ing to the porphyrinato-N atoms may also play a role (N···H = 2.48–2.51 Å; Figure 2).

Trapped deeply in a hydrophobic environment and bonded to an unusually hybridized oxygen atom, the acidity of the μ-hydroxo proton is of both thermodynamic and kinetic interest. There is a conceptual parallel to acidic protons buried in protein structures. Obtaining a pK_a value in a suitable solvent for such measurements (e.g., CH_3CN, dimethyl sulfoxide (DMSO)) is complicated by the tendency of such solvents to act as ligands. The chemical shift of the ^2H NMR signal of the hydroxo group proton of **1** or **2** ($\delta = 11.6$) in bromobenzene solvent cannot be used as a criterion of acidity because of chemical shift contributions from the paramagnetism of iron. Nevertheless, the acidity can be bracketed by $H_9O_4^+$ in dry arene solvents (which protonates the μ-oxo conjugate base) and a two-phase arene/aqueous H^+ system. Addition of a drop of water to a solution of the μ-hydroxo species in bromobenzene causes deprotonation.

Kinetically, the lack of angular change at the oxygen atom upon protonation/deprotonation should contribute to a fast rate of proton transfer.[5] On the other hand, the iron atoms must move about 0.15 Å upon proton transfer and this will contribute to a slowing of the rate. Experimentally, there is no proton exchange between the μ-oxo and μ-hydroxo species on the ^1H NMR timescale. In [D_5]bromobenzene at 25 °C, separate pyrrole resonances are observed in a mixture of the two species and the chemical shifts are unchanged from those of single component measurements ($\delta = 13.8$ and -42, respectively). This probably reflects the steric impossibility of close approach of the protonated Fe–O(H)–Fe moiety to the unprotonated Fe–O–Fe moiety. Traces of smaller proton carriers such as hydronium ions, which must inevitably be present even in dried solvents, are apparently also ineffective at mediating proton exchange on the NMR timescale. This experiment suggests that the nature of the proton carrier and the accessibility of the base must be considered along with structural and electronic reorganizational barriers when rationalizing slow proton transfer rates. Given the interest currently being paid to proton transfer rates in bioinorganic chemistry,[22, 23] and the possibility that systems such as [(tpp)Fe–O(H)–Fe(tpp)]$^+$ may be useful in partitioning the various contributions to these rates, these aspects warrant more detailed study.

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[14] Crystal data **1** (**2**): purple (purple), $0.3 \times 0.3 \times 0.4$ mm^3 ($0.4 \times 0.3 \times 0.4$ mm^3), monoclinic $P2(1)/c$ (triclinic ($P\bar{1}$), $a = 17.550(4)$, $b = 23.381(7)$, $c = 22.372(6)$ Å ($a = 16.491(2)$, $b = 17.928(3)$, $c = 20.601(3)$ Å), $\beta = 110.69(2)°$ ($\alpha = 109.52(1)$, $\beta = 105.45(1)$, $\gamma = 104.12(1)°$), $V = 8588(4)$ Å^3 ($V = 5148(2)$ Å^3), $\rho_{calcd} = 1.389$ g cm^{-3} for $Z = 4$ ($\rho_{calcd} = 1.490$ g cm^{-3} for $Z = 2$), $\mu = 4.856$ mm^{-1} (3.096 mm^{-1}). Data collection: $Cu_{K\alpha}$, 1.54178 Å, scan mode: ω (ω), 153 K (173 K), $2\theta_{max} = 104.5°$ ($2\theta_{max} = 104.0°$), 10624 (12256) measured reflections, 9332 (10766) independent reflections. Full-matrix least-squares refinement on $|F^2|$ with 4223 (8390) reflections having $I > 2\sigma(I)$ (SHELXL-93). Direct methods and difference Fourier techniques (SHELXL PLUS), 662 (818) parameters, absorption correction (psi scans) max 1.000 (0.8275), min 0.105 (0.4923), residual electron density max 0.599 (0.912) -0.454 (-0.486) e Å^{-3}, $R_1 = 0.010$ (0.068) $wR_2 = 0.020$ (0.015). All H atoms were idealized except the hydroxo-H atom whose coordinates and temperature factors were refined by full-matrix least-squares methods. The hexachlorocarborane anion in **1** was disordered over two sets of positions which was successfully modeled as a 0.88:0.12 disorder. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406151 and CSD-406152.
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Tetraphosphasemibullvalene: First Valence Isomerizations in the Phosphaalkyne Cyclotetramer System**

