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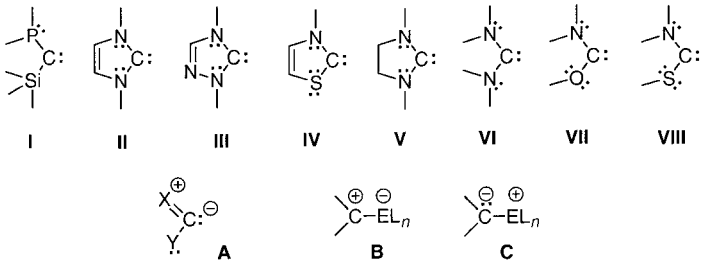
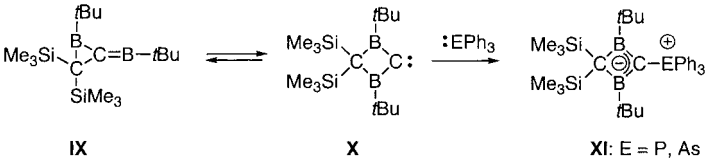
## The Electrophilic Behavior of Stable Phosphanylcarbenes Towards Phosphorus Lone Pairs**

Stéphanie Goumri-Magnet, Orest Polishchuk, Heinz Gornitzka, Colin J. Marsden, Antoine Baceiredo, and Guy Bertrand*

All the known stable carbenes **I**–**VIII**[1, 2] feature two heteroatom substituents. According to calculations,[3] all these carbenes are strongly stabilized by electron donation from the

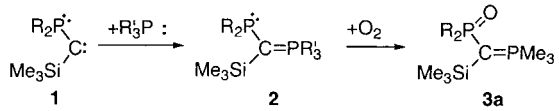



nitrogen or phosphorus lone pair into the formally "empty" $p_\pi$ orbital. In other words, the peculiar stability of these compounds is due to the crucial contribution of the ylide form **A**. Therefore, carbenes **I**–**VIII** show strong nucleophilic character and readily react with Lewis acids to give reverse ylides **B**.[1, 4] On the other hand, transient electrophilic carbenes are known to react with Lewis bases to give normal ylides **C**. For example, carbene–pyridine adducts have been spectroscopically characterized and used as a proof for the formation of carbenes.[5] The reaction of transient dihalocarbenes with phosphanes is even a preparative method for *C*-dihalo phosphorus ylides.[6] Lastly, addition of triphenylphosphane and triphenylarsane to the borandiylborirane **IX**, the hidden form of the electrophilic carbene **X**, led to the corresponding ylides **XI**.[7] These reactions which involve the vacant orbital of singlet carbenes have not yet been observed with the stable carbenes **I**–**VIII**.




Moss et al. have shown that in contrast to dialkoxycarbenes, carbenes featuring only a weak π-donor substituent, such as acetoxyphenylcarbene, give carbene–Lewis base adducts.[8] Among the stable carbenes **I**–**VIII**, only the phosphanylsilylcarbene **I** has a single π-donor substituent. Moreover, it has been theoretically[9] and experimentally[10] demonstrated that phosphorus is a weaker π donor than nitrogen. Here we report that the stable carbene **1** indeed reacts with phosphanes to give the corresponding phosphorus ylides; the extension of this reaction to a bimetallic complex containing a side-on-coordinated :P≡P: moiety is also presented.

Instantaneous and quantitative formation of phosphorus ylides **2** occurred when one equivalent of phosphane was added at 0 °C to a solution of carbene **1** in pentane (Scheme 1).[11] The coupling of the phosphane with the




Scheme 1. Synthesis of *C*-phosphanyl phosphorus ylides **2** and oxidation of **2a** to **3a**. R = *c*Hex$_2$N; R′$_3$ = Me$_3$P (**a**), Et$_3$P (**b**), Me$_2$PhP (**c**), MePh$_2$P (**d**), Ph$_3$P (**e**).

carbene center was indicated by AX systems in the $^{31}$P NMR spectra. Ylides **2** are highly sensitive to oxygen. Attempted recrystallizations of **2a** led to the corresponding phosphane oxide **3a**, which was isolated in 90% yield, as colorless crystals suitable for an X-ray diffraction study (Figure 1).[12] The formation of **2** clearly demonstrates that the derivative **1** possesses an available vacant orbital at the carbene center, as

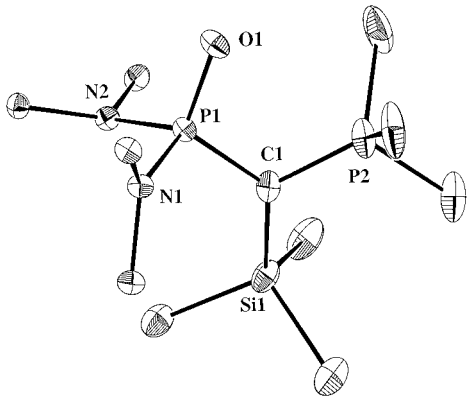



Figure 1. Crystal structure of **3a** (a part of the cyclohexyl groups and the hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–C1 1.755(2), P1–O1 1.4867(16), P2–C1 1.707(2), C1–Si1 1.849(2); P1-C1-P2 110.58(13), P1-C1-Si1 130.04(13), P2-C1-Si1 118.69(12).

