[1] An overview on molecular knots: a) G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**; b) *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**; c) J.-P. Sauvage, C. Dietrich-Buchecker in *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**, pp. 105 – 142; d) N. C. Seeman in *Molecular Catenanes, Rotaxanes and Knots* (Eds.: J.-P. Sauvage, C. Dietrich-Buchecker), Wiley-VCH, Weinheim, **1999**, pp. 323 – 356; e) P. R. Ashton, O. A. Matthews, S. Menzer, F. M. Raymo, N. Spencer, J. F. Stoddart, D. J. Williams, *Liebigs Ann.* **1997**, 2485 – 2494; f) G. A. Breault, C. A. Hunter, P. C. Mayers, *Tetrahedron* **1999**, *55*, 5265 – 5293; g) for nomenclature and absolute configuration of chiral knots, see: C. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, A. De Cian, J. Fischer, *Chem. Eur. J.* **1999**, *5*, 1432 – 1439.

[2] a) O. Safarowsky, M. Nieger, R. Fröhlich, F. Vögtle, *Angew. Chem.* **2000**, *112*, 1699 – 1701; *Angew. Chem. Int. Ed.* **2000**, 39, 1616 – 1618; b) P. Zurer, *Chem. Eng. News* **2000**, *78*(19), 14; c) S. Albus, *Nachr. Chem.* **2000**, *7/8*, 887.

[3] O. Safarowsky, B. Windisch, A. Mohry, F. Vögtle, *J. Prakt. Chem.* **2000**, *5*, 437 – 444.

[4] So far racemic knotane mixtures have not been separated by chromatography, instead separation has been achieved through diastereomers: "Unfortunately, this technique seemed to be inappropriate to the resolution of the knot" (ref. [1b], p. 36).

[5] N. Enomoto, S. Furukawa, Y. Ogasawara, H. Akano, Y. Kawamura, E. Yashima, Y. Okamoto, *Anal. Chem.* **1996**, *68*, 2798 – 2804.

[6] a) For the PPP-SCF method (overview: M. Scholz, H. J. Köhler, *Quantenchemie*, *Vol. 3*, Hüthig, Heidelberg, **1981**), standard parameters (J. Pancir, I. Matousek, R. Zahradnik, *Collect. Czech. Chem. Commun.* **1973**, *38*, 3039) and the Mataga – Nishimoto and Ohno – Klopman approximations (N. Mataga, K. Nishimoto, *Z. Phys. Chem. NF* **1957**, *12*, 335; K. Ohno, *Theor. Chim. Acta* **1964**, 219; G. J. Klopman, *J. Am. Chem. Soc.* **1964**, *86*, 4450) were used for the two-electron integrals ($\gamma = 1.2\gamma_{MN} - 0.2\gamma_{OK}$). Contracted cartesian Gaussian functions (STO-6G) and standard Slater exponents were used as the basis for the p atomic orbitals (pAOs). The electrical (velocity form) and magnetical dipol integrals were calculated exactly with the Löwdin-deorthogonalized ZDO basis. To describe the nonplanarity of the conjugated units, the oriented pAOs were represented by the sum of the $c_{x^*}p_x$, $c_{y^*}p_y$, and $c_{z^*}p_z$ AOs, while the coefficient $c_x - c_z$ was determined by the plane's orientation in space, as defined by its closest π neighbors. The entire program, which also includes the solution of the TDPPP equation, can be downloaded from the WWW as a fortran source code from: http://www.uni-muenster.de/Chemie/OC/research/grimme/. b) The broadening of the oscillation of each transition was simulated by summing up Gaussian curves that have been weighted based upon rotational strength, with a width of 0.2 eV at a height of e^{-1}. The theoretical $\Delta\varepsilon$ values are obtained as absolutes, that is, they can be directly compared with the experimental data. See also: S. Grimme, J. Harren, A. Sobanski, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 1491 – 1509; c) AM1: M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902 – 3909; MOPAC 6.0: J. J. P. Stewart, *QCPE Bull.* **1985**, *5*, 133; d) MMX force field: PCModel 7.0, Serena Software, Bloomington, **1999**.