Andreas Mack, Bernhard Breit, Thomas Wettling, Uwe Bergsträsser, Stefan Leininger, and Manfred Regitz*

Dedicated to Professor Michael Hanack on the occasion of his 65th birthday

Thermal or metal-induced cyclooligomerizations of phosphaalkynes in many cases provide a surprisingly simple access to polycyclic phosphorus–carbon cage compounds.[1, 2] The phosphaalkyne cyclotetramers have been investigated in most detail and are available in good yields by specific syntheses. Thus, for example, the tetraphosphacubane **1**,[3] the tetraphosphatricyclooctadiene **2**,[4] and the tetraphosphabarrelene **3**[5] may be considered as milestones along this road.

[*] Prof. Dr. M. Regitz, Dipl.-Chem. A. Mack, Dr. B. Breit, Dr. T. Wettling, Dr. U. Bergsträsser, Dr. S. Leininger
Fachbereich Chemie der Universität
Erwin Schrödinger Strasse, D-67663 Kaiserslautern (Germany)
Fax: Int. code +(631)205-3921

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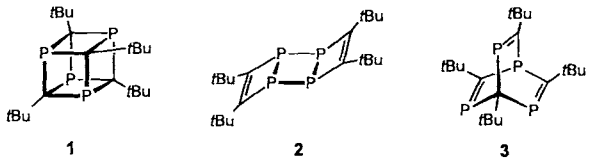
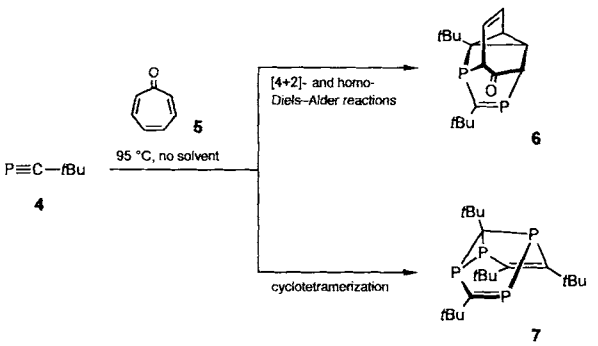


1 2 3

We now report on a new phosphaalkyne cyclotetramer, the tetraphosphasemibullvalene **7**. Although no valence isomerizations have yet been described for **1**–**3**, compound **7** can be both final and starting product for reactions of this type.

First evidence for the formation of the tetraphosphasemibullvalene **7** during the thermal cyclotetramerization of the phosphaalkynes **4** was surprisingly found in the reaction of **4** with tropone (**5**) at 95 °C, in which the diphosphatetracyclodienone **6** was formed by a sequence of Diels–Alder and homo-Diels–Alder reactions (Scheme 1).[6]



Scheme 1.

Work-up of the reaction mixture by column chromatography at −30 °C gave in addition to **6** the tetraphosphasemibullvalene **7** as an orange-red oil that was still contaminated with ≤5% (by ^{31}P NMR spectroscopy) of a further novel phosphaalkyne cyclotetramer. The latter was assigned the tetracyclic structure **13** on the basis of its NMR data (see Scheme 3).

The presence of tropone (**5**) has a significant but not yet understood influence on the course of the reaction. This is evident from the fact that the thermolysis of pure **4** at 95 °C[7] leads to the formation of a different cyclotetrameric distribution: after 8 h the main product is the tetraphosphatetracyclooctene **13**,[8] formed together with **7** and **12**[3c] in a ratio of 55:25:20 (by ^{31}P NMR spectroscopy).

