

173.5(8), Fe1-S 218.2(2), Fe2-S 227.9(2), Fe1-Fe2 267.5(1), C=C1 134.0(12) pm.

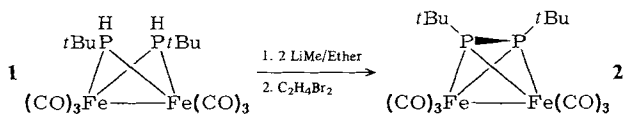
[5] Details of the crystal structure investigation can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen by quoting the depository number CSD 50259, the name of the author and the citation of the journal.

A Diphosphene as Tetrahedrane Building Block: Synthesis of $[\text{Fe}_2(\text{CO})_6(\text{P}_2t\text{Bu}_2)]^{**}$

By Heinrich Vahrenkamp* and Doris Wolters

Diorganodiphosphenes R_2P_2 are stable in the free form only when bearing very bulky substituents $\text{R}^{[1]}$. To our knowledge, unlike the analogous compounds Ph_2As_2 and Ph_2Sb_2 , they were previously unknown in the form of complex ligands^{[2]***}. We have now succeeded in carrying out a directed synthesis of an R_2P_2 species ($\text{R} = t\text{Bu}$) in the ligand sphere of a complex.

The doubly $t\text{BuPH}$ -bridged dinuclear complex **1**^[3] was deprotonated with MeLi (ether, 0°C); *in situ* oxidation of the intermediate with 1,2-dibromoethane (ether, $0^\circ\text{C} \rightarrow \text{RT}$), evaporation to dryness, dissolution in *n*-hexane, and chromatography on silica gel, (*n*-hexane/benzene, 10:1) furnished the complex **2** (red crystals, m.p. 120°C (decomp.) 11% yield).



Complex **2** was identified by elemental analysis and spectra: IR (C_6H_{12}): $\nu = 2053$ (m), 2015 (s), 1988 (vs), 1968 (s), 1958 (m) cm^{-1} ; NMR (CDCl_3): $\delta = 1.52$, $J = 22.0$ Hz, EI-MS: m/z 456 (M^+). A crystal structure analysis revealed the molecular geometry given in Figure 1^[4].

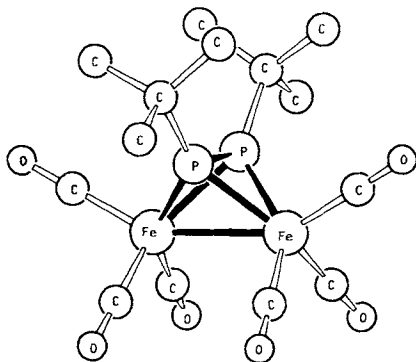


Fig. 1. Structure of $[\text{Fe}_2(\text{CO})_6(\text{P}_2t\text{Bu}_2)]$ **2** in the crystal [4]. Bond lengths: Fe-Fe 274.0(1), P-P 205.9(3), Fe-P 221.2–223.2(2) pm.

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[***] Note added in proof (January 10, 1983): A mononuclear complex of $\text{P}_2(\text{SiMe}_3)_2$ has recently been described: B. Deppisch, H. Schäfer, *Z. Anorg. Allg. Chem.* 490 (1982) 129.

The tetrahedrane molecule **2** is isoelectronic and structurally related to the R_2N_2 - and S_2 -analogues^[5]. However, whereas the N-N bond in $[\text{Fe}_2(\text{CO})_6(\text{N}_2\text{Me}_2)]$ and the S-S bond in $[\text{Fe}_2(\text{CO})_6\text{S}_2]$ are about the same length as a normal N-N or S-S single bond, the P-P bond in **2**, with a length of ca. 206 pm, is markedly shorter than a P-P single bond in oligophosphanes; it is almost the same length as the P-P bond in the diphosphene $\text{P}_2(\text{C}_6\text{H}_2t\text{Bu}_3)_2$ (203 pm)^[1]. Hence, the classification of the ligand P_2tBu_2 in **2** as diphosphene appears justified.

To achieve an 18-electron balance for each iron atom, the diphosphene must function as a 6-electron ligand (one π -electron pair and two n -electron pairs). According to Hoffmann's isolobal relationship^[6] $[(\text{CO})_3\text{Fe}^\ominus \leftarrow \delta \text{CH}$ and $\text{RP}^\ominus \leftarrow \delta \text{CH}]$ the complex **2** can be regarded as a derivative of the tetrahedrane $(\text{CH})_4$.

