[4] a) A. Alexakis, J. Vastra, J. Burton, P. Mangeney, *Tetrahedron: Asymmetry* **1997**, *8*, 3193; b) A. Alexakis, J. Vastra, J. Burton, C. Benhaim, P. Mangeney, *Tetrahedron Lett.* **1998**, *39*, 7869; c) A. Alexakis, C. Benhaim, X. Founioux, A. van den Heuvel, J.-M. Leveque, S. March, S. Rosset, *Synlett* **1999**, 1811; d) A. Alexakis, C. Benhaim, *Org. Lett.* **2000**, *2*, 2579; e) A. Alexakis, J. Burton, J. Vastra, C. Benhaim, X. Fournioux, A. van den Heuvel, J.-M. Leveque, F. Maze, S. Rosset, *Eur. J. Org. Chem.* **2000**, *24*, 4011; f) X. Hu, H. Chen, X. Zhang, *Angew. Chem.* **1999**, *111*, 3720; *Angew. Chem. Int. Ed.* **1999**, *38*, 3518; g) B. L. Feringa, M. Pineschi, L. A. Arnold, R. Imbos, A. H. M. De Vries, *Angew. Chem.* **1997**, *109*, 2733; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2620; h) R. Naasz, L. A. Arnold, M. Pineschi, E. Keller, B. L. Feringa, *J. Am. Chem. Soc.* **1999**, *121*, 1104; i) R. Imbos, M. H. G. Brilman, M. Pineschi, B. L. Feringa, *Org. Lett.* **1999**, *1*, 623; j) J. P. G. Versleijen, A. M. van Leusen, B. L. Feringa, *Tetrahedron Lett.* **1999**, *40*, 5803; k) L. A. Arnold, R. Imbos, A. Mandolini, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865; l) I. Chataigner, C. Gennari, U. Piarulli, S. Ceccarelli, *Angew. Chem.* **2000**, *112*, 953; *Angew. Chem. Int. Ed.* **2000**, *39*, 916; m) A. K. H. Knoebel, I. H. Escher, A. Pfaltz, *Synlett* **1997**, 1429; n) I. H. Escher, A. Pfaltz, *Tetrahedron* **2000**, *56*, 2879.

[5] a) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, *J. Am. Chem. Soc.* **1998**, *120*, 5579; b) Y. Takaya, M. Ogasawara, T. Hayashi, *Tetrahedron Lett.* **1998**, *39*, 8479; c) Y. Takaya, M. Ogasawara, T. Hayashi, *Tetrahedron Lett.* **1999**, *40*, 6957; d) T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **1999**, *121*, 11591; e) Y. Takaya, T. Senda, K. Hiroaki, M. Ogasawara, T. Hayashi, *Tetrahedron: Asymmetry* **1999**, *10*, 4047; f) Y. Takaya, M. Ogasawara, T. Hayashi, *Chirality* **2000**, *12*, 469; g) T. Hayashi, T. Senda, M. Ogasawara, *J. Am. Chem. Soc.* **2000**, *122*, 10716.

[6] J. M. Chong, L. Shen, N. J. Taylor, *J. Am. Chem. Soc.* **2000**, *122*, 1822.

[7] D. Seebach, *Angew. Chem.* **1979**, *91*, 259; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239.

[8] a) A. Boudier, C. Darcel, F. Flachsmann, L. Micouin, M. Oestreich, P. Knochel, *Chem. Eur. J.* **2000**, *6*, 2748; b) A. Boudier, E. Hupe, P. Knochel, *Angew. Chem.* **2000**, *112*, 2396; *Angew. Chem. Int. Ed.* **2000**, *39*, 2294; c) E. Hupe, P. Knochel, *Org. Lett.* **2001**, *3*, 127.

[9] H. C. Brown, A. K. Mandal, N. M. Yoon, B. Singaram, J. R. Schwier, P. K. Jadhav, *J. Org. Chem.* **1982**, *47*, 5069.