Although semibullvalene itself undergoes a rapid, degenerate Cope rearrangement at −110 °C,[9] a Cope rearrangement for the tetraphosphasemibullvalene **7** cannot be detected even at room temperature. Higher temperatures cannot be used on account of thermal isomerization of **7** to furnish **12** (see Scheme 3). The constitution of **7** is confirmed by its NMR spectroscopic data. In the ^{31}P NMR spectrum the four phosphorus nuclei give rise to signals at $\delta = -49.0$ (P-7), −14.9 (P-1), 127.7 (P-4), and 332.0 (P-3); in the ^{13}C NMR spectrum the P=C and C=C units are characterized by signals at $\delta = 156.8$ (C-6), 170.5 (C-5), and 208.8 (C-2), while, as expected, the signal for C-8 is shifted markedly to high field ($\delta = 57.9$). The coupling patterns as well as the P,C coupling constants (Table 1) are in accord with the proposed structure.

Compound **7** reacts with [W(CO)$_5$·thf] by extrusion of tetrahydrofuran to furnish exclusively the dark-red complex **8** (Scheme 2), which is thermally more stable than the noncomplexed molecule. A skeletal rearrangement to afford the

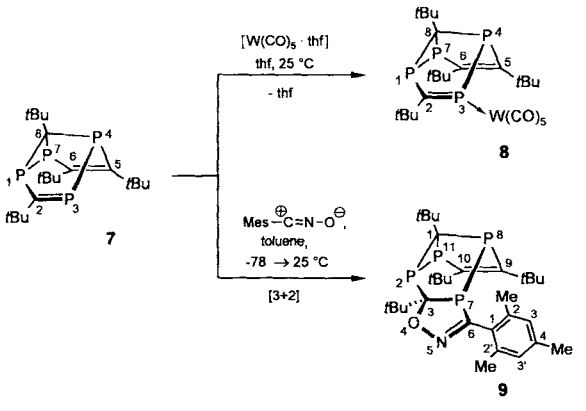
Table 1. Selected spectroscopic data for the tetraphosphapolycyclic compounds **7**–**9** [a].

7: ^{1}H NMR (400 MHz): $\delta = 0.87$ (s, 9H; C(CH$_3$)$_3$), 1.29 (d, ^4J(P,H) = 1.6 Hz, 9H; C(CH$_3$)$_3$), 1.45 (d, ^4J(P,H) = 1.6 Hz, 9H; C(CH$_3$)$_3$), 1.47 (d, ^4J(P,H) = 1.8 Hz, 9H; C(CH$_3$)$_3$); ^{13}C NMR (100.64 MHz): $\delta = 29.4$ (m; C(*C*H$_3$)$_3$), 34.7 (d, ^3J(P,C) = 14.4 Hz; C(*C*H$_3$)$_3$), 34.9 (dd, ^3J(P,C) = 12.3 and 9.3 Hz; C(*C*H$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 35.6 (d, ^3J(P,C) = 11.9 Hz; C(*C*H$_3$)$_3$), 38.4 (d, ^2J(P,C) = 28.8 Hz; *C*(CH$_3$)$_3$), 39.5 (d, ^2J(P,C) = 21.2 Hz; *C*(CH$_3$)$_3$), 42.1 (dd, ^2J(P,C) = 22.0 Hz, ^3J(P,C) = 12.7 Hz; *C*(CH$_3$)$_3$), 57.9 (ddd, ^1J(P,C) = 49.0 and 42.2 Hz (2×); C-8), 156.8 (d, ^1J(P,C) = 65.5 Hz; C-6), 170.5 (d, ^1J(P,C) = 34.2 Hz; C-5), 208.8 (pseudo-t, ^1J(P,C) = 79.7 Hz; C-2); ^{31}P NMR (161.98 MHz): $\delta = -49.0$ (dd, ^1J(P,P) = 167.9 Hz, ^2J(P,P) = 22.9 Hz; P-7), −14.9 (ddd, ^1J(P,P) = 167.9 Hz, ^2J(P,P) = 22.9 and 15.3 Hz; P-1), 127.7 (ddd, ^1J(P,P) = 259.4 Hz, ^2J(P,P) = 22.9 and 15.3 Hz; P-4), 332.0 (dd, ^1J(P,P) = 259.4 Hz, ^2J(P,P) = 22.9 Hz; P-3); MS (EI, 70 eV): *m*/*z* (%): 400 (52) [M^+], 343 (3) [$M^+ - t$Bu], 300 (4) [$M^+ - t$BuCP], 262 (89) [$M^+ - (t$BuC)$_2$], 247 (8) [$M^+ - (t$BuC)$_2 - CH_3$)], 200 (9) [$M^+ - 2t$BuCP], 169 (100) [P(*t*BuC)$_2^+$], 131 (29) [P$_2$(*t*BuC)$^+$], 100 (11) [*t*BuCP$^+$], 57 (47) [*t*Bu$^+$].