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[**] Thanks are due to the CNRS for financial support of this work, and to the "Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche" for a postdoctoral fellowship (O.P.).

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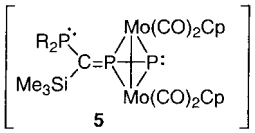
expected for a genuine singlet carbene. In contrast, it has been shown that the free electron of the radical anion formed by reduction of a carbene of type **III** is not located in the area of the carbenic center but on the NBO-LUMO of the C=N bond.[13] This might explain the absence of reactivity of N-heterocyclic carbenes with Lewis bases.

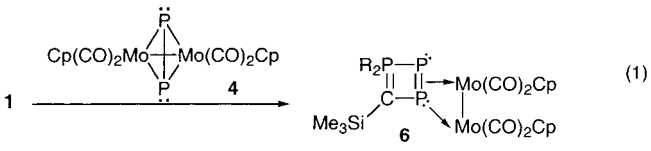
The lone pairs of the :P≡P: fragment in complexes such as **4**[14] are available for further complexation reactions.[15] Therefore, in the hope of synthesizing the hitherto unknown

$[\{Cp(CO)_2Mo\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}P_2)]$ **4**

phosphorus analogue **5** of a diazo compound, complex **4** was added at 0 °C to a solution of carbene **1** in toluene. After workup, a new complex was isolated as dark yellow crystals in 69 % yield. Here also, the coupling of the carbene center with the phosphorus complex was clearly indicated by an AMX system in the $^{31}P$ NMR spectrum (see the Experimental Section). A single-crystal X-ray diffraction study[12] revealed, instead of the desired product **5**, the heterocyclic structure **6** [Eq. (1), R = *c*Hex$_2$N; Figure 2].



**5**



(1)

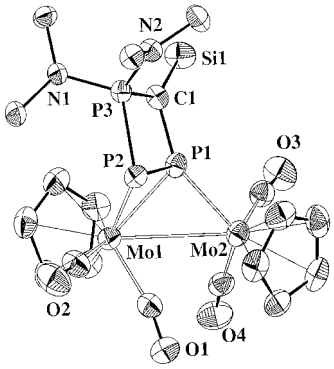
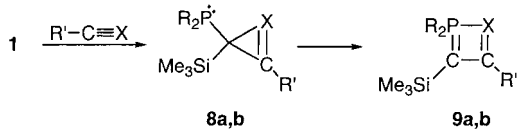


Figure 2. Crystal structure of **6** (a part of the cyclohexyl groups and the hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2 2.152(3), P2–P3 2.220(3), P3–C1 1.733(6), P1–C1 1.754(7), P1–Mo2 2.340(2), P1–Mo1 2.492(2), P2–Mo1 2.636(2), Mo1–Mo2 3.279(1); C1-P1-P2 97.0(2), P1-P2-P3 72.33(9), P2-P3-C1 95.2(3), P1-C1-P3 95.5(3).

The symmetrical tetrahedrane structure of the starting $P_2Mo_2$ complex is no longer present, the two Mo atoms now showing different coordination geometries: Mo1 is linked to phosphorus atoms P1 and P2 (2.492(2) and 2.636(2) Å), while Mo2 is only bonded to P1 (Mo2 ··· P1 2.340(2), Mo2 ··· P2 3.765(2) Å). Both the four-membered P-P-P-C ring (maximum deviation 0.008(3) Å) and the ring carbon atom (sum of angles 359.8°) are planar. Together, these geometric parameters along with the P1–P2 bond length (2.152(3) Å) describe what can be regarded as an ylidic four π electron four-membered heterocycle[16] featuring a $\mu\text{-}\eta^1\text{:}\eta^2$-diphosphene fragment.[17] The ligand in complex **6** is the first example of a $1\lambda^3,2\lambda^3,3\lambda^5$-triphosphete.[18]

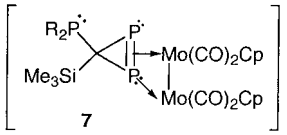
We have already shown that carbene **1** reacts with benzonitrile[19a, b] and *tert*-butylphosphaalkyne[19c, d] to give the corresponding three-membered heterocycles **8a**, **b**, which readily rearrange to afford the four-π-electron four-membered heterocycles **9a**, **b** (Scheme 2). Therefore the transient