[7] For nomenclature of molecular knots and their chirality, see ref. [1c], as well as D. M. Walba, *Tetrahedron* **1985**, *41*, 3161 – 3212; M. Epple, *Die Entstehung der Knotentheorie*, Vieweg, Wiesbaden, **1999**, pp. 31 – 43.

[8] In supplement to ref. [3]: The determination of the relative positions of the knot's cross-over sections is carried out as follows (Figure 4): If it is possible to project the line crossing below (broken arrow) onto the line running above (complete arrow) by a rotation of less than 180°, the cross-over section is marked by a superscript p (clockwise rotation) or m (counterclockwise rotation). To determine the direction of the arrows, they have to be moved along the graph in a clockwise motion. The molecular knots described here can therefore be characterized as 3_1^{ppp} or 3_1^{mmm}, depending on the enantiomer.

[9] a) E. Francotte, *J. Chromatogr. A* **2001**, *906*, 379 – 397; b) N. M. Maier, P. Franco, W. Lindner, *J. Chromatogr. A* **2001**, *906*, 3 – 33.

[10] a) *Templated Organic Synthesis* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **2000**; b) N. V. Gerbeleu, V. B. Arion, J. Burgess, *Template Synthesis of Macrocyclic Compounds*, Wiley-VCH, Weinheim, **1999**; c) R. Hoss, F. Vögtle, *Angew. Chem.* **1994**, *106*, 389 – 398; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 375 – 384; d) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469 – 475.

[11] O. Safarowsky, PhD Thesis, Universität Bonn, **2000**.

[12] Preliminary results: a) M. Knott, Diploma Thesis, Universität Bonn, **2000**; b) E. Vogel, Dissertation, Universität Bonn, **2001**.

[13] Molecular knots of this type measure 4 – 5 nm across.

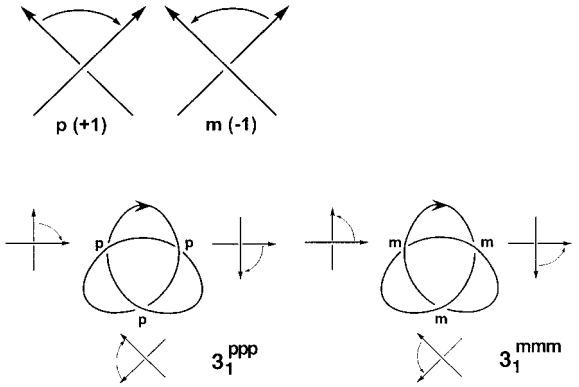

Figure 4. Determination of the chirality of knotted molecules.

Synthesis of the First 1,3,4-Triphosphole Complex**

Rainer Streubel,* Udo Schiemann, Peter G. Jones, Jörg Grunenberg, Hans-Martin Schiebel, and Dietrich Gudat*

Dedicated to Professor Manfred Regitz on the occasion of his 65th birthday

The development of phosphorus-containing 6π-arenes such as phosphinines (phosphabenzenes) is currently attracting attention because of the considerable interest from industry in novel directing ligands for catalytic processes,[1, 2] yet it still suffers from a lack of rational and efficient synthetic methods. Interesting candidates as novel ligands with 6π-electron systems besides phosphinines are phosphorus-rich hetero-