8: ^{1}H NMR (400 MHz): $\delta = 0.87$, 1.28, 1.46 (each s, 9H; C(CH$_3$)$_3$), 1.47 (d, ^4J(P,H) = 2.6 Hz, 9H; C(CH$_3$)$_3$); ^{13}C NMR (100.64 MHz, skeletal carbon atoms only): $\delta = 55.2$ (ddd, ^1J(P,C) = 44.1 and 37.2 Hz (2×); C-8), 159.4 (d, ^1J(P,C) = 59.4 Hz; C-6), 167.5 (dd, ^1J(P,C) = 35.6 Hz, ^2J(P,C) = 10.2 Hz; C-5), 196.9 (d, ^2J(P,C) = 6.8 Hz, ^1J(W,C) = 125.5 Hz; *C*O-eq.), 200.6 (d, ^2J(P,C) = 27.2 Hz; *C*O-ax.), 210.6 (dd, ^1J(P,C) = 89.9 and 25.4 Hz; C-2); ^{31}P NMR (161.98 MHz): $\delta = -61.9$ (ddd, ^1J(P,P) = 188.2 Hz, ^2J(P,P) = 15.3 Hz (2×); P-7), 9.2 (ddd, ^1J(P,P) = 188.2 Hz, ^2J(P,P) = 15.3 Hz (2×); P-1), 144.2 (ddd, ^1J(P,P) = 305.2 Hz, ^2J(P,P) = 15.3 Hz (2×); P-4), 312.6 (d, ^1J(P,P) = 305.2 Hz, ^1J(W,P) = 218.7 Hz; P-3).