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- [1] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* 103 (1981) 4587; however, see also A. H. Cowley, J. E. Kilduff, T. H. Newman, M. Pakulski, *ibid.* 104 (1982) 5820; C. Couret, J. Escudié, J. Satgé, *Tetrahedron Lett.* 23 (1982) 4941; E. Niecke, R. Rüger, *Angew. Chem.* 95 (1983) 154; *Angew. Chem. Int. Ed. Engl.* 22 (1983) 155.
[2] M. Jacob, E. Weiss, *J. Organomet. Chem.* 153 (1978) 31; G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, *Angew. Chem.* 94 (1982) 210; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 215; *Angew. Chem. Suppl.* 1982, 411.
[3] P. M. Treichel, W. K. Dean, W. M. Douglas, *Inorg. Chem.* 11 (1972) 1609.
[4] Monoclinic; $\text{P}2_1/n$; $a = 1543.5(2)$, $b = 1543.1(2)$, $c = 853.9(1)$ pm; $\beta = 91.34(1)^\circ$; $Z = 4$; 3336 reflections, R (anisotropic, without H atoms) = 0.051. Further details about the crystal structure investigation can be obtained on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein Leopoldshafen, quoting the depository number CSD 50242, the name of the authors and full citation of the journal.
[5] Cf. B. K. Teo, M. B. Hall, R. F. Fenske, L. F. Dahl, *Inorg. Chem.* 14 (1975) 3103.
[6] R. Hoffmann, *Angew. Chem.* 94 (1982) 725; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 711 (Nobel lecture).

Photochemical Four-Electron Redox Reaction of Hexaazidoplatinate(IV)**

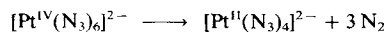
By Arnd Vogler* and Joachim Hlavatsch

In many transition-metal complexes intramolecular photoredox reactions occur, in which an electron is transferred from a ligand to the metal (one photon-one electron redox reaction). In contrast, only a few photo-induced two-electron transfer reactions are known. Reactions of this type are meeting with increasing interest in connection with photosynthesis or in the photochemical cleavage of water^[1]. Reductive eliminations are particularly straightforward intramolecular two-electron redox reactions of metal complexes. Here, two ligands are oxidatively cleaved off and the metal is reduced by two units by the electrons from the ligands. Some reactions of this type have also been observed to occur photochemically^[2] (one photon—two electron redox reaction). We now report on two consecutive reductive photoeliminations (two photon—four electron redox reaction). By this means Pt^{IV} is reduced to Pt^0 via Pt^{II} , whereas in total four ligands are oxidatively cleaved off.

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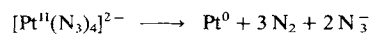
[**] This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

The complex ion $[\text{Pt}(\text{N}_3)_6]^{2-}$, first synthesized and characterized by Beck *et al.*^[3], has a charge-transfer band ($\text{N}_3 \rightarrow \text{Pt}$) at $\lambda_{\text{max}} = 308 \text{ nm}$ ($\epsilon = 37\,154$)^[3]. Irradiation of a solution of $[\text{Pt}(\text{N}_3)_6]^{2-}$ in CH_2Cl_2 with light of wavelength $\lambda = 314 \text{ nm}$ led to photolysis of the complex ion. Over the complete absorption region of the ion between 590 and 285 nm^[4] the extinction decreased by the same ratio at all wavelengths. Simultaneously, bubbles of nitrogen were evolved from the solution. From this observation we conclude that photolysis according to



occurs. The decrease in extinction is accounted for by the considerably smaller absorption of the primary photolysis product $[\text{Pt}(\text{N}_3)_4]^{2-}$ over the entire absorption range relative to that of $[\text{Pt}(\text{N}_3)_6]^{2-}$ ^[3]. Upon complete absorption of light ($A \geq 2$) by $[\text{Pt}(\text{N}_3)_6]^{2-}$ the photolysis proceeds with zero order. Irradiation with light of wavelength $\lambda = 314 \text{ nm}$ gives a quantum yield $\Phi = 0.27$.

If irradiation is further continued the solution becomes black due to precipitation of colloidal platinum. As a consequence this caused an increase in extinction which became larger with decreasing wavelength, such as is expected for light scattering by the colloidal particles. Simultaneously, evolution of bubbles of nitrogen continued. Moreover, azide was released, which could be quantitatively determined by spectrophotometry of its Fe^{III} complex^[2a]. These observations are consistent with the following secondary photolysis.



The same result was also obtained by direct photolysis of $[\text{Pt}^{\text{II}}(\text{N}_3)_4]^{2-}$ ^[3] in a separate experiment. The quantum yield for the photolysis of $[\text{Pt}(\text{N}_3)_4]^{2-}$ is $\Phi = 0.17$ at an excitation wavelength of $\lambda = 314 \text{ nm}$.

Formation of colloidal platinum during the photolysis of $[\text{Pt}(\text{N}_3)_6]^{2-}$ and of $[\text{Pt}(\text{N}_3)_4]^{2-}$ is also interesting in connection with heterogeneous catalysis by platinum metal. It is known that the catalytic activity increases as the size of the colloidal particles decreases^[1]. Photolysis of azidoplatinate complexes could lead to better control of the particle size.

