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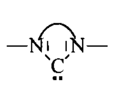
1,3-Diphosphacyclobutane-2,4-diyl-2-ylidenide: A Unique Carbene and Its Trimethylalane Complex[**]

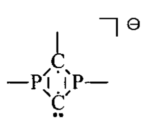
Edgar Niecke,* André Fuchs, Martin Nieger,
Olaf Schmidt, and Wolfgang W. Schoeller

Dedicated to Professor Konrad Sandhoff
on the occasion of his 60th birthday

The chemistry of N-heterocyclic carbenes **I** has, through the synthesis of stabilized derivatives by Arduengo et al.,[1] experienced an unexpected renaissance.[2] Heterocycles, in which the position neighboring the carbene atom is not occupied by nitrogen atoms, are not known in free form. On the other hand "push/pull" substituted λ^5-phosphaacetylenes **II** ("kryptocarbenes"[3]) are stable and reveal a carbene-analogous reactivity.[4] In connection with our work on four-membered π-delocalized phosphorus heterocycles (1,3-diphosphacyclobutane-2,4-diyls), which, owing to the pyramidalized carbon and[5]/or[6] phosphorus atoms, are ascribed more or less pronounced diradical character, we became interested in the corresponding isoelectronic anions **III** (1,3-diphosphacyclobutane-2,4-diyl-2-ylidenides). Here we report on the synthesis and bonding analysis of the first representative of this type as well as on the structure of its trimethylalane adduct.


I


II


III

Deprotonation of 1,3-diphosphacyclobutane-2,4-diyl[6] **1** with one equivalent of lithium diisopropylamide (LDA) led to the formation of a deep red solution from which $\mathbf{2}\cdot[\mathrm{Li(thf)}_n]^+$ can be isolated as a dark red, amorphous solid[7] (Scheme 1). In the pure state $\mathbf{2}\cdot[\mathrm{Li(thf)}_n]^+$ can be stored under an inert atmosphere without decomposition; in solution (25 °C, THF) **1** is re-formed within one day (ca. 60% according to ^{31}P NMR control). With the Lewis acid trimethylalane, **2** can easily be transformed into the adduct $\mathbf{2}\cdot\mathrm{AlMe_3}$ (**3**), and isolated as the lithium salt $\mathbf{3}\cdot[\mathrm{Li(thf)}_4]^+$ in the form of red, hydrolysis-sensitive crystals (Scheme 1).

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[*] Prof. Dr. E. Niecke, Dr. A. Fuchs, Dr. M. Nieger,
Dipl.-Chem. O. Schmidt
Institut für Anorganische Chemie der Universität
Gerhard-Domagk-Strasse 1, D-53121 Bonn (Germany)
Fax: (+49) 228-735-327
E-mail: e.niecke@uni-bonn.de

Prof. Dr. W. W. Schoeller
Fakultät für Chemie der Universität
Postfach 8640, D-33615 Bielefeld (Germany)

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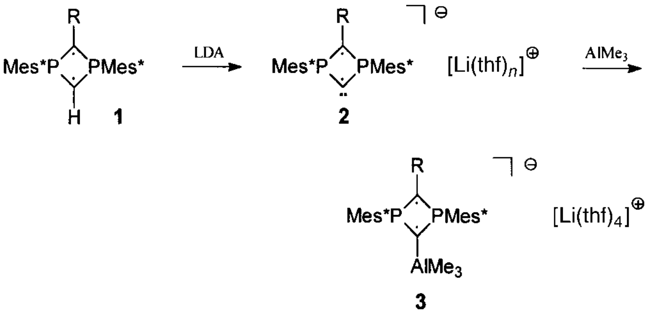


Scheme 1. Synthesis of **2** · $[Li(thf)_n]^+$ and of **3** · $[Li(thf)_4]^+$.

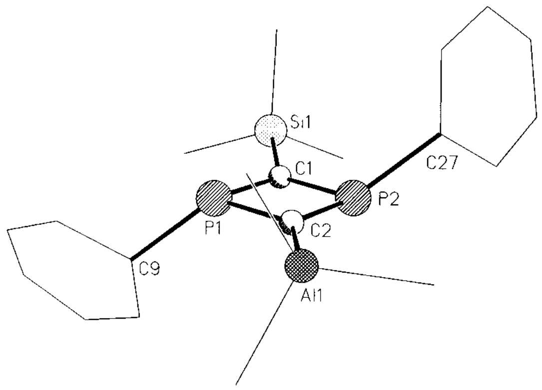
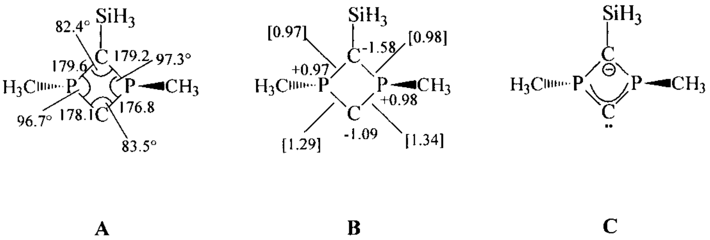