9: ^{1}H NMR (400 MHz): $\delta = 1.15$ (d, ^4J(P,H) = 2.0 Hz, 9H; C(CH$_3$)$_3$), 1.18, 1.38, 1.48 (each s, 9H; C(CH$_3$)$_3$), 2.04 (s, 3H; 4-CH$_3$), 2.52 (s, 6H; 2,2′-CH$_3$), 6.70 (s, 2H; 3,3′-CH$_3$); ^{13}C NMR (100.64 MHz): $\delta = 20.9$ (s; 4-*C*H$_3$), 22.0 (d, ^4J(P,C) = 5.7 Hz; 2,2′-*C*H$_3$), 29.0 (dd, ^3J(P,C) = 7.2 Hz (2×); C(*C*H$_3$)$_3$), 30.8 (s; C(*C*H$_3$)$_3$), 34.1 (dd, ^3J(P,C) = 14.0 Hz, ^4J(P,C) = 2.7 Hz; C(*C*H$_3$)$_3$), 34.4 (d, ^3J(P,C) = 13.6 Hz; C(*C*H$_3$)$_3$), 35.5 (m, *C*(CH$_3$)$_3$), 38.8, 38.9 (each s, *C*(CH$_3$)$_3$), 40.0 (dd, ^2J(P,C) = 21.9 and 17.8 Hz; *C*(CH$_3$)$_3$), 56.2 (ddd, ^1J(P,C) = 49.9 and 37.8 Hz (2×); C-1), 125.9 (dd, ^1J(P,C) = 71.2 and 53.8 Hz; C-3), 127.2 (d, ^2J(P,C) = 16.1 Hz; C-1 arom.), 129.6 (s; C-3,3′ arom.), 137.6 (s; C-2,2′ arom.), 138.3 (s; C-4 arom.), 150.2 (dd, ^1J(P,C) = 63.4 Hz, ^2J(P,C) = 15.2 Hz; C-10), 158.9 (dd, ^1J(P,C) = 48.2 Hz, ^2J(P,C) = 8.0 Hz; C-6), 164.3 (dd, ^1J(P,C) = 20.3 Hz, ^2J(P,C) = 9.3 Hz; C-9); ^{31}P NMR (161.98 MHz): $\delta = -2.8$ (ddd, ^1J(P,P) = 219.1 Hz, ^2J(P,P) = 16.3 and 9.1 Hz; P-2), 2.7 (dd, ^1J(P,P) = 219.1 Hz, ^2J(P,P) = 21.4 Hz; P-11), 62.5 (dd, ^1J(P,P) = 272.0 Hz, ^2J(P,P) = 9.1 Hz; P-7), 154.1 (ddd, ^1J(P,P) = 272.0 Hz, ^2J(P,P) = 21.4 and 16.3 Hz; P-8); MS (CI, 200 eV): *m*/*z* (%): 562 (2) [$M^+ + $H]; MS (EI, 70 eV): *m*/*z* (%): 561 (0.02) [M^+], 504 (2) [$M^+ - t$Bu], 416 (12) [$M^+ -$ MesCN], 400 (5) [$M^+ -$ MesCNO], 300 (2) [$M^+ -$ MesCNO, $-t$BuCP], 262 (18) [$M^+ -$ MesCNO, $-(t$BuC)$_2$], 169 (100) [P(*t*BuC)$_2^+$], 131 (11) [P$_2$(*t*BuC)$^+$], 119 (4) [Mes$^+$], 57 (51) [*t*Bu$^+$].

[a] NMR: Bruker AMX-400, ^{1}H and ^{13}C NMR in C$_6$D$_6$; ^{31}P NMR in C$_6$D$_6$ with 85% H$_3$PO$_4$ as external reference, all spectra recorded at $T = 25$ °C; MS: Finnigan MAT 90.



Scheme 2.

W(CO)$_5$ complex of the structure **12** does not occur either in the solid state or in solution. Coordination of the metal fragment at P-3, the signal of which is shifted only slightly to higher field ($\delta = 312.6$), is confirmed by the ^{183}W satellites [^1J(P,W) = 218.7 Hz] (for further NMR data, see Table 1).

Mesityl nitrile oxide undergoes rapid addition to the phosphaalkene unit of **7** in toluene to furnish the crystalline, polycyclic product **9** (Scheme 2), which is isolated in 92% yield after work-up by column chromatography. The NMR data unequivocally demonstrate the cycloaddition to the P–C double bond as well as the regiochemistry of the reaction. The signals for both reaction centers in **7** are shifted significantly to higher field: P-7 from $\delta = 332.0$ to $\delta = 62.5$, C-3 from $\delta = 208.8$ to $\delta = 125.9$. The unusual lowfield position of the signal for C-3 is reasonable when the oxygen of the dipole is bonded at this position. The remaining question of the stereochemistry of the cycloadduct **9** was resolved in favor of an *exo*-arrangement of the newly formed five-membered ring by a crystal structure analysis (Figure 1); an *endo* attack of the dipole is apparently prevented by the *tert*-butyl substituents at the C–C double bond. At the same time the structure of this novel phosphaalkyne cyclotetramer is confirmed.[10]

