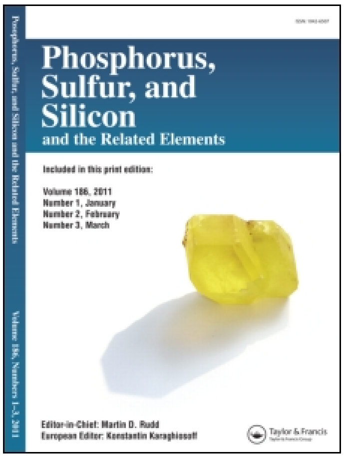

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,3-Diphosphetane-2,4-diyles--Cryptocarbenes?

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To cite this Article Fuchs, Andre , Nieger, Martin , Niecke, Edgar , Nyulaszi, Laszlo , Schmidt, Olaf , Schoeller, Wolfgang and Sebastian, Manuel(2002) '1,3-Diphosphetane-2,4-diyles--Cryptocarbenes?', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1605 — 1608

To link to this Article: DOI: 10.1080/10426500212310

URL: http://dx.doi.org/10.1080/10426500212310

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1605–1608
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1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290093694

1,3-DIPHOSPHETANE-2,4-DIYLES—CRYPTOCARBENES?

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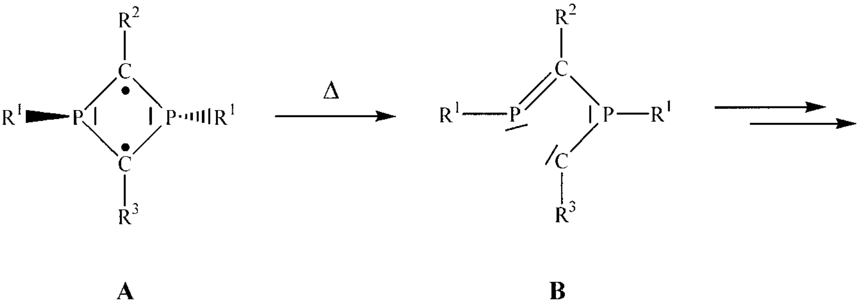
(Received July 29, 2001; accepted December 25, 2001)

*1,3-Diphosphetane-2,4-diyles (**A**) possess a diradical molecular structure. Experimental studies reveal interconversions of different valence isomers of the diradicals. As a consequence of the facile thermal ring opening of 1,3-diphosphetane-2.4-diyles **A**, we obtained cryptophosphinocarbenes (**B**), confirmed by the results of intramolecular rearrangements as well as reactions with multiple bonded systems. A new range of five- and six-membered phosphorus heterocycles are isolated, including transition-metal complexes. The mechanism for the ring-expansion are predicted by quantum chemical calculations.*

Keywords: Carbene-complexes; diradicals; insertion; phosphinocarbenes

Non-Kekule compounds reveal a particular type of structure and bonding. The 1,3-diphosphetane-2,4-diyles **A** (Scheme 1) were isolated with R^1 = Mes* and R^2, R^3 = Cl for the first time in 1995.[1] Their chemistry



SCHEME 1

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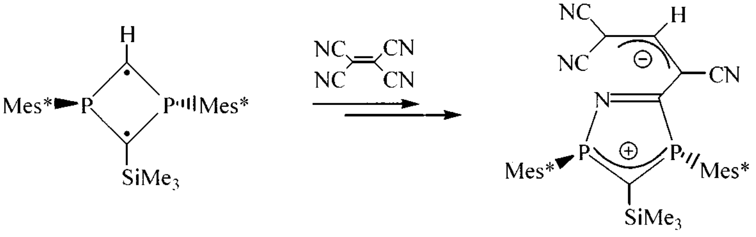
exhibit two facets: they undergo bond-stretch isomerism[2] or behave like phosphinocarbenes.[3,4]

The intermediate **B** allows the syntheses of five- and six-membered ring systems. Reaction of **1** with isocycnide affords, via phosphinocarbene **B**, a six-membered heterocyclus containing a bis(ylene)phosphorane fragment [cyclo-{P(Mes*)–C($SiMe_3$)=P(Mes*)= N–C(O)–CH_2}].[4]

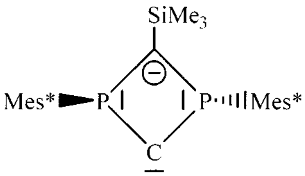
Furthermore, the novel diphospholium species **2** is achieved by reaction of **1** with tetracyanoethylene (Scheme 2).[6]



1 **2**

SCHEME 2

A versatile synthetic building block is the 1,3-diphosphetane-2,4-diyle-2-id **3** (Scheme 3). According to quantum chemical calculations, **3** can be regarded as an anionic bis(phosphino)carbene.[7]