[10] The purpose of the treatment with Et_2BH is to replace the bulky isopinocampheyl ligand by an ethyl group or a hydrogen atom.

[11] The enantiomeric excess was determined by chiral GC analysis of the alcohol obtained from oxidation with aqueous H_2O_2 after the asymmetric hydroboration step.

[12] The absolute configuration of **14**–**17** was determined by deprotection and reduction of the corresponding *trans*-alcohol, obtained after asymmetric hydroboration and oxidative workup, to *trans*-2-(hydroxymethyl)cyclohexanol. The $[\alpha]_D^{20}$ values were compared with those reported in the literature. See: L. J. Dolby, F. A. Meneghini, T. Koizumi, *J. Org. Chem.* **1968**, *33*, 3060.

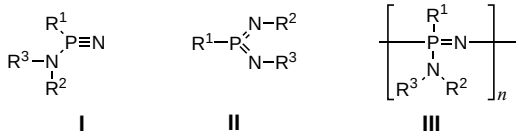
[13] The absolute configuration of **20a** and **20b** was determined according to method applied by: K. Ishihara, S. Kondo, H. Yamamoto, *J. Org. Chem.* **2000**, *65*, 9128.

Reversible Tautomeric Transformation between a Bis(amino)cyclodiphosph(v)azene and a Bis(imino)cyclodiphosph(v)azane**

Jürgen Tirreé, Dietrich Gudat, Martin Nieger, and Edgar Niecke*

Dedicated to Professor Rolf Appel on the occacion of his 80th birthday

Amino-substituted phosphinonitrenes (**I**) with suitable substitution patterns can be rearranged to tautomeric bis(imino)phosphoranes (**II**).[1] In the absence of the possibility



I **II** **III**

to rearrange, oligo- and polyphosphazenes (**III**) are formed.[2] Whereas in general the formation of tri- and tetramers appears to be thermodynamically favored,[2] a sterically overcrowded bisamino-substituted phosphinonitrene (**I**, $R^1 = NR^2R^3$, $R^2,R^3 = iPr_2N$) was noted to undergo instead an unusual cyclodimerization to give a cyclodiphosph(v)azene.[3] In connection with studies on NH-functionalized bis(imino)-phosphoranes and the anions derived therefrom[4] we also became interested in [2+2] cycloadditions of these species which yielded as yet unknown bis(imino)diphosph(v)azanes. Herein, we report on the synthesis of a cyclodiphosph(v)azane as well as on its reversible conversion into a tautomeric cyclodiphosph(v)azene.

Treatment of the azidophosphane **2**,[6] which is accessible from reaction of pentamethylcyclopentadienyl-(2,4,6-tri-*tert*-butylphenyl)iminophosphane, Cp*P=NMes* (**1**),[5] with hydrogen azide under dry pyrolysis (pure substance, 130 °C) conditions produced a mixture of the tautomeric four-membered-ring P–N heterocycles **5** and **7** in 1:9 ratio (Scheme 1). Colorless crystals of the bis(amino)cyclodiphosp(v)azene **7** were isolated by crystallization of the mixture from a little toluene.[7] Probable intermediates during the elimination of nitrogen from **2** are the phosphinonitrene **3** and the bis(imino)phosphorane **4**, which is formed from **3** by subsequent 1,3-H shift.[8] Metalation of **7** (MeLi, 0 °C) to the dilithiated complex **8**[9] and subsequent protonation with *t*BuOH gave a quantitative yield of the tautomeric bis(imino)cyclodiphosph(v)azane **5**, which was likewise isolated in crystalline form.[10]