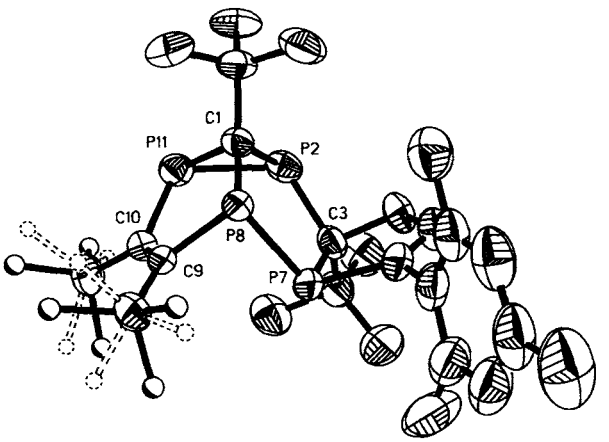
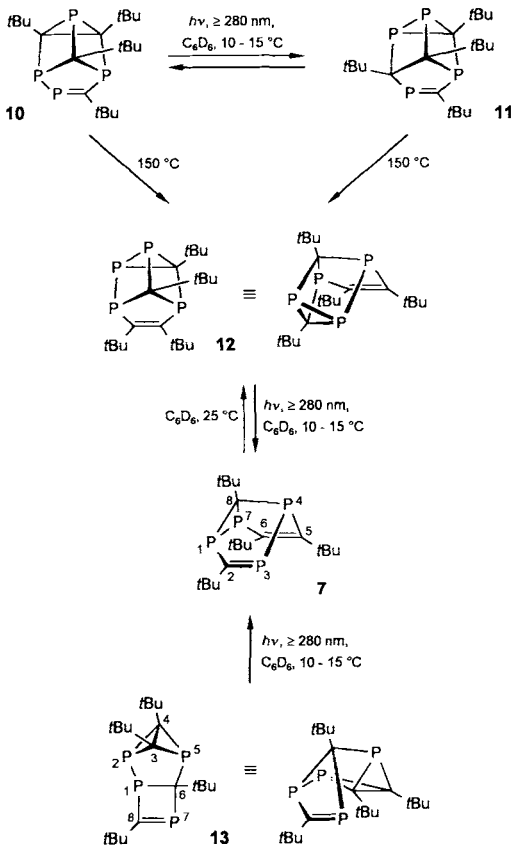


Figure 1. Structure of **9** in the crystal (XP-Plot, thermal ellipsoids drawn at 50% probability level). Selected bond lengths [Å] and angles [°]: P2–P11 2.2185(13), P7–P8 2.2095(12), P7–C3 1.865(3), P2–C3 1.892(3), P8–C9 1.869(3), P2–C1 1.855(3), P8–C1 1.845(3), P11–C1 1.836(3), P11–C10 1.851(3), C10–C9 1.357(4); C1-P2-P11 52.65(10), C1-P2-C3 103.49(14), C3-P2-P11 116.12(10), C1-P11-C10 100.21(14), C1-P11-P2 53.45(10), C10-P11-P2 115.66(11), P11-C1-P8 108.0(2), P11-C1-P2 73.89(12), P8-C1-P2 116.9(2).

The P–C single bond lengths in the tricyclic phosphorus–carbon skeleton of **9** are between 1.836 and 1.892 Å (average value 1.856 Å) and thus in good agreement with those of other polycyclic compounds.[11] The P2–P11 bond length of 2.219 Å lies at the upper limit for diphosphiranes.[12] In accord with this, the angle P2-C1-P11 in the three-membered ring is larger (73.9°) and the angles C1-P11-P2 (53.5°) and C1-P2-P11 (52.7°) are smaller than those in other polycyclic systems containing a diphosphirane element.[13]

Valence isomerizations in phosphaalkyne cyclotetramer systems were previously unknown. We report here on reactions of this type that also make the tetraphosphasemibullvalene **7** accessible from the polycyclic systems **10**–**13** (Scheme 3).

The compounds **10** and **11** are known[13a,14] and coexist as a 1:1 equilibrium mixture (by ^{31}P NMR spectroscopy) upon irradiation of the one or the other in C_6D_6 (mercury high-pressure lamp Phillips, HPK 125W, Duran-50 filter). When each of the two isomers is heated separately at 150 °C, compound **12** (100 and 48%, respectively) is formed by a skeletal rearrangement; the latter product is also accessible directly from the thermal cyclotetramerization of the phosphaalkyne **4** at 180 °C.[3c] When **12** is photolyzed under the conditions mentioned for the equilibrium **10**⇌**11**, the valence isomer **7** is formed (up to 75%);



Scheme 3.

the reverse isomerization of **7** occurs relatively slowly at 25 °C in C_6D_6 (ca. 20% **12** after 7 d, both by ^{31}P NMR spectroscopy). Finally, **13** can undergo complete photochemical isomerization to furnish an isomeric mixture of **7** and **12** (80:20).