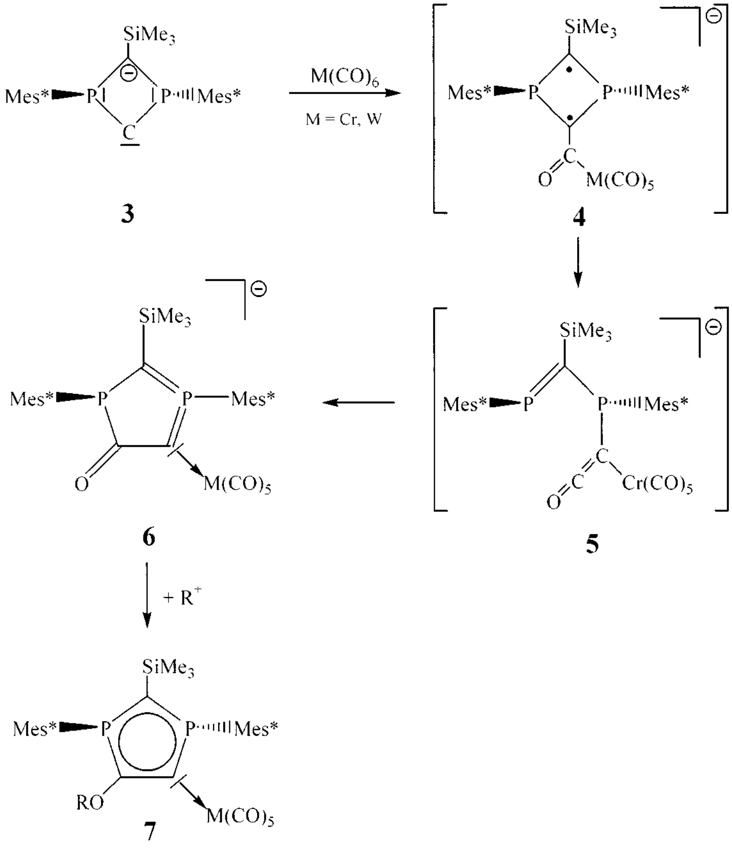


3

SCHEME 3

Derivative **3** reacts with the *Lewis*-acid trimethylalane to the 1:1 adduct [cyclo-{P(Mes*)–C($SiMe_3$)–P(Mes*)–C($AlMe_3$)}]$^{(-)}$.[7]

Treatment of **3** with chromium or tungsten hexacarbonyl affords the anionic complexes **6** by formal insertion of CO (Scheme 4). Computational studies indicate that this reaction proceeds via two intermediates, which can be formulated as the cyclic metal acyl and the acyclic ketenyl complex (**4**, **5**). Furthermore, the anionic complexes **6** react with electrophiles to the neutral complexes **7** (with R = H, Me, $SiMe_3$).[8] Their bonding situation is comparable to those of imidazoyl carbene complexes.



SCHEME 4

Ab initio calculations on the parent compound **A** (with R^1, R^2, R^3 = H) indicate an electronic structure best described by a superposition of two dominant contributions and a small singulet/triplet (S/T) energy splitting.[1,5] Due to the high inversion barrier at the phosphorus atoms (40 kcal/mol), a planarisation of all substituents—accompanied by a strong π-delocalization—seems to be not profitable.[5]

The 1,3-diphophetane-2,4-diyle **A** can be regarded as a bond stretch isomer of the energetically favored 2,4-diphosphabicyclobutane, but the interconversion is symmetrically forbidden.[1,5] The isomers are separated by a significant energy barrier. Computational studies show the influence of the inductive effects of the substituents on the S/T energy barrier.[5] A very small S/T energy difference is predicted, e.g. for a *pull-pull* substitution pattern.

Isomer **A** (with $R^1 = 2,2,6,6\text{-}Me_4C_5H_6N$; R^2, $R^3 = Cl$) can be isolated as a deep purple coloured solid.[3] Recrystallization affords the corresponding 1,2-diphosphete. Investigations on the basis of UV-, CP-MAS, ^{31}P- and ^{13}C-NMR measurements proved that the conversion also occurs in the solid state.[3] According to quantum chemical calculations, the valence isomerization to the 1,2-diphosphete proceeds by a two-step process via an additional stationary point on the hypersurface, identified as a singulet-phosphinocarbene **B** (Scheme 1). The rate-determinating step is the ring opening of the biradical **A** to the phosphinocarbene **B**, which is slightly higher in energy. Further conrotatory movement of the substituents afford the 1,2 diphosphete, the lowest point on the electronic hypersurface.[3]

As already mentioned, computational studies predict that a silyl group at the ring carbon atoms should enhance cyclic π-delocalization. Compound **1** is used as a synthon for a series of different derivatives of type **A** ($R^1 = Mes^*$; $R^2 = SiMe^3$; $R^3 =$ alkyl, silyl, phosphanyl). Furthermore, **1** is photochemically converted into the corresponding bicyclobutane derivative. The formation of the *trans* annular C,C-linkage proceeds via a conrotatory twist of all substituents.[2]

Since the relative energies of the closed (**A**) and open (**B**) species are comparable, isomer **B** can be regarded as a cryptocarbene. This thesis is confirmed by the results of thermal isomerisation of **A** (with $R^1 = Mes^*$, $R^2 = SiMe_3$, $R^3 = Me$) into the corresponding 1,3-diphosphapenta-1,4-diene, $Mes^*P{=}C(SiMe_3){-}P(Mes^*){-}CH{=}CH_2$.[4] Moreover, the 1,1-addition reaction of hydrogen chloride to **A** (with $R^1 = Mes^*$, $R^2 = Cl$, $R^3 = Cl$) results in the formation of the 1,3-diphosphabutene derivative ($Mes^*P{=}C(Cl){-}P(Mes^*){-}CHCl_2$).[4]

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