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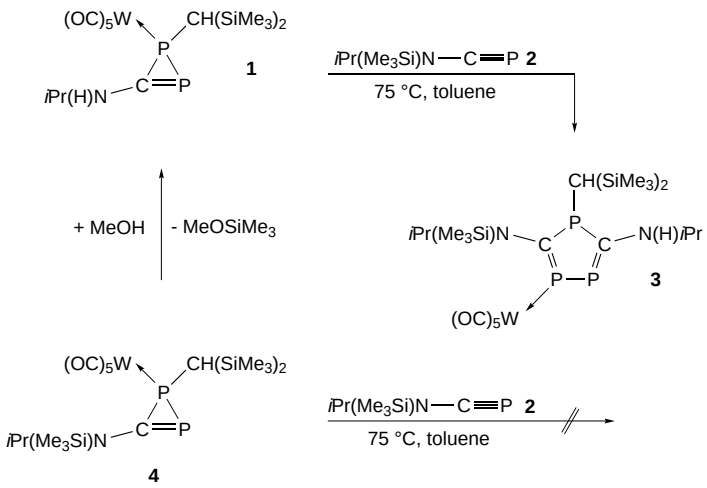
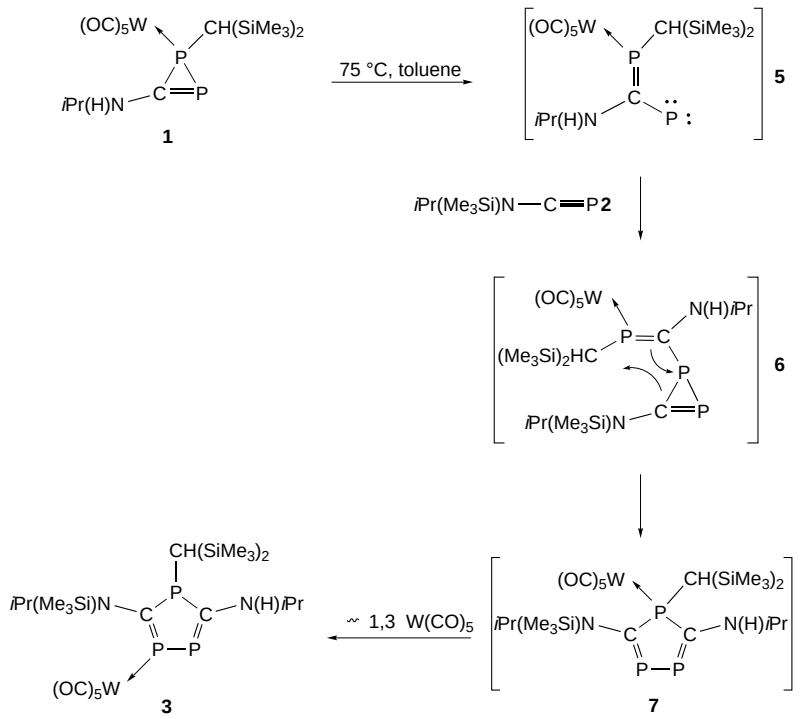
phospholes, in which, according to theoretical studies, the replacement of CH groups by P atoms induces an increasing tendency towards planarization of the tricoordinate phosphorus center in the ring.[3, 4] A milestone in this field was the first synthesis of aromatic 1,2,4-triphosphole derivatives.[5, 6]

In the course of our systematic investigations towards the synthesis of novel heterophosphole complexes with a tricoordinate phosphorus atom and one[7] or two[8–10] further heteroatoms in the ring, we have now obtained the first 1,3,4-triphosphole complex **3** in good yield (>90% of crude product) by thermally induced, regiospecific insertion of the phosphaalkyne **2**[11] into the P–P bond of the 1*H*-diphosphirene complex **1** (Scheme 1); preliminary results will be reported, hereafter. The starting material **1** is readily available by methanolysis of **4**.[12] Formation of a regioisomer of **3** was not observed.

As a possible reaction mechanism for the formation of **3** we postulate the initial formation of a phosphanediyl **5**, which then undergoes a [2+1] cycloaddition with **2** to give the 1*H*-diphosphirene derivative **6**, which in turn undergoes a ring expansion to afford the 1,3,4-triphosphole complex **7**. A subsequent 1,3-shift



Scheme 1. Reactions of the 1*H*-diphosphirene complexes **1** and **4** with phosphaalkyne **2.**



Scheme 2. Proposed reaction mechanism for the formation of the 1,3,4-triphosphole complex **3**.