Experimental Section

7: In a 15-mL-pressure Schlenk tube, tropone (**5**) (0.14 g, 1.3 mmol) was added to phosphaalkyne **4** [15] and the two-phase system was heated with magnetic stirring under argon pressure (5 bar) for 17 h at 95 °C. After the mixture had cooled to 25 °C, unconverted phosphaalkyne **4** (2.15 g, 21.5 mmol) was recovered by condensation (0.003 mbar, received −192 °C). Column chromatography (1.4 × 30 cm) on silica gel (63–200 μm, baked for 16 h at 175 °C and 10^{-3} mbar and deactivated with 4% argon-saturated water) at −30 °C afforded the following in sequence: a) elution with *n*-pentane (500 mL) gave after evaporation of the solvent at 10^{-3} mbar/25 °C the orange-red, oily **7**. Yield: 32 mg (4.9%, with respect to converted **4**); stored at −25 °C; b) elution with *n*-pentane/diethyl ether 10/1 (50 mL) gave a dark orange-red, unidentified "polymer"; c) elution with *n*-pentane/diethyl ether 5/1 (70 mL) gave the pale yellow, oily tetracyclic product **6**.

8: Compound **7** (70 mg, 0.17 mmol) in tetrahydrofuran (5 mL) was added to a solution of $[W(CO)_5 \cdot thf]$,[16] prepared by irradiation of $[W(CO)_6]$ (92.3 mg, 0.26 mmol) in tetrahydrofuran (60 mL). After 17 h the solvent was evaporated at 25 °C/10^{-3} mbar, the oily residue was eluted with *n*-pentane (20 mL) and subjected to chromatography on silica gel (column: 1.8 × 37 cm) with *n*-pentane. Yield: 85.5 mg (69%) dark red oil, which could be crystallized from *n*-pentane at −80 °C. M.p. 8–13 °C (in thawing cold bath).

9: Mesityl nitrile oxide (40 mg, 0.25 mmol) in toluene (3 mL) was added dropwise with stirring at −78 °C to the tetraphosphasemibullvalene **7** (100 mg, 0.25 mmol) in toluene (3 mL), and the mixture was stirred for further 3 h at 25 °C. After evaporation (25 °C/10^{-3} mbar), dissolution in *n*-pentane (1.5 mL), and chromatography on silica gel (as described for **7**, but with water-cooling) the following were obtained in sequence: a) elution with *n*-pentane (80 mL) gave after evaporation about 5 mg of **12** formed by isomerization of **7**; identification by a comparison of the NMR spectrum with that of an authentic sample [3c]; b) elution with *n*-pentane/diethyl ether 25/1 (50 mL) gave the pale yellow cycloadduct **9**. Yield: 129 mg (92%), m.p. 123 °C (from *n*-pentane at −20 °C).

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[8] The spectroscopic characterization of **13** was carried out in an admixture with **7** and **12**; the assignments of the skeletal atoms were based on the values for the corresponding 1-adamantyl compound, which was isolated in the pure state. ^1H NMR (400 MHz): $\delta = 1.15$ (s, 9H; $C(CH_3)_3$), 1.17 (d, $^4J(P,H) = 1.6$ Hz, 9H; $C(CH_3)_3$), 1.34 (s, 9H; $C(CH_3)_3$), 1.48 (s, 9H; $C(CH_3)_3$); ^{13}C NMR (100.64 MHz): $\delta = 77.4$ (ddd, $^1J(P,C) = 51.6$, 45.1 and 6.2 Hz; C-6), 234.4 (dd, $^1J(P,C) = 57.3$ and 35.0 Hz; C-8), the remaining skeletal carbon atoms could not be assigned because of signal overlap; ^{31}P NMR (161.98): $\delta = 0.9$ (ddd, $^2J(P,P) = 35.2$, 26.9 and 25.6 Hz; P-5), 4.4 (dd, $^1J(P,P) = 282.3$ Hz, $^2J(P,P) = 26.9$ Hz; P-2), 107.0 (ddd, $^1J(P,P) = 282.3$ Hz, $^2J(P,P) = 28.3$ and 25.6 Hz; P-1), 348.5 (dd, $^2J(P,P) = 35.2$ and 28.2 Hz; P-7).