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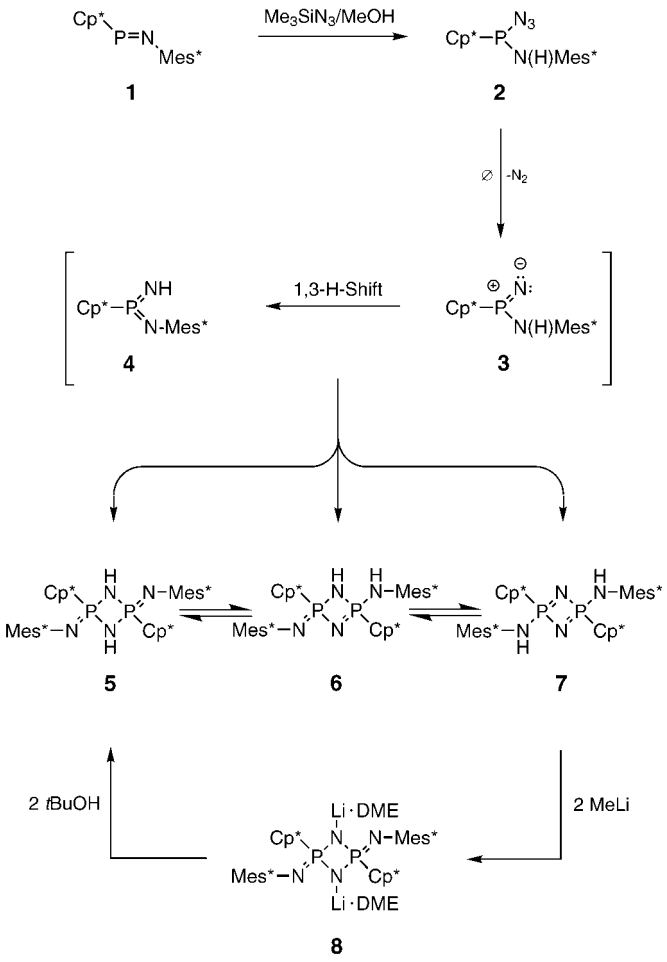

Scheme 1. Synthesis of the cyclodiphosph(v)azane **5** and cyclodiphosph(v)azene **7**. Cp* = C_5Me_5, Mes* = $tBu_3C_6H_2$, DME = 1,2-dimethoxyethane.

The molecular structures[11] of the cyclodiphosph(v)azane **5** and the tautomeric cyclodiphosph(v)azene **7** are shown in Figures 1 and 2, respectively. A common feature of both molecules is the planar P_2N_2 ring, which both display C_i symmetry and exhibit a rhombic distortion; the latter is more pronounced in **5** (bond angles: **5**: N-P-N 85.0(1), P-N-P 95.0(1)°; **7**: N-P-N 91.5(1), P-N-P 88.5(1)°). The arene moieties in the exocyclic amino (**7**) and imino groups (**5**) are found in *endo*, and the pentamethylcyclopentadienyl substituents in *exo* positions with respect to the central ring; regardless of the protonation, the P-N-C angles remain essentially unchanged (**7**: 130.99(12)°, **5**: 133.0(2)°). Thus, all four substituents adopt a "paddle-wheel" conformation which can be interpreted to arise as a consequence of the minimization of steric interactions. As expected, **5** displays substantial differences between endocyclic (P1–N1 167.2(3), P1–N1a 166.7(3) pm) and exocyclic P–N distances (P1–N2 156.5(2) pm), which lie in the expected range for compounds with the same molecular skeleton.[13] In contrast, the tautomeric cyclodiphosph(v)azene **7** exhibits an equalization of all P–N distances (P1–N1 165.87(15), P1–N1a 165.94(15), P1–N2 162.56(14) pm). A similar finding was noted for the cyclodiphosph(v)azene $[(iPr_2N)_2PN]_2$[3] and is in agreement with the results of quantum-chemical computations which suggest that the bonding situation in cyclodiphosph(v)azenes