of the $(CO)_5W$ fragment in **7** yields the final product **3** (Scheme 2). These hypotheses are based on former results and model considerations of the chemical behavior of reactive 1*H*-diphosphirene complexes, for which P–P[13] or P–C bond cleavage processes[14] have also been suggested as primary reaction steps. Likewise, migrations of coordinated metal complex fragments from $\sigma^3\lambda^3$- to $\sigma^2\lambda^3$-phosphorus centers have been reported repeatedly.[12, 15] Surprisingly, control experiments revealed that the 1*H*-diphosphirene complex **4** failed to react with **2** under similar conditions. Even though the lack of significant differences between the molecular structures of complexes **1** and **4** (vide infra) gave no explicit clue for a different bonding situation, we propose as the most reasonable explanation of this remarkable chemoselectivity that the activation energy required for the formation the reactive intermediate of type **5** is liable to considerable electronic substituent influences.

The constitution of complexes **1**, **3**, and **4** follows unequivocally from their NMR and MS data.[16] In addition, the molecular structures of complexes **1** (Figure 1) and **4** were determined from single-crystal X-ray diffraction studies.[17]

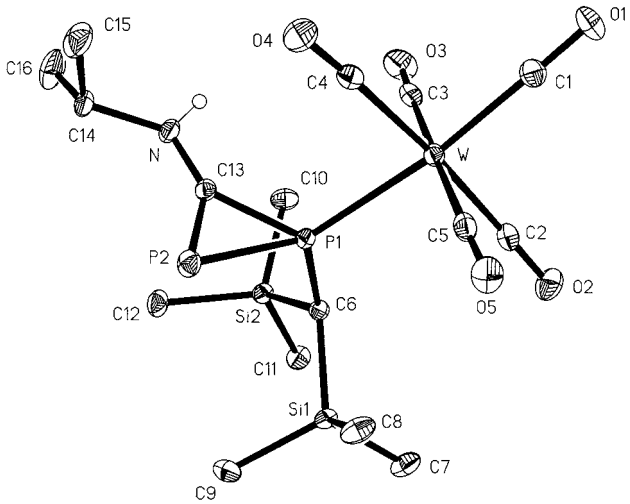


Figure 1. Molecular structure of compound **1** in the crystal (thermal ellipsoids at 30% probability level; H atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: W-P1 251.97(12), P1-C6 183.2(3), P1-C13 178.8(3), P1-P2 217.56(14), P2-C13 169.6(3), C13-N 132.7(4); P2-P1-C13 49.49(10), P2-C13-P1 77.22(13), C13-P2-P1 53.28(10), P2-C13-N 142.4(2).

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The individual bond lengths and angles exhibit no peculiarities and show close similarities in both complexes. The dihedral angle C14-N-C13-P2 in **1** (−173.7°) indicates an almost coplanar orientation of the amino group relative to the plane of the three-membered ring, with the bulky substituent on the nitrogen atom pointing away from the coordinated phosphorus atom. Conjugation between the P–C double bond and the lone pair of electrons at the nitrogen atom is indicated by the relatively short C–N distance. Interestingly, and in contrast to other 1*H*-diphosphirene complexes that have less sterically demanding substituents at the σ^3-phosphorus atom,[18, 19] only a single conformer of **1** is observed even in solution.

The postulated constitution of **3** was further substantiated by an X-ray diffraction study, even though an adequate final refinement of the structure proved impossible owing to severe disorder of the *i*Pr(Me$_3$Si)N group. Nevertheless, the available data provided evidence for a weakly pyramidal configuration at the σ^3-phosphorus atom[20] which points to the presence of a low inversion barrier and can be understood as a step towards aromatization of the cyclic π system.[5, 6]

