CO_2CH_3), 4.28 (AB, $J_1 = 13.7$ Hz, $J_2 = 3.0$ Hz, 2H, C*H*), 9.61 (s, 1H, COOH); ^{13}C NMR (25.2 MHz, $CDCl_3$): $\delta = 52.2$ (CO_2CH_3), 59.3, 59.5 ($CHOCH_3$) 81.2 (CH), 168.9 (CO_2CH_3), 172.4 (COOH); MS: *m/z* 192 ($M^{\oplus}$); $[\alpha]_D = +6.25°$ ($c = 7.2$, $CHCl_3$).

[8] K. Freudenberg, *Ber. Dtsch. Chem. Ges. 66* (1933) 177; J. H. Brewster, *J. Am. Chem. Soc. 81* (1959) 5475, 5483, 5493; K. Freudenberg, F. Brauns, H. Siegel, *Ber. Dtsch. Chem. Ges. 56* (1923) 193; K. Freudenberg, L. Markert, *ibid. 58* (1925) 1753; K. Freudenberg, *Monatsh. Chem. 85* (1954) 537; D. H. R. Barton, W. Klyne, *Chem. Ind. (London) 1948*, 755.

[9] H. J. Kleiner, H. Wissmann, *Angew. Chem. 92* (1980) 129; *Angew. Chem. Int. Ed. Engl. 19* (1980) 133.

[10] (+)-**6**: oil (purified chromatographically on silicagel 60, eluted with petroleum ether/ether 2:1); IR: $\tilde{\nu} = 1735$ cm^{-1} (CO); ^1H NMR (60 MHz, $CDCl_3$): $\delta = 0.85$ (t, 3H, CH_2CH_3), 1.00–1.90 (m, 14H, $(CH_2)_7$), 2.35 (t, 2H, $COCH_2$), 3.20 (s, OH), 3.40 (s, 6H, OCH_3), 3.60–4.60 (m, 6H, $CHCH_2$), 4.75 (s, 4H, OCH_2O); ^{13}C NMR (25.2 MHz, $CDCl_3$): $\delta = 13.9$, 22.5, 24.7, 29.1, 29.2, 31.7, 34.0 (7 signals, C_9H_{19}), 55.6 (CH_3O), 61.7 (CH_2OH), 63.1 (CH_2OCO), 74.5 ($CHCH_2OCO$), 79.0 ($CHCH_2OH$), 96.2, 96.6 (OCH_2O), 173.4 (CO); $[\alpha]_D = +19.2°$ ($c = 2.2$, methanol).

[11] H. S. Mosher, J. A. Dale, D. L. Dull, *J. Org. Chem. 34* (1969) 2543.

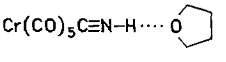
Molecular and Ionic Hydrogen Isocyanide (CNH) Adducts with N-H···O- and "Super-Short" N-H···N-Hydrogen Bridges: Metal-Stabilized Hydrogen Bisisocyanides[**]

By *Eberhard Bär, Joachim Fuchs, Dirk Rieger, Francisco Aguilar-Parrilla, Hans-Heinrich Limbach,* and *Wolf P. Fehlhammer*[*]

Short and super-short hydrogen bonds, particularly as occur in homonuclear molecule-ion associates $AHA^{\ominus}$ ($A^{\ominus}$ = anion base, e.g. $Hal^{\ominus}$) and $BHB^{\oplus}$ (B = neutral base, e.g. N-heterocycle), are currently a subject of intensive theoretical and experimental investigations.[1] Interest in H-bridged *cyanide* and *hydrogen cyanide* systems[2] may well originate from their capability of spontaneous aggregation and self-condensation to give biologically relevant secondary products $[HCN]_n$ (