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Rotational Spectroscopy of Mixtures of Trimethylamine and Fluorine: Identification of the Ion Pair $[(CH_3)_3NF]^+ \cdots F^-$ in the Gas Phase**

Hannelore I. Bloemink, Stephen A. Cooke, John H. Holloway, and A. C. Legon*

Reactions of elemental fluorine with organic compounds are notorious for their violence. They are assumed usually to proceed by a chain mechanism that is initiated by the facile homolytic dissociation of F_2 into atoms. The next step (propagation) is presumably the abstraction of an H atom from a CH_n group to give $\cdot CH_{n-1}$ and HF, which is strongly exothermic and makes the reaction difficult to control. Consequently, the products are often predominantly HF, CF_4, and carbon. The large value for the energy of heterolytic dissociation $F_2 = F^+ + F^-$ ($1370\ kJ\,mol^{-1}$)[1] means that reactions in the gas phase involving the F^+ ion are unlikely to be common. Are there reactions of F_2 in which heterolysis of the diatomic molecule needs to be invoked?

We report herein the identification and characterization of a complex formed by trimethylamine with F_2 in the gas phase. Interpretation of spectroscopic constants derived from analyses of the rotational spectra of three isotopomers leads to the conclusion that the observed species is best described as a Mulliken complex $[(CH_3)_3NF]^+ \cdots F^-$ of the inner type, that is, one in which the F^+ ion has been transferred from F_2 to the Lewis base. This is a surprising result, not only because of the reluctance of F_2 to dissociate heterolytically but also because, for all complexes $B \cdots F_2$ previously investigated ($B = NH_3$,[2] HCN,[3] CH_3CN,[4] H_2S,[5] and H_2O[6]), the interaction between the Lewis base and F_2 is very weak.

The rotational spectrum of the complex $[(CH_3)_3N, F_2]$ was observed by using a pulsed-nozzle, Fourier-transform microwave spectrometer[7] fitted with a fast-mixing nozzle.[8] This latter device consists of two concentric, nearly coterminal tubes and ensures that the two components (trimethylamine flowing continuously through the inner tube and F_2/Ar mixture pulsed down the outer tube) do not mix until they expand simultaneously into the evacuated Fabry–Pérot cavity of the spectrometer. The reasons why the fast-mixing nozzle is effective in inhibiting the production of F atoms, and therefore in precluding violent chain reactions of the type alluded to earlier, have been discussed elsewhere.[6]

The ground-state rotational spectrum of the isotopomer $[(CH_3)_3{}^{14}N, F_2]$ is characteristic of a symmetric-top molecule carrying a ^{14}N ($I = 1$) nucleus on the unique axis. Analysis of the ^{14}N nuclear quadrupole hyperfine structure in the $J = 2 \leftarrow 1$, $3 \leftarrow 2$, $4 \leftarrow 3$, and $5 \leftarrow 4$ transitions yielded the rotational constant B_0, the centrifugal distortion constants D_J and D_{JK}, and the ^{14}N-nuclear quadrupole coupling constant $\chi(^{14}N)$ (Table 1). A partially resolved substructure, arising from coupling of the various $I = 1/2$ (H and F) nuclei, together with the small magnitudes of $\chi(^{14}N)$ and D_{JK}, resulted in a complex and congested

[*] Prof. A. C. Legon, Dr. H. I. Bloemink, S. A. Cooke
Department of Chemistry, University of Exeter
Stocker Road, Exeter EX4 4QD (UK)
Fax: Int. code +(1392) 263434
e-mail: ACLegon@exeter.ac.uk

Prof. J. H. Holloway
Department of Chemistry, University of Leicester
University Road, Leicester LE1 7RH (UK)

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