The assumption of a low inversion barrier at the σ^3-phosphorus atom was corroborated by solution NMR studies. The ^{1}H NMR spectrum of **3** at 25 °C displays a broad signal for the methyl protons of the (Me$_3$Si)$_2$CH substituent, which decoalesces when the temperature is lowered, and finally splits into two equally intense singlets at −45 °C. Similar splittings were observed for the methyl protons in both *N*-isopropyl groups. The results of lineshape analyses revealed that all three exchange processes occur at the same rate and can thus be assigned to a single dynamic process whose activation parameters were determined from an Eyring plot as $\Delta H^{\neq} = 41.4 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\neq} = -50 \pm 5$ eu. Based on the analysis of 2D ^{1}H ROESY spectra taken at different temperatures, the observed effects can be explained as the result of hindered rotation of the *i*Pr(Me$_3$Si)N group which at −45 °C is frozen in a notably twisted orientation relative to the ring plane.[21] Additional NMR measurements gave no evidence of further dynamically induced signal-broadening effects down to −92 °C. In summary, these findings prove that the P inversion in **3** must proceed at the same rate as or a higher rate than the rotation of the *i*Pr(Me$_3$Si)N group, and that the activation barrier for the amine rotation can thus be regarded as an upper limit for the P-inversion barrier.

To gain a better estimate of the magnitude of the P-inversion barrier in the 1,3,4-triphosphole **3**, quantum-mechanical model calculations (at the B3LYP/6-31+G(d)+ZPE level)[22, 23] were carried out. The results indicate an increase of the inversion energies for the compounds $H_2C_2P_3H$ (**8**), $H_2N(H)C_2P_3H$ (**9**), and $(H_2N)_2C_2P_3H$ (**10**) with increasing number of amino groups ($\Delta E = 25.2$ (**8**), 53.6 (**9**), 70.7 (**10**) kJ mol^{-1}). This trend is markedly reduced when one considers for **9** and **10** interconversion between conformers that represent transition states with respect to C–N bond rotation and feature a nearly orthogonal arrangment of the lone pairs of electrons on the NH_2 groups and the π orbitals in the ring, respectively ($\Delta E =$ 16.8 (**9**), 21.3 (**10**) kJ mol^{-1}). A stabilization of an appropriate conformation for the *i*Pr(Me$_3$Si)N group in **3** together with the influence of the sterically demanding (Me$_3$Si)$_2$CH substituent, which acts in favor of a planarization of the σ^3-phosphorus atom,[5] should be sufficient to decrease the P-inversion barrier to a few kJ mol^{-1}.

Fragmentation of **3** in negative-ion CI mass spectra occurs by elimination of 1,1-dimethylsilaethene and 1,1-dimethyl-1-silapropene to give first a triphospholide complex $[\{(i\text{Pr(H)N})_2C_2P_3\}^{182}W(CO)_5]^-$ (*m*/*z* 555), and further by cleavage of the W(CO)$_5$ fragment to yield the free triphospholide $[(i\text{Pr(H)N})_2C_2P_3]^-$ (*m*/*z* 233). Additional studies aimed at the realization of reductive cleavage of the exocyclic (SiMe$_3$)$_2$CH group in condensed phases and the achievement of π tuning in the 1,3,4-triphosphole ring system by transformation of the amino functions in **3** are currently in progress.

Experimental Section

1: Complex **4** (0.688 g, 1 mmol) was dissolved in *n*-pentane (10 mL), methanol (2 mL) was added at room temperature, and the solution was stirred for approximately 60 min at 30 °C; the end of the reaction was determined by ^{31}P NMR spectroscopy. The solution was evaporated in vacuum (ca. 0.1 mbar) and the solid residue was dissolved in *n*-pentane (5 mL), cooled to −25 °C, and the resulting precipitate separated from the supernatant solvent. The obtained solid was washed several times with small quantities of *n*-pentane, and dried in vacuum. Yield: 295 mg (48 %), m.p. 47 °C (decomp). Selected NMR data: ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C, ext. TMS): $\delta = 1.88$ (dd, ^3J(P,C) = 3.7, ^4J(P,C) = 4.3 Hz; Si(CH$_3$)$_3$), 2.10 (d, ^3J(P,C) = 2.2 Hz; Si(CH$_3$)$_3$), 21.5 (s; NCH*C*H$_3$), 22.0 (s; NCH*C*H$_3$), 26.9 (dd, ^1J(P,C) = 42.2, ^2J(P,C) = 10.0 Hz; PCH), 52.3 (d, ^3J(P,C) = 2.2 Hz; N*C*H(CH$_3$)$_2$), 193.3 (dd, J(P,C) = 79.1, 33.3 Hz; PPC), 197.2, (d, ^2J(P,C) = 8.2, ^1J(W,C) = 126.8 Hz; *cis*-CO), 200.4 (d, ^2J(P,C) = 30.3 Hz; *trans*-CO); ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 25 °C, ext. 85 % H_3PO_4): $\delta = -31.6$ (d, J(P,P) = 127.5 Hz), −150.6 (d, J(P,P) = 127.5, ^1J(W,P) = 264.4 Hz).

