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Communications to the Editor

Synthesis and X-ray Crystal Structure of the First Diphosphirenium Salt

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The story of 3-membered heterocycles began as early as 1859 with the discovery of oxirane, but the first phosphorus-containing 3-membered ring **A** was only reported in 1963.[1] In recent years several types of neutral 3-membered carbon–phosphorus heterocycles[2a] have been described: diphosphiranes **B**,[2b] $1H$- and $2H$-phosphirenes **C**[2c] and **D**,[2d] and diphosphirenes **E**.[2e] In contrast, the phosphirenium ions **F** are the only cationic phosphorus–carbon 3-membered rings known;[3] their stability has been explained in terms of aromaticity.[2a] Here we wish to report the synthesis of a diphosphirenium salt **G** (Chart I).

Grützmacher has recently shown that the addition of 2 equiv of boron trifluoride to ((bis(diisopropylamino)phosphino)-methylene)triphenylphosphoranes **H** afforded the corresponding phosphonio-substituted phosphaalkenes **I**.[4] This result prompted us to investigate the reaction of a Lewis acid with the *C*-[bis(diisopropylamino)phosphino)] *C*-(diisopropylamino) *P*-(diisopropylamino)phosphaalkene **1**[5] in the hope of obtaining the hitherto unknown σ^2,σ^2- or σ^1,σ^3-diphosphaallylic cations **2**[6] or **3** (Scheme I).

When a toluene solution of phosphaalkene **1** was treated with 2 equiv of boron trifluoride–ethylamine complex at room temperature, a clean reaction occurred leading to a new compound **4a** and (diisopropylamino)difluoroborane. Derivative **4a** was obtained as non-air-sensitive pale-yellow crystals from a saturated THF solution at −20 °C (mp 118 °C, 60% yield). The ionic structure of **4a** was indicated by its very low solubility in nonpolar solvents and by the presence of a sharp signal at +0.60 (CD_2Cl_2) in the ^{11}B NMR spectrum, due to tetrafluoroborate. Moreover, an exchange reaction with potassium hexafluorophosphate occurred in acetonitrile giving **4b** (mp 133 °C). Mass spectral data and elemental analysis demonstrated that one of the starting four diisopropylamino groups had been cleaved off. The ^{31}P NMR spectrum showed a doublet of broad quintets at −46.6 (J_{PP} = 247.4 Hz, J_{PH} = 19.8 Hz) and a doublet at +58.5 (J_{PP} = 247.4 Hz), strongly suggesting the presence of two diisopropylamino groups on one phosphorus and none on the other. Selective $^1H[^{31}P]$ and $^{13}C[^{31}P,^1H]$ decoupling experiments[7] confirmed this hypothesis and showed that the two isopropyls of the third R_2N group are not equivalent. These results totally excluded the symmetrical structure **2** but did not agree either with the diphosphaallenic cation **3**. Indeed, although it is difficult to predict the chemical

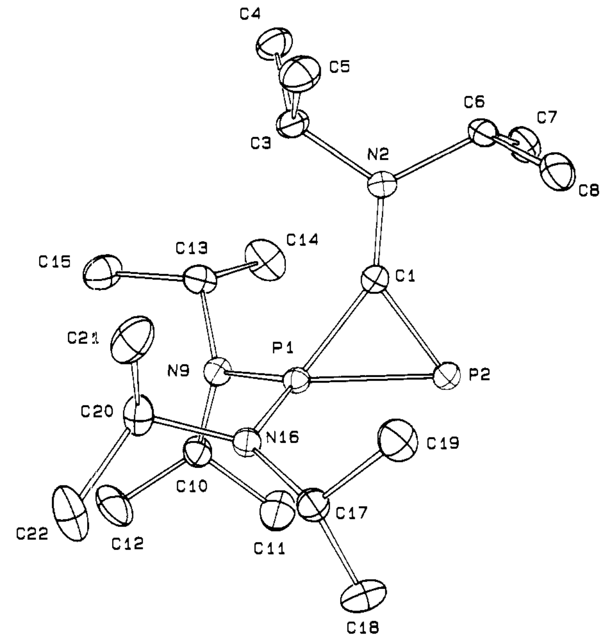
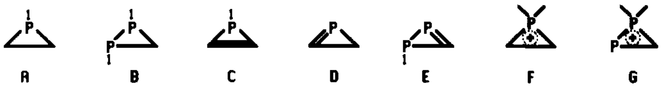
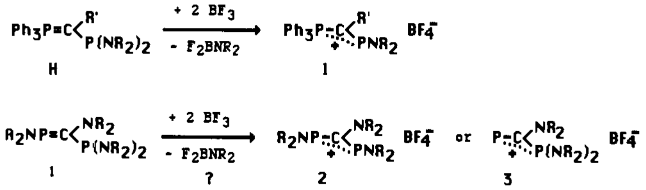


