatic stabilization. However, the diphosphirenylium salts **V** are more strongly related to the cyclopropenium salts **C** due to the similar nature of the empty p-type orbital involved in the electronic delocalization; in the case of the diphosphirenium salts **W**, instead of a 3p nonbonding orbital, it is a σ^*_{PX} -type antibonding orbital that is involved.

Nucleophiles attack at the dicoordinate phosphorus center of **V**, inducing ring-opening or ring-expansion reactions, while they react at the highly electrophilic phosphorus centers of diphosphirenylium salts **W**, afford-

ing the corresponding 1*H*-diphosphirenes with retention of the cyclic structure.

Clearly, diphosphirenylium salts merit further study. The synthesis of a noncomplexed diphosphirenylium salt remains an exciting challenge. These cations can be regarded as two-, four-, or six-electron donors, but so far, only monometallic η^2 -complexes have been isolated. Their reactivity is governed by the electrophilicity of the phosphorus centers, and it would be particularly interesting to attempt to force the system to react at carbon, which should lead to the hitherto unknown 3*H*-diphosphirenes **T**. The latter compounds, which are the phosphorus analogues of 3*H*-diazirines **J**, could be alternative precursors for carbenes. Moreover, the diphosphirenyl radical **23**, which formally results from the reduction of a diphosphirenylium salt **W**, dimerizes via a $\pi^*-\pi^*$ (SOMO-SOMO) interaction, giving the [3.1.0.0^{2,4}]tricyclic derivative **24**, which features a very long one-electron PP bond (2.634 Å). This result opens a brand new research area in phosphorus chemistry, since we believe that derivative **24** is not unique, and it is likely that many other derivatives featuring phosphorus-phosphorus half bonds will be prepared in the future.

Throughout this Account, the role of the amino groups on the structure, stability, and reactivity of both diphosphirenium and diphosphirenylium salts has been stressed. What would be the fate of non-amino-substituted derivatives, and could amino substituents allow the preparation of other heteroatom-containing cyclopropenium analogues?

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