Figure 1. Molecular structure of the anion **3** (H atoms and peripheral groups omitted for clarity). Selected bond lengths [pm] and angles [°]: P1–C1 175.6(3), P1–C2 176.9(3), P2–C1 173.2(3), P2–C2 172.6(3), C1–Si1 182.9(3), C2–Al1 201.3(3), Al1–C6 200.9(3), Al1–C7 200.8(3), Al1–C8 201.1(3); C1-P1-C2 94.0(1), C1-P2-C2 96.4(1), P1-C1-P2 84.9(1), P1-C2-P2 84.7(1).

A comparison of the NMR data (^{31}P, ^{13}C) of **2** · $[Li(thf)_n]^+$ with those of the protonated form **1**[6] undoubtedly proves the cyclic structure of the anion as a 2,4-diphosphacyclobutane-2,4-diyl-2-ylidenide. The appearance of only one ^{31}P NMR signal in solution ($\delta = 4.5$) confirms the chemical equivalence of both phosphorus atoms, which reveal a chemical shift ($\delta = -11.3$) comparable to that in **1**. The chemical equivalence of the phosphorus atoms is indicated in the ^{13}C NMR spectrum by a triplet structure of the C(SiMe$_3$) signal (**2**: $\delta = 120.9$, $^1J(C,P) = 21.0$ Hz; **1**: $\delta = 111.0$, $^1J(C,P) = 20.2$ Hz). The signal of the C(H) ring carbon atom in **1** ($\delta = 104.1$) experiences a strong deshielding upon protonation and is shifted downfield (**2**: $\delta = 158.8$; $\Delta\delta = 55$). $\Delta\delta$ values of 50–65 ppm indicate the difference between lithiated arenes and their corresponding protonated forms.[7, 8] An even stronger deshielded carbene carbon atom is observed in the *push-pull* substituted "kryptocarbenes" of Bertrand et al.,$[(R_2N)_2P]CSiMe_3$ ($120 < \delta > 145$).[3c] The ^{13}C NMR spectra of ^6Li-doped samples of **2** · $[Li(thf)_n]^+$[9] in THF show even at -90 °C no coupling with the carbene carbon atom, indicating a fast intermolecular exchange of the solvated lithium ion between the different anions **2**. In the case of the phosphanyl carbenoid, [Mes*P=CCl][Li(thf)$_3$][10] such an exchange mechanism can be proven by temperature-dependent ^{13}C NMR experiments and can be frozen in at -100 °C. The adduct formation **2** → **3** causes no signifcant changes in the ^{31}P or ^{13}C NMR spectrum, apart from a considerable highfield shift of the "carbene carbon atom" signal ($\Delta\delta = 18.5$). In the alane adduct of the 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene the deshielding of the carbene carbon atom is $\Delta\delta = 46.4$.[11]

The constitution of anion **3**, derived from the NMR data, is confirmed by X-ray analysis[12] (Figure 1). It indicates the presence of a salt **3** · $[Li(thf)_4]^+$ (thf = tetrahydrofuran). The anion is a planar P_2C_2 ring with phosphorus atoms in the 1,3-position; the aryl substituents are in a *trans* arrangement. The aluminum-substituted carbon atom lies in the ring plane (sum of angles $\Sigma = 360°$), while the carbon atom attached to the silicon is slightly pyramidalized ($\Sigma = 357.4°$). The C(sp^2)–Al(sp^3) distance (201.3(3) pm) is significantly longer than the terminal Al–C distance in $(AlPh_3)_2$ (195.8 pm)[14] and corresponds to the one in the alane complex of the imidazol-2-ylidene.[11] The significant pyramidalization of the phosphorus atoms (sum of valence angles: 336° (P1), 343°(P2)) leads to the formation of two distinct pairs of endocyclic P–C distances (P1–C1 175.6(3) and P1–C2 176.9(3) as well as P2–C1 173.2(3), P2–C2 172.6(3) pm), the shorter of which correspond to the less pyramidalized phosphorus atom P(2). The residual structural parameters are similar to the structural characteristics in the 1,3-diphosphetane-2,4-diyls.[5, 6]



Scheme 2. Bonding parameters (**A**), charge densities and Wiberg indices (**B**), and canonical valence bond structure (**C**) of the 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide $[(H_3C)PC(SiH_3)P(CH_3)C]^-$ (**X**).