Figure 1. ORTEP plot of **4a** showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P1–P2 2.095 (1), P1–C1 1.747 (4), P1–N9 1.643 (3), P1–N16 1.637 (3), P2–C1 1.737 (4), C1–N2 1.322 (4), N2–C3 1.478 (5), N2–C6 1.496 (5); P2–P1–C1 52.8 (1), P1–P2–C1 53.3 (1), P1–C1–P2 73.9 (1), P1–C1–N2 144.5 (3), P2–C1–N2 141.2 (3), C1–N2–C3 122.0 (3), C1–N2–C6 119.9 (3), C3–N2–C6 118.1 (3).

Chart I



Scheme I



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‡ Université Louis Pasteur.

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[7] **4a**: ^1H NMR (CD_2Cl_2, 250 MHz) δ 1.35 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHNP_{IV}), 1.38 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHNP_{IV}), 1.39 (d, J_{HH} = 6.6 Hz, 6 H, CH_3CHNC), 1.48 (d, J_{HH} = 6.8 Hz, 6 H, CH_3CHNC), 3.71 (sept d, $J_{P_{IV}H}$ = 19.8 Hz, J_{HH} = 6.9 Hz, 4 H, CH_3CHNP_{IV}), 3.89 (sept, J_{HH} = 6.6 Hz, 1 H, CH_3CHNC), 4.18 (sept d, $J_{P_{IV}H}$ = 2.4 Hz, J_{HH} = 6.8 Hz, 1 H, CH_3CHNC); ^{13}C NMR (CD_2Cl_2, 62.0 MHz) δ 18.22 (d, $J_{P_{II}C}$ = 6.4 Hz, CH_3CHNC), 20.17 (s, CH_3CHNC), 22.62 (d, $J_{P_{IV}C}$ = 2.6 Hz, CH_3CHNP_{IV}), 23.21 (d, $J_{P_{IV}C}$ = 3.4 Hz, CH_3CHNP_{IV}), 50.11 (d, $J_{P_{IV}C}$ = 4.0 Hz, CH_3CHNP_{IV}), 50.84 (d d, $J_{P_{IV}C}$ = 9.1 Hz, $J_{P_{II}C}$ = 2.2 Hz, CH_3CHNC), 66.41 (d d, $J_{P_{IV}C}$ = 7.8 Hz, $J_{P_{II}C}$ = 4.4 Hz, CH_3CHNC), 185.88 (d, $J_{P_{II}C}$ = 81.2 Hz, PCP).

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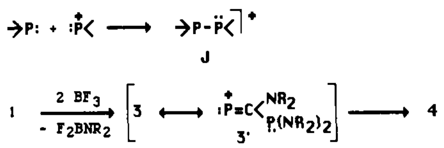
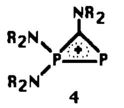
Scheme II



shift of the σ^1-phosphorus, it is quite likely that the σ^3-phosphorus atom should appeared at much higher frequency and that the PP coupling constant should be smaller. In contrast, the high-field ^{31}P chemical shift[2a] and the large J_{PP} were in favor of the diphosphirenium structure **4**. The ^{13}C signal for the quaternary carbon appearing at 185.9 as a doublet, coupled only with the σ^2-P (J_{PC} = 81.2 Hz), confirmed this hypothesis, since it has been shown that in phosphirenes the $^1J_{PC}$ coupling constant drastically decreases when the phosphorus coordination number increases.[2a]



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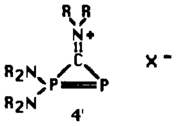
X^- $X = BF_4$, **4a** ; PF_6, **4b**
R = iPr

The structure of **4a** has been clearly established by a single X-ray diffraction study.[8] The thermal ellipsoid diagram of the molecule is shown in Figure 1, as well as the pertinent metric parameters. Several aspects of the structure merit discussion. No interaction with the tetrafluoroborate is observed, demonstrating the ionic character of **4a**. The P1–P2 distance (2.095 (1) Å) is the range expected for a phosphinylidene-σ^4-phosphorane (–P=P<);[9] the P1–C1 (1.747 (4) Å) and P2–C1 (1.737 (4) Å) bond lengths are quite similar, and the C1–N2 distance (1.322 (4) Å) is comparable to that found in the tris(dimethylamino)cyclopropenium ion.[10] These results as a whole and the fact that the geometry at both C1 and N2 is planar indicate a substantial participation of resonance structure **4'**. This resonance form also explains the non-equivalence of the diisopropyl groups at the nitrogen bonded to the ring carbon, observed by NMR.