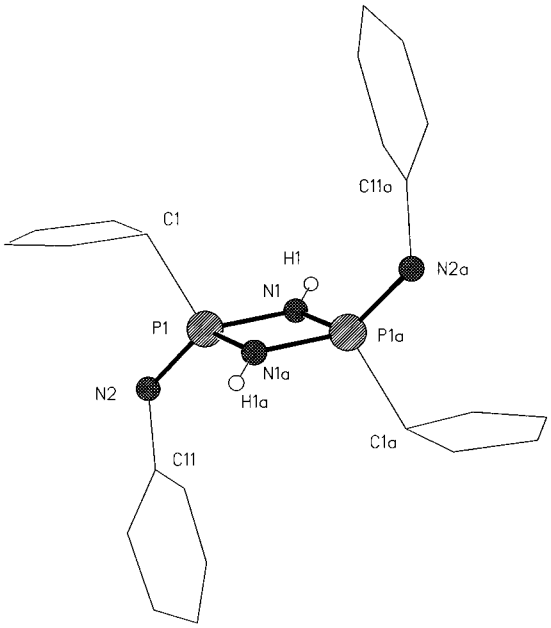

Figure 1. Molecular structure of **5** in the crystal (without hydrogen atoms (apart from H1 and H1a) and peripheral groups). Selected bond lengths [pm] and angles [°]: P1-N1 167.2(3), P1-N2 156.5(2), P1-N1a 166.7(3), P1-C1 185.4(3), N1-H1 85(2), N2-C11 142.6(3); N2-P1-N1 122.04(13), N2-P1-N1a 121.54(13), N1-P1-N1a 84.98(15), N2-P1-C1 105.66(13), N1-P1-C1 109.99(13), N1a-P1-C1 111.54(14), P1-N1-P1a 95.02(15), P1-N1-H1 133(2), C11-N2-P1 133.0(2), P1a-N1-H1 128(2).

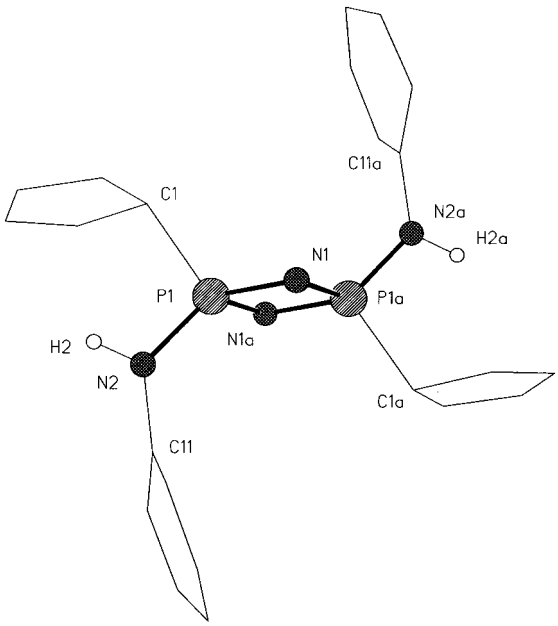

Figure 2. Molecular structure of **7** in the crystal (without hydrogen atoms (apart from H2 and H2a) and peripheral groups). Selected bond lengths [pm] and angles [°]: P1-N1 165.87(15), P1-N2 162.56(14), P1-N1a 165.94(15), P1-C1 186.27 (17), N2-H2 87(2), N2-C11 143.8(2); N2-P1-N1 119.09(8), N2-P1-N1a 119.34(8), N1-P1-N1a 91.52 (8), N2-P1-C1 102.20(7), N1-P1-C1 113.02(8), N1a-P1-C1 112.16(8), P1-N1-P1a 88.48(8), C11-N2-P1 130.99(12), P1-N2-H2 110(1), C11-N2-H2 119(1).

can be described in terms of a quadrupolar resonance structure.[14]

The reversible interconversion between **5** and **7** in solution was confirmed by temperature-dependent ^1H and ^{31}P NMR