**8a,b** **9a,b**

Scheme 2. Synthesis of **8a**,**b** and subsequent rearrangement to **9a**,**b**. R = *c*Hex$_2$N; X = N, R′ = Ph (**a**); X = P, R′ = *t*Bu (**b**).

formation of the 3*H*-diphosphirene complex **7**, which could undergo a ring expansion reaction to give **6** is quite likely. By analogy with the results observed by addition of phosphanes to **1**, the formation of the P-analogue **7** of a 3H-diazirine could result from the cycloisomerization of the initial P-analogue **5** of a diazoalkane.[20, 21]



**7**

The reactivity of stable phosphanylcarbenes with various Lewis bases, and of the $P_2$-complex **4** towards various transient carbenes, is currently being investigated.

## *Experimental Section*

All operations were carried out under argon using Schlenk techniques. In a typical experiment, to a solution of **1**[11] (0.1 g, 0.2 mmol) in pentane (1 mL) was added at 0 °C a stoichiometric amount of phosphane or complex **4**.[14] According to $^{31}P$ NMR spectroscopy, in all cases the reaction was quantitative.

**2a**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 4.1$ ($\sigma^4$-P), 97.2 ($\sigma^3$-P), $^2J(P,P) = 218$ Hz; $^1H$ NMR($C_6D_6$): $\delta = 0.40$ (s, 9H, $CH_3Si$), 1.24 (dd, 9H, $^2J(P,H) = 11.6$, $^4J(P,H) = 2.4$ Hz, $PCH_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta = 7.7$ (d, $^3J(P,C) = 3.1$ Hz, $CH_3Si$), 19.8 (dd, $^1J(P,C) = 57.9$, $^3J(P,C) = 17.6$ Hz, $PCH_3$). **2b**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 25.2$ ($\sigma^4$-P), 101.7 ($\sigma^3$-P), $^2J(P,P) = 192$ Hz. **2c**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 7.1$ ($\sigma^4$-P), 98.1 ($\sigma^3$-P), $^2J(P,P) = 224$ Hz. **2d**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 13.4$ ($\sigma^4$-P), 100.4 ($\sigma^3$-P), $^2J(P,P) = 229$ Hz. **2e**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 24.6$ ($\sigma^4$-P), 108.4 ($\sigma^3$-P), $^2J(P,P) = 265$ Hz.

**3a**: Attempted recrystallization of **2a** in pentane at −20 °C gave colorless crystals of **3a** (0.10 g, 90 %). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 8.5$ ($PCH_3$), 46.2 ((*c*Hex$_2$N)$_2$PO), $^2J(P,P) = 16.0$ Hz; $^1H$ NMR ($C_6D_6$): $\delta = 0.40$ (s, 9H, $CH_3Si$), 1.36 (d, 9H, $^2J(P,H) = 12.3$ Hz, $PCH_3$); $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta =$ 7.1 (s, $CH_3Si$), 19.5 (dd, $^1J(P,C) = 56.7$, $^3J(P,C) = 16.0$ Hz, $PCH_3$); MS (DCI, $NH_3$): *m*/*z*: 569 ([*M*+1]); m.p. > 250 °C.

**6**: Recrystallization from heptane/toluene at −20 °C gave dark yellow crystals of **6** (0.13 g, 69 %). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta = 250.3$ (P1), −47.3 (P2), 63.8 (P3), $J(P1,P3) = 15$, $J(P1,P2) = 285$, $J(P2,P3) = 256$ Hz; $^1H$ NMR ($C_6D_6$): $\delta = 0.20$ (s, 9H, $CH_3Si$), 5.05 (s, 10H, $C_5H_5$); $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta = 4.1$ (dd, $^3J(P,C) = 2.5$, 1.0 Hz, $CH_3Si$), 58.2 (d, $^2J(P,C) = 5.6$ Hz, P–NCH), 58.5 (d, $^2J(P,C) = 5.0$ Hz, P–NCH), 91.9 and 93.3 (2 × s, $C_5H_5$); m.p. 155–157 °C (decomp.); elemental analysis calcd for $C_{42}H_{63}Mo_2N_2O_4P_3Si$: C 51.85, H 6.53, N 2.88; found: C 52.27, H 6.63, N 3.00.

Received: February 9, 1999
Revised version: September 9, 1999 [Z13015IE]
German version: *Angew. Chem.* **1999**, *111*, 3938–3941

  1433-7851/99/3824-3728 $ 17.50+.50/0 

**Keywords:** carbenes · heterocycles · phosphorus · ylides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