3: 1*H*-diphosphirene complex **1** (0.246 g, 0.4 mmol) was dissolved in toluene (6 mL), *N*-trimethylsilyl(isopropyl)aminophosphaethyne (0.14 g (0.80 mmol) was added, and the solution was stirred for 3 h at 75–80 °C. Completion of the reaction was determined by ^{31}P NMR control. The solution was then evaporated in vacuum (0.01 bar), the red oily residue was dissolved in *n*-pentane (3 mL), and complex **3** was crystallized at −20 °C. Complex **3** was obtained as a bright red solid after drying in vacuum. Yield: 110 mg (35 %), m.p. 108 °C (decomp). Selected NMR data: ^{13}C{^{1}H} NMR (75.4 MHz, C_7D_8, −50 °C, ext. TMS): $\delta = 6.8$ (d, J(P,C) = 2.3 Hz; CH(Si*C*H$_3$)$_3$), 7.1 (d, J(P,C) = 2.3 Hz; CH(Si*C*H$_3$)$_3$), 8.6 (s; N(SiCH$_3$)$_3$), 20.4 (dd, J(P,C) = 55.5, 7.1 Hz; (Me$_3$Si)$_2$CH), 25.6 (s; HNCH*C*H$_3$), 28.9 (s; SiNCH*C*H$_3$), 29.6 (d, J(P,C) = 3.8 Hz; SiNCH*C*H$_3$), 54.3 (d, J(P,C) = 15.3 Hz; HNCH), 61.1 (d, J(P,C) = 7.6 Hz; SiN*C*H), 186.6 (ddd, J(P,C) = 21.8, 5.9, 5.5 Hz; P^{1}C), 201.5 (dd, J(P,C) = 4.1, 3.2 Hz; *cis*-*C*O), 204.7 (dm, J(P,C) = 28.2 Hz; *trans*-*C*O), 216.3 (ddd, J(P,C) = 77.6, 28.0, 4.9 Hz; P^{2}C); ^{31}P{^{1}H} NMR (121.5 MHz, C_7D_8, −30 °C, ext. 85 % H_3PO_4): $\delta = 220.9$ (dd, J(P^1,P^2) = 422, J(P^1,P^3) = 126, J(W,P^1) = 230 Hz; P^1), 88.3 (dd, J(P^2,P^1) = 422, J(P^2,P^3) = 26, J(W,P^2) = 25 Hz; P^2), 40.4 (dd, J(P^3,P^1) = 126, J(P^3,P^2) = 26 Hz; P^3).

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[1] a) F. Mathey, *Coord. Chem. Rev.* **1994**, *137*, 1; b) P. LeFloch, F. Mathey, *Coord. Chem. Rev.* **1998**, *179–180*, 771.

[2] a) E. J. M. Boer (Shell), World Patent Application 95/04087, **1995**; b) B. Breit, *Chem. Commun.* **1996**, 2071; c) E. J. M. Boer, I. Gilmore, F. Korndorfer, A. D. Horton, *J. Mol. Catal. A* **1998**, *128*, 155; d) B. Breit, *J. Mol. Catal. A* **1999**, *134*, 143; e) B. Breit, R. Paciello, B. Geißler, M. Röper (BASF AG), DE 19621967 A1, **1999**; f) R. Paciello, E. Zeller, B. Breit, M. Röper (BASF AG), DE 19743167 A1, **1999**.