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studies. The results of these experiments showed that both tautomers exist in dynamic equilibrium with a further species which was formulated on the basis of the available NMR data as the 1,2-dihydro-1,3,2λ^5,4λ^5-diazadiphosphete **6** (Scheme 1).[15] The adjustment of the position of the equilibrium is concentration independent and requires several hours at ambient temperature or a few minutes at 80–120 °C; all attempts to speed up the reaction by addition of acids (imidazole, tertiary ammonium salts) or bases (4-dimethylaminopyridine) were unsuccessful. Direct proof for the reversible interconversion of **6** and **7** was obtained from appropriate correlation signals in 2D-^{31}P{^{1}H}EXSY-NMR spectra recorded at 120 °C. The absence of cross peaks connecting the resonance signals of **7** or **6**, respectively, with those of the cyclodiphosph(v)azane **5** suggested this reaction step to occur more slowly; nonetheless, the interconversion was unequivocally proven by the reversible changes in signal intensities following a temperature change. Evaluation of the temperature dependence of the overall equilibrium constant $K = c(\mathbf{5})/c(\mathbf{7})$, which could be computed from the observed intensities of the signals of **5** and **7** at different temperatures, yielded values of $\Delta H^0 = -13.4(9)$ kJ mol^{-1} and $\Delta S^0 = 26.0(25)$ J mol^{-1} K^{-1} for the tautomeric equilibrium **5** $\rightleftharpoons$ **7**.

Taking into account all results obtained from the NMR investigations, one may conclude that the tautomerization of the cyclodiphosph(v)azene **7** can be mechanistically described in terms of an intramolecular reaction and proceeds through two subsequent 1,3-hydrogen shifts, for which the second step (transformation **6** $\rightarrow$ **5**) is rate-determining. The cyclodiphosph(v)azene **7** is both enthalpically and entropically favored with respect to the cyclodiphosph(v)azane **5**. In the light of these findings, the formation of the thermodynamically less favorable tautomer **5** during the protonation of the dilithiated salt **8** is considered to be the result of a kinetically controlled reaction.

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[1] a) R. H. Neilson, *Inorg. Chem.* **1981**, *20*, 1679; b) M. Larbig, M. Nieger, V. von der Gönna, A. V. Ruban, E. Niecke, *Angew. Chem.* **1995**, *107*, 505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 460.

[2] Review: R. H. Allcock, *Chem. Rev.* **1972**, *72*, 315.

[3] A. Baceireido, G. Bertrand, J. P. Majoral, *J. Am. Chem. Soc.* **1984**, *106*, 6088.

[4] M. Larbig, J. Tirreé, M. Nieger, E. Niecke, unpublished results.

[5] D. Gudat, H. M. Schiffner, M. Nieger, D. Stalke, A. J. Blake, H. Grondey, E. Niecke, *J. Am. Chem. Soc.* **1992**, *114*, 8857.

[6] **Caution**: Hydrogen azide must be handled exclusively in ethereal solution. For the generation of such solutions, azidotrimethylsilane (0.96 g, 8.4 mmol) was dissolved in anhydrous THF (4 mL), and ethanol (0.39 g, 8.4 mmol) was added with stirring. The solution is immediately ready for use. **2**: Compound **1** (3.1 g, 7.29 mmol) was dissolved in THF (10 mL), and a stochiometric amount of a solution of hydrogen azide (prepared as described above) was added. Completion of the reaction was indicated by a change of color to yellow. Volatile components were removed by evaporation under vacuum, and **2** was isolated after crystallization of the residue at −30 °C from *n*-hexane. Yield: 1.61 g (47.2 %). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 30 °C, H_3PO_4): $\delta = 126.2$ (s); ^{1}H NMR (300 MHz, C_6D_6, 30 °C, TMS): $\delta = 1.36$ (dd, ^3J(P,H) = 14.6, ^5J(H,H) = 0.9 Hz, 3H; $PCCH_3$), 1.42 (s, 9H; *p*-*t*Bu), 1.61 (s, 18H; *o*-*t*Bu), 1.87 (s, 3H; $PCCCH_3$), 2.04 (s, 3H; $PCCCCH_3$), 2.14 (s, 3H; $PCCCCH_3$), 4.91 (d, ^2J(P,H) = 10.5 Hz, 1H; NH), 7.54 (s, 2H, Aryl-H).