In order to understand the bonding situation in the 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide **2** and its Lewis acid adduct **3**, we performed ab initio calculations (B3LYP/6-31 + g*)[15] on the model compounds *cyclo*-$[(H_3C)PC(SiH_3)P(CH_3)C]^-$ **X** and *cyclo*-$[(H_3C)PC(SiH_3)P(CH_3)C(AlMe_3)]^-$ **Y**.[16] The calculations indicate a planar P_2C_2 heterocycle with C_i symmetry for the anion **X**. Likewise, the silicon atom is situated in the plane with the ring, while the substituents at both pyramidalized phosphorus atoms are arranged *trans* to each other. The structural properties in the free anion **X** correspond to those of the lithium complex *cyclo*-$[(H_3C)PC(SiH_3)P(CH_3)C][Li(Me_2O)_3]$.[17] Scheme 2 presents structural data (**A**) as well as the results of a NBO analysis (**B**)[18] for the anion **X**. Both carbon atoms bear a negative charge, which is preferentially localized in the p_π orbital orthogonal to the ring plane. The π population at the trigonal carbon atom is 1.63 (for the localization of two electrons in the p orbital 2.0 are expected). The empty p orbital at the carbene carbon atom suffers a homoallylic resonance with the neighboring lone pairs of electrons at the phosphorus atoms (the π population at the carbene carbon atom is 1.02). Hence, the 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide can be viewed as a cyclic, anionic bis(phosphanyl)carbene (**C**), which is stabilized by p-electron density of the carbanionic center. A comparable bonding situation is given in the imidazol-2-ylidene ("Arduengo-carbene"); here the π-electron density of the C–C double bond distal to the carbene carbon center contributes to the stability of the cyclic bis(amino)carbene.[19] The singlet–triplet energy separation for the parent compound of the cyclic, anionic bis(phosphanyl)carbene *cyclo*-$[P_2C_2H_3]^-$ is calculated to be 7.4 kcal mol^{-1}.[20] Hence it is comparable to that for dibromocarbene[21] and the hypothetical bis(phosphanyl)carbene $C(PH_2)_2$ ($\Delta E(S/T) = 7.3$ kcal mol^{-1}).[22] Nevertheless, it is about a factor of 10 smaller than that of the imidazol-2-ylidene, *cyclo*-[C-(NHCH)$_2$] (ΔE(S/T) kcal mol^{-1}).[23]

The structural changes on going from **X** to the adduct **Y**, leads to a distortion of the ring moiety ($C_i \rightarrow C_1$) giving two different pairs of P–C distances, in agreement with the solid-state structure of **3**. The electronic perturbation of the carbene fragments experienced by complexation with the Lewis acid $AlMe_3$ is evident from the NBO analysis[18] of the density functional theory (DFT) wave function of **Y.** According to this, 0.28 electrons flow into the $AlMe_3$ fragment. The aluminum atom is bound weakly covalent to the carbene carbon atom (Wiberg bond index 0.48).[24] The nature of the donor–acceptor complex is also apparent from the Laplace distribution of the electron density (Figure 2), which shows a domain of the electron pair at the carbene carbon, directing towards the aluminum atom.

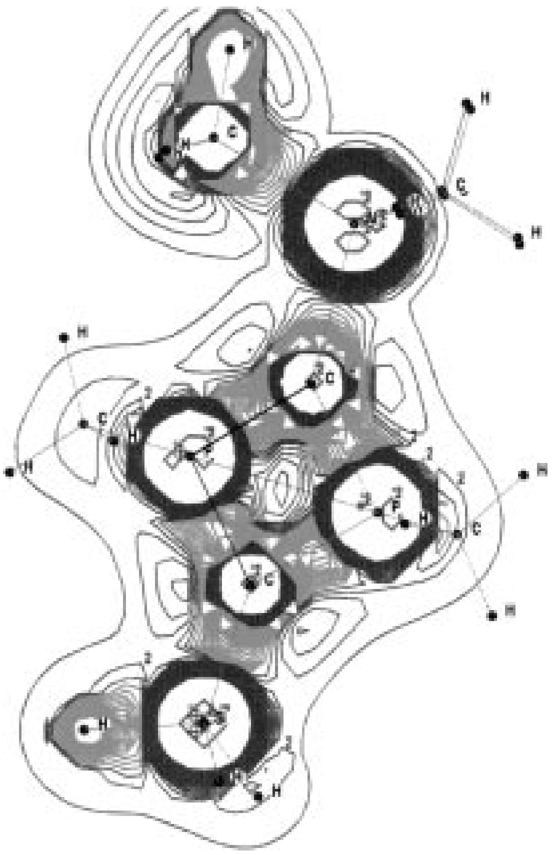


Figure 2. La Place distribution of the electron density of the 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide trimethylalane adduct *cyclo*-$[(H_3C)PC(SiH_3)P(CH_3)C(AlMe_3)]^-$ (**Y**).