[3] L. Nyulászi, *J. Phys. Chem.* **1996**, *100*, 6194.

  1433-7851/01/4013-2473 $ 17.50+.50/0

[4] a) L. Nyulászi, *Inorg. Chem.* **1996**, *35*, 4690; b) M. N. Glokhotsev, A. Dransfeld, P. von R. Schleyer, *J. Phys. Chem.* **1996**, *100*, 13447.

[5] F. G. N. Cloke, P. B. Hitchcock, P. Hunnable, J. F. Nixon, L. Nyulászi, E. Niecke, V. Thelen, *Angew. Chem.* **1998**, *110*, 1139; *Angew. Chem. Int. Ed.* **1998**, *37*, 1083.

[6] F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, B. Wibbeling, *Angew. Chem.* **2000**, *112*, 2393; *Angew. Chem. Int. Ed.* **2000**, *39*, 2307.

[7] 2*H*-1,2-Azaphospholes: a) R. Streubel, H. Wilkens, A. Ostrowski, C. Neumann, F. Ruthe, P. G. Jones, *Angew. Chem.* **1997**, *109*, 1549; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1492; b) H. Wilkens, A. Ostrowski, J. Jeske, F. Ruthe, P. G. Jones, R. Streubel, *Organometallics* **1999**, *18*, 5627.

[8] 2*H*-1,3,2-Diazaphospholes: a) H. Wilkens, F. Ruthe, P. G. Jones, R. Streubel, *Chem. Eur. J.* **1998**, *4*, 1542; b) R. Streubel, U. Schiemann, N. Hoffmann, Y. Schiemann, P. G. Jones, D. Gudat, *Organometallics* **2000**, *19*, 475.

[9] 2*H*-1,4,2-Diazaphospholes: R. Streubel, H. Wilkens, P. G. Jones, *Chem. Eur. J.* **2000**, *6*, 3997.

[10] 2*H*-1,2,3-Azadiphospholes: G. N. Cloke, P. B. Hitchcock, U. Schiemann, R. Streubel, J. F. Nixon, D. J. Wilson, *Chem. Commun.* **2000**, 1659.

[11] R. Appel, M. Poppe, *Angew. Chem.* **1989**, *101*, 70; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 53.

[12] R. Streubel, L. Ernst, J. Jeske, P. G. Jones, *J. Chem. Soc. Chem. Commun.* **1995**, 2113.

[13] F. Mercier, L. Ricard, F. Mathey, M. Regitz, *J. Chem. Soc. Chem. Commun.* **1991**, 1305.

[14] M. Julino, M. Slany, U. Bergsträßer, F. Mercier, F. Mathey, M. Regitz, *Chem. Ber.* **1995**, *128*, 991.

[15] R. Matos, M. F. Meidine, J. F. Nixon, B. F. Trigo Passos, E. Niecke, D. Barion, *J. Organomet. Chem.* **1990**, *390*, C89.

[16] **1**: MS (EI, 70 eV, ^{182}W): *m*/*z* (%): 613 (18) $[M]^+$; **3**: MS (EI, 70 eV, 10000 resolution (10%-Tal-Def.)) *m*/*z* (%): 788.1188 ± 2 ppm (16) $[M]^+$ $C_{23}H_{43}N_2O_5P_3Si_3{}^{184}W$; negative-ion MS (CI, NH_3, ^{182}W): *m*/*z* (%): 785 (6) $[M-H]^-$, 713 (9) $[M-H-(H_3C)_2SiCH_2]^-$, 627 (78) $[M-H-(H_3C)_2SiCH_2\text{-}(H_3C)_2SiCHCH_3]^-$, 555 (69) $[\{(i\text{Pr(H)N})_2C_2P_3\}^{182}W(CO)_5]^-$.