[7] **Caution**: Thermolysis of the azidophosphane **2** was carried out with special precautions in a fume cupboard using a plexiglass safety shield. **5**: Azidophosphane **2** (1.6 g, 3.4 mmol) was heated in vacuum to 130 °C (oil bath temperature), and this temperature was maintained for about 15 min. After the mixture had been cooled to ambient temperature, the residue was dissolved in a small amount of toluene. Compound **5** crystallized over a period of several days. Yield: 0.4 g (26.5 %). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 30 °C, H_3PO_4): $\delta = 49.1$ (s); ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 0.16$ (m, $|^3J$(P,H) + ^5J(P,H)$| =$ 20.6 Hz, 3H; $PCCH_3$), 1.21 (s, 9H; *p*-*t*Bu), 1.43 (br s, 18H; *o*-*t*Bu), 1.69 (br s, 6H; Cp*-CH_3), 1.88 (s, 6H; Cp*-CH_3), 3.72 (m, $|^2J$(P,H) + ^4J(P,H)$| = 13.9$ Hz, 2H; NH); 7.21 (s, 1H; Aryl-H); MS (16 eV): *m*/*z* (%): 880 (8) [M^+], 689 (5) [$M^+ - t$Bu − Cp*], 135 (100) [Cp*$^+$].

[8] J. Böske, E. Ocando-Mavarez, E. Niecke, J. P. Majoral, G. Bertrand, *Inorg. Chem.* **1986**, *25*, 2695.

[9] The existence of **7** was proven on the grounds of NMR spectroscopic evidence and a crystal structure analysis of a cyclodiphosph(v)azane with a similar substitution pattern: J. Tirreé, M. Nieger, A. V. Ruban, E. Niecke, unpublished results.

[10] To a cooled (0 °C) suspension of the cyclodiphosph(v)azene **7** (250 mg, 0.28 mmol) in DME (2 mL) was added a solution of methyllithium (0.57 mmol, 0.35 mL of a 1.6 M solution in hexane). The formed lithium salt was quenched after 12 h by addition of *tert*-butyl alcohol (0.05 g in 2 mL DME), and the product **5** was crystallized from DME. Yield: 235 mg (94 %). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 30 °C, H_3PO_4): $\delta = -15.3$ (s); ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C, TMS): $\delta = 0.38$ (m, $|^3J$(P,H) + ^5J(P,H)$| = 25.5$ Hz, 3H; $PCCH_3$), 1.18 (s, 9H; *p*-*t*Bu), 1.31 (br s, 18H; *o*-*t*Bu), 1.53 (br s, 6H; Cp*-CH_3), 1.79 (s, 6H; Cp*-CH_3), 3.98 (t, ^2J(P,H) = 7.6 Hz, 2H; NH), 7.00 (d, ^5J(P,H) = 2.6 Hz), 2H; Aryl-H); MS (16 eV): *m*/*z* (%): 880 (8) [M^+], 747 (2) [M^+ − Cp*], 486 (25) [M^+ − Mes* − Cp*], 135 (100) [Cp*$^+$]. The adjustment of the equilibrium proceeds over several days at 25 °C in DME.