Experimental Section

2: A solution of **1** (325 mg, 0.5 mmol) in THF (10 mL) was added to a solution of LDA (0.25 mL, a 2 M solution in *n*-hexane) at room temperature. Further stirring of the red reaction mixture for 3 h resulted in a deepening of the color. After evaporation of the solvent and the resulting amine, the residue was washed with fresh cold *n*-pentane to give **2**$\cdot[Li(thf)_n]^+$ in the form of a deep red solid. NMR data (25 °C, without aryl groups): $^{31}P\{^1H\}$ NMR (THF): $\delta = 4.6$; ^1H NMR (THF): $\delta = -0.57$ (s, $SiCH_3$); ^{13}C NMR(THF): $\delta = 2.5$ (t, $^3J(C,P) = 2.7$ Hz, P_2CSiC), 121.4 (t, $^1J(C,P) = 21.0$ Hz, P_2CSi), 158.8 (br, J(C,P) = not resolved, P_2CLi).

3: To a stirred solution of **2** (0.2 mmol) in THF (10 mL) was added dropwise a equimolar solution of trimethylaluminum in toluene. Removal of the solvent in vacuo afforded **3**$\cdot[Li(thf)_4]$ in the form of red crystals (280 mg, 55 %). NMR (25 °C, without aryl groups): $^{31}P\{^1H\}$ NMR (THF): $\delta = -0.1$; ^1H NMR (THF): $\delta = -0.65, -0.18$ (s, $SiCH_3$, $AlMe_3$); ^{13}C NMR (THF): $\delta = 2.0, 2.6$ (t, $^3J(C,P) = 3.1, 3.6$ Hz, P_2CSiC and P_2CAl), 118.3 (t, $^1J(C,P) = 28.4$ Hz, P_2CSi), 140.3 (t, $J(C,P) = 29.9$ Hz, P_2CAl).

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*p-t*Bu groups and two THF molecules are disordered. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-130277. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[24] Further Wiberg bond indices for **Y** are: P–C(Al): 1.33, 1.14; P–C(Si) 1.07, 0.99; C–Si:0.90; P–C(H_3) 0.86, 0.89; all Al–C(H_3): 0.56.

Charting No-Man's Land in d^0 Transition Metal Six-Coordination: Structure Predictions for the Complexes $[WCl_5CH_3]$, $[WCl_4(CH_3)_2]$, and $[WCl_3(CH_3)_3]$**

Martin Kaupp*

Among the growing number of early, high-valent transition metal complexes that defy the traditional structural rules, the computationally predicted[1–3] and experimentally confirmed[4] distorted trigonal-prismatic structure of hexamethyltungsten, $[W(CH_3)_6]$, holds a central role. Related, more ionic d^0 complexes such as $[Zr(CH_3)_6]^{2-}$ or $[Ta(CH_3)_6]^-$ have regular trigonal-prismatic structures.[2c, 4b, 5] In contrast to these fascinating compounds, the majority of hexacoordinate d^0 systems are octahedral, such as the Group 6 hexahalides.[3, 6] A major difference[1, 3, 7] between these two sets of complexes is that cylindrical π-donor halide (or related) ligands favor the octahedron, whereas exclusively σ-bonding ligands prefer nonoctahedral arrangements (the latter preference can be rationalized within relatively simple valence bond[2a, 8] or molecular orbital[1, 2b,c, 3, 7, 9] frameworks). We are thus facing two seemingly very different structural paradigms within closely related series of compounds. This suggests that one should be able to find complexes with preferences *between* octahedral and distorted or regular trigonal-prismatic structures. There are different routes into this "no-man's land". One route consists of replacing the cylindrical halide π-donor ligands by effectively single-faced π donors, for example as in thiolate complexes. This leads into the large and interesting field of dithiolene, dithiolate, and related complexes, the trigonal twist angles of which do indeed cover a large range between octahedral and trigonal prismatic,[10] depending on bond polarity and on the actual π-donor abilities of the ligands. Herein are reported the first computational results along a different route into this intermediate region, on which practically nothing has been known: Starting from octahedral WCl_6 complexes, we replace successively π-donor chloride ligands by σ-donor methyl groups. Structural predictions for the first three members of this $[WCl_{6-n}(CH_3)_n]$ series ($n = 1-3$) and for the fluoride complex $[WF_5CH_3]$ are made.

Figure 1 shows the most important stationary points computed at the gradient-corrected density functional theory (DFT) level[11] for $[WCl_5CH_3]$ (**1**). We note that this complex has been prepared and was characterized by IR and ^{1}H NMR spectroscopy,[12] but nothing is known about its structure. The

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[*] Priv.-Doz. Dr. M. Kaupp
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, D-70569 Stuttgart (Germany)
Fax: (+49) 711-689-1702
E-mail: kaupp@vsibm1.mpi-stuttgart.mpg.de

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Supporting information for this article (one Figure with computed IR spectra for $[WCl_5CH_3]$) is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.