[17] Crystal structure analysis of complex **1** ($C_{16}H_{27}NO_5P_2Si_2W$): triclinic, space group $P\bar{1}$, $a = 10.577(4)$, $b = 11.441(4)$, $c = 11.970(4)$ Å, $\alpha = 70.47(2)$, $\beta = 79.07(2)$, $\gamma = 62.66(2)^\circ$, $V = 1211.6$ Å^3, $Z = 2$, $\mu = 5.0$ mm^{-1}, $T = -130\,^\circ$C. A crystal (yellow plate, ca. $0.5 \times 0.4 \times 0.2$ mm) was mounted in perfluoropolyether at $-130\,^\circ$C on a Stoe STADI-4 diffractometer. Intensities were registered up to $2\theta_{max}$ 50° using $Mo_{K\alpha}$ radiation; 4277 reflections of a total of 5117 were independent ($R_{int} = 0.015$). After a semiempirical absorption correction (ψ scans, transmittance 0.61–0.96), the structure was solved by the heavy-atom method and refined with full-matrix least-squares methods on F^2 (program SHELXL-93, G. M. Sheldrick, Universität Göttingen). The hydrogen atom at the nitrogen center was refined free, all others with a riding model or as rigid methyl groups. The final *wR*2 based on F^2 for all data was 0.045, and the conventional $R(F)$ value was $R1 = 0.019$; 257 parameters, $S = 1.07$, max. residual electron density 0.85 e Å^{-3}. 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-160390. 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). Note: The crystal structure of **4** will be published elsewhere in the near future.

[18] R. Streubel, N. H. T. Huy, L. Ricard, F. Mathey, *Phosphorus Sulfur Relat. Elem.* **1993**, *77*, 229.

[19] R. Streubel, U. Schiemann, unpublished results.

[20] Several attempts were made to determine the crystal structure of **3**; the measurement (at $-130\,^\circ$C) gave a value of 322° for the sum of bond angles at the $\sigma^3\lambda^3$-phosphorus atoms in two independent molecules which matches approximately the value found for a 3,4-bisphosphonio-1,2-diphosphole: G. Jochem, H. Nöth, A. Schmidpeter, *Chem. Ber.* **1996**, *129*, 1083.

[21] The key to the assignment of the conformation was the appearance of cross peaks that connect the protons in the *N*-*i*Pr and *N*-$SiMe_3$ groups, respectively, with *only one* of the anisochronous $CSiMe_3$ groups. This suggested a static, quasi-orthogonal orientation of the $(Me_3Si)_2CH$ and *i*Pr(Me_3Si)N groups with respect to the plane of the five-membered ring. The onset of rotation with increasing temperature led to the appearance of the missing cross peaks. Analysis of the cross peaks originating from the N(H)*i*Pr signals revealed that the amino group has either a static and coplanar orientation relative to the ring, or undergoes fast rotation.

[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[23] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998** Note: The barrier which was determined here for **8** with the B3LYP/6-31+G(d)-method lies approximately 2.5 kcal mol^{-1} higher than the earlier results;[3, 4] it is known, however, that the MP2/6-31G(d)-method underestimates the P-inversion barrier by 8–12 kJ mol^{-1}.

Unexpected Splitting of ansa-Ytterboacene and ansa-Calcoacene: Formation of $[(\eta^2\text{-}C_{12}H_8)ZrCl_2(thf)_3]$ and $(Me_3Si)_2C_{12}H_8$**

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Recently we reported on the synthesis of the C_2-symmetric *trans-rac*-ansa-lanthanoacenes[1] $[(\eta^5\text{-}C_{12}H_8)_2M(thf)_2]$ (M = Yb, **1**; Sm, **2**) by reductive coupling of acenaphthylene (acene) with activated metallic ytterbium or samarium.[2] The acenyl radical anions formed in the course of these redox reactions dimerize to biacenyl dianions which stereoselectively coordinate the simultaneously formed M^{2+} cations. In contrast, the

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