[11] Crystal data of **5**: $C_{56}H_{90}N_4P_2$, colorless crystals, crystal dimensions $0.10 \times 0.05 \times 0.05$ mm; $M_r = 881.26$; triclinic, space group $P\bar{1}$ (no. 2), $a = 9.8354(11)$, $b = 12.2683(11)$, $c = 12.9324(14)$ Å, $\alpha = 64.466(6)$, $\beta = 83.540(5)$, $\gamma = 73.735(6)°$, $V = 1351.6(2)$ Å^3, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.12$ mm^{-1}, $T = 123(2)$ K, $F(000) = 484$. Of 10923 reflections which were collected on a Nonius Kappa-CCD diffractometer using $Mo_{K\alpha}$ radiation up to $2\theta_{max} = 50°$, 4734 were independent and used in all further calculations. The structure was solved by direct methods and refined anisotropically against F^2; hydrogen atoms were refined by using a riding model (programs SHELXS-97[12a] and SHELXL-97[12b]). The final $wR2(F^2)$ was 0.162 and the conventional $R(F) = 0.068$ for 288 parameters and 1 restraint. Crystal data of **7**: $C_{56}H_{90}N_4P_2$, colorless crystals, crystal dimensions $0.35 \times 0.35 \times 0.30$ mm; $M_r = 881.26$; triclinic, space group $P\bar{1}$ (no. 2), $a = 10.0227(2)$, $b = 12.3369(3)$, $c = 12.8896(3)$ Å, $\alpha = 63.980(2)$, $\beta = 83.314(2)$, $\gamma = 72.876(2)°$, $V = 1368.60(5)$ Å^3, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.12$ mm^{-1}, $T = 173(2)$ K, $F(000) = 484$. Of 21195 reflections which were collected on a Nonius Kappa-CCD diffractometer using $Mo_{K\alpha}$ radiation up to $2\theta_{max} = 56.5°$, 5034 were independent and used in all further calculations. The structure was solved by direct methods and refined anisotropically against F^2; hydrogen atoms were refined by using a riding model (programs SHELXS-97[12a] and SHELXL-97[12b]). The final $wR2(F^2)$ was 0.123 and the conventional $R(F) = 0.045$ for 326 parameters with 142 restraints. The *p*-*tert*-butyl group in one of the Mes* substituents is disordered. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160512 (**5**) and CCDC-160511 (**7**). 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).

[12] a) SHELXS-97: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467; b) G. M. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

[13] "Cyclic Phosphorus–Nitrogen Compounds—Three-, Four-, and Five-Membered Ring-Systems": L. Riesel in *Gmelins Handbuch der Anorganischen Chemie*, *P-Phosphorus*, *Suppl. Vol. C5a*, Springer, Heidelberg, **1996**.

[14] R. Ahlrichs, H. Schiffer, *J. Am. Chem. Soc.* **1985**, *107*, 6494.

  1433-7851/01/4016-3027 $ 17.50+.50/0

[15] Compound **6**: $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_8]$xylene, 50 °C, H_3PO_4): $\delta = 36.6$ (d, $^2J(P,P) = 25.4$ Hz), 0.6 (d, $^2J(P,P) = 25.4$ Hz). ^1H NMR (300 MHz, $[D_8]$xylene, 50 °C, TMS): $\delta = 0.71$(d, $^3J(P,H) = 21$ Hz, 3H; $PCCH_3$), 0.73(d, $^3J(P,H) = 23$ Hz, 3H; $PCCH_3$), 4.12 (d, $^2J(P,H) = 15.4$ Hz, 1H; NH), 4.50 (br, 2H; NH), 7.18 (d, $^4J(H,H) = 2.3$ Hz, 1H; Aryl-H), 7.29 (d, $^4J(H,H) = 2.0$ Hz, 1H; Aryl-H), 7.32 (d, $^4J(H,H) = 2.0$ Hz, 1H; Aryl-H), 7.44 (d, $^4J(H,H) = 2.3$ Hz, 1H; Aryl-H). Signal assignments were aided by 2D $^1H\{^{31}P\}$-HMQC spectra; the remaining resonance signals could not be unequivocally assigned.

[16] See: J. Böske, E. Niecke, B. Krebs, M. Läge, G. Henkel, *Chem. Ber.* **1992**, *125*, 2631.