4'

X^-

Since it is well-known that dicoordinated phosphenium cations react with phosphanes to give the corresponding adduct **J**,[11] it seems reasonable to postulate the transient formation of the σ^1,σ^3-diphosphaallenic cation **3** to rationalize the formation of **4**. Indeed, compound **4** can be regarded as resulting from the intramolecular interaction of a monocoordinated phosphorus cation with a phosphane (Scheme II).

From these results the question arises of the relative stability of 1,3-diphosphaallenic cations and of the corresponding diphosphirenium cations, depending on the coordination of both phosphorus atoms. The only other relevant molecule is **I** which possesses a linear structure.[4] We are currently investigating other $1\sigma^x,3\sigma^y$-diphosphaallenic cations.

Acknowledgment. Thanks are due to Dr. Grützmacher for valuable discussions and to CNRS for financial support of this work.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and angles and ORTEP plots of the two molecules of **4a** (17 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for **4a**: $C_{19}H_{42}BN_3F_4P_2$, mol wt = 461.3, monoclinic, $P2_1/c$, a = 15.122 (4) Å, b = 18.422 (5) Å, c = 18.284 (5) Å, β = 95.14 (2)°, V = 5073 Å^3, Z = 8 (asymetric unit contains two independent molecules of **4a** which are identical within the experimental errors), D(calcd) = 1.208 g cm^{-3}, λ(Cu Kα) = 1.5418 Å (graphite monochromator), T = –100 °C. A Philips PW1100/16 diffractometer, equipped with a locally-build low-temperature device, was used to collect 5885 reflections ($3° < 2\theta < 51°$) on a yellow crystal 0.20 × 0.20 × 0.28 mm. Of these, 4357 were observed [$I > 3\sigma(I)$]. Empirical absorption corrections and Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were located by direct methods, and they were refined anisotropically. The hydrogen atoms were included as idealized contributions. R = 0.046, R_w = 0.074, GOF = 1.62, final residual = 0.28 e Å^{-3}. All computation used MOLEN on a VAX computer: Frenz, B. A. The Enraf-Nonius CAD4-SDP. In *Computing in Crystallography*: Schenk, H., Olthof-Hazekamp, R., Van Koningveld, H., Bassi, G. C., Eds.; Delft University Press, 1978; pp 64–71.

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"Kinetic" Higher Order Cyanocuprates: Applications to Biaryl Synthesis

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A common side reaction associated with lithio organocuprates is their inadvertent oxidation leading to coupling between the ligands on copper (eq 1).[1,2] With mixed-ligand reagents (i.e.,

$$R_2CuLi/R_2Cu(CN)Li_2 \xrightarrow{[O]} RR \qquad (1)$$

R ≠ R', eq 2), statistical ratios of three products are usually produced,[1c] rendering this carbon-carbon bond forming process in most circumstances synthetically unattractive.[3]

$$RR'CuLi/RR'Cu(CN)Li_2 \xrightarrow{[O]} RR + RR' + R'R' \qquad (2)$$

We now report that extremely high levels of unsymmetrical ligand couplings can be consistently achieved with diaryl higher order (HO) cuprates by controlling both temperature and mode of reagent formation, thereby resulting in a novel route to the biaryl nucleus.[4]

Combining *m*-anisyllithium (*m*-ArLi),[5] *p*-anisyllithium (*p*-ArLi),[5] and CuCN (1:1:1) in THF, cooling to –75 °C, and carrying out oxidation (with gaseous O_2)[6] affords a 1:2:1 mix of biaryls. However, preformation of *m*-ArCu(CN)Li in 2-methyl tetrahydrofuran, cooling[7] to –125 °C, and then introduction of *p*-ArLi followed by oxidation at this lowered temperature now leads to a 3.5;93:3.5 ratio favoring *m*-ArAr-*p*, Scheme I.[8] Ex-

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(6) Early experiments using *o*-dinitrobenzene or -toluene gave similar ratios; however, the yields and percent conversions were much lower.

(7) External, bath temperature.

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