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- [1] M. Grätzel, *Acc. Chem. Res.* 14 (1981) 376.
[2] a) A. Vogler, A. Kern, B. Fusseder, J. Hüttermann, *Z. Naturforsch. B* 33 (1978) 1352; b) A. Vogler, R. E. Wright, H. Kunkely, *Angew. Chem.* 92 (1980) 745; *Angew. Chem. Int. Ed. Engl.* 19 (1980) 717; c) A. Vogler, H. Kunkely, *J. Am. Chem. Soc.* 103 (1981) 6222.
[3] W. Beck, W. P. Fehlhammer, P. Pöhlmann, E. Schuierer, K. Feldl, *Chem. Ber.* 100 (1967) 2335.
[4] $[\text{Pt}(\text{N}_3)_6]^{2-}$ was studied as its $[\text{As}(\text{C}_6\text{H}_5)_4]^+$ salt. The cation exhibits intense self-absorption below 285 nm.

Tetrakis(trimethylsilyl)diaminodiphosphene**

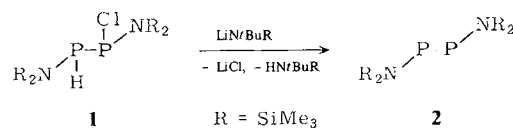
By Edgar Niecke* and Reinhold Rüger

The synthesis of the first stable diphosphene has recently been reported^[1]. We have now found that base-in-

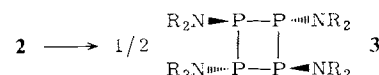
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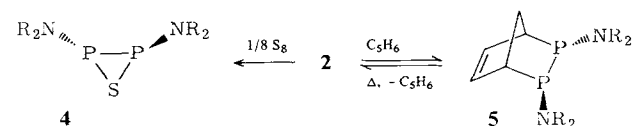
duced "HCl"-elimination from the diphosphene **1** affords entry to a novel, further example of this interesting class of compounds with phosphorus-phosphorus (p-p) π bonding.



The pyrophoric diaminodiphosphene **2** is a ruby-red liquid at room temperature. In solution, the compound is stable for several days; without solvent it dimerizes within hours to the cyclotetraphosphane **3**^[3a,b], which can be isolated as a crystalline, colorless, almost inert solid.



The synthetic potential of **2** has already been demonstrated by its reactions with sulfur or cyclopentadiene, which lead to cycloaddition products—the thiadiphosphirane **4**^[3a,c] and the 2,3-diphosphanorbornene **5**, respectively, each of which forms only one isomer. According to the NMR data^[4] only the *trans*-form of **5** is formed.



No cycloreversion takes place in the case of **4**, at least up to 150 °C, whereas **5** already decomposes above 40 °C into its components, and it can thus serve as a storable source of the diphosphene.

The composition and structure of the tetrasilylated diaminodiphosphene **2** and its reaction products **3**–**5** are confirmed by elemental analysis, mass spectra (**2**–**4**), and NMR data^[4]. Noteworthy is the extremely large downfield shift of the ³¹P-NMR signal of $\delta = 572$ in the case of **2** (30% in CD_2Cl_2 , H_3PO_4 ext.)^[5]. The ¹H-, ¹³C{¹H}- and ²⁹Si{¹H}-NMR spectra (30%, in CD_2Cl_2 , TMS int.) show the groups of signals with pseudo-triplet structure that are to be expected for free rotation about the P–N bond: $\delta(^1\text{H}) = 0.32$ (1.2 Hz), $\delta(^{13}\text{C}) = 3.4$ (8.4 Hz), $\delta(^{29}\text{Si}) = 7.1$ (2.8 Hz).

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- [1] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* 103 (1981) 4587; B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, H. Goldwhite, *J. Chem. Soc. Chem. Commun.* 1982, 691; G. Bertrand, C. Couret, J. Escudie, S. Majid, J. P. Majoral, *Tetrahedron Lett.* 23 (1982) 3567.
[2] E. Niecke, R. Rüger, *Z. Naturforsch. B* 37 (1982) 1593.
[3] The stereochemistry of **2**, **3**, and **4** cannot be derived unequivocally from the NMR data; structural investigations on similar compounds indicate that **2**, **3**, and **4** might also contain *trans*-oriented amino groups.—b) **3** has already been identified as a decomposition product of tetraphosphabicyclobutane, $\text{P}_4(\text{NR}_2)_2$: E. Niecke, R. Rüger, B. Krebs, *Angew. Chem.* 94 (1982) 553; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 544.—c) The synthesis of a thiadiphosphirane by cyclocondensation has been reported: M. Baudler, H. Suchomel, G. Fürstenberg, U. Schings, *ibid.* 93 (1981) 1087 and 20 (1981) 1044.