Parallel Analysis of the Reaction Products from Combinatorial Catalyst Libraries**

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The combinatorial approach has great potential in many disciplines to optimize systems that have large parameter spaces. Recently, this concept has been introduced to the field of materials science.[1] The ultimate goal of the combinatorial approach is to efficiently optimize and discover new formulations, be they pharmaceutical products, catalysts, or other materials. Practically, this is accomplished by a systematic and efficient exploration of the parameter space that controls the properties of the final product. The two key components to a successful combinatorial approach are the controlled synthesis of a collection of materials with systematic variations in properties and the subsequent high-throughput analysis of libraries of these materials. Speed, through parallel synthesis and characterization, consequently becomes critical for the success of the combinatorial discovery process. Herein, we report the first analytical technique for truly parallel high-throughput screening of the reaction products from libraries of heterogeneous supported catalysts.

A number of experimental approaches have been reported for screening catalyst libraries. These are based on conventional serial techniques, which have been automated to decrease the screening time. Scanning mass spectrometry is based on rapidly analyzing the gases from one sample in a combinatorial library at a time, in a sequential manner. One approach uses a single probe composed of coaxial gas delivery and gas analysis tubes.[2] Libraries are analyzed by sequentially placing the tube over each element of the library, feeding reactant gases, and analyzing product gases. This approach is applicable to the initial screening of libraries deposited onto flat, solid substrates due to its gas delivery design. A second approach uses array microreactors with supported catalysts, coupled with capillary microprobe sampling.[3] Reactants, products, and carrier gas are withdrawn from each microreactor channel using a capillary sampling probe. By repeating this approach for each microreactor, the entire library can be screened. Another experimental method is based on photoionization of reaction products using tunable UV lasers.[4] The resulting photoions are detected by a microelectrode in close proximity to the sample. One disadvantage of this technique is that a suitable laser frequency for each species of interest must be known and accessible. In general, all of these techniques have the shortcoming that the screening time is proportional to the library size.

In contrast, truly parallel screening techniques gather information simultaneously from all the elements in a library. This category so far only includes heat-sensing techniques. Infrared thermography and thermistor arrays detect heat evolved from active library members and have been used to detect activity for exothermic reactions in combinatorial libraries.[5] These techniques, however, cannot chemically resolve product composition, which is often the most important issue when studying catalytic reactions, and therefore cannot determine the selectivity of a catalyst. Also, the assumption is made that the exothermicity is derived solely from the desired reaction, and not from any unforeseen side reactions, limiting these techniques to the study of well-known, simple reactions.

FT-IR imaging has the ability to gather chemically sensitive information from all library elements simultaneously. This approach has been demonstrated in recent work, where our group has pioneered infrared spectral imaging for the rapid analysis of reactions on solid bead materials.[6] IR spectroscopy is a well-established tool for the analysis of the composition of gas mixtures. The lower detection limit depends on several factors, such as the absorptivity of the absorption bands of the specific gas, the path length of the cell, the concentration of the species of interest, the spectral noise level, and the strength and structure of the bands of interfering gases. The true power of FTIR imaging for high-throughput analysis lies in its capability for parallel examination of product streams from multiple reactors. For this purpose, we have developed a novel gas-phase array attached to a multiple sample reactor, which currently allows us to perform parallel screening of the product stream of 16 supported catalyst samples.

To demonstrate the applicability of gas-phase IR imaging to parallel reaction product analysis, we present results, in which the parallel FTIR analysis was used to determine conversion during temperature-programmed complete oxidation of propene. This reaction is important for the automotive three-way catalyst and, in general, hydrocarbon oxidation is mainly catalyzed by platinum group metals.[7]

The samples examined in this study were commercial catalyst monoliths as well as custom-synthesized supported catalyst powders. Additionally, some channels of the reactor were filled with blank support material. After approximately 0.2 g of each catalyst sample was loaded into the 16-catalyst parallel reactor; all samples were pretreated simultaneously by alternate oxidation and reduction cycles. After the reactant gases were introduced, a temperature ramp of 10 K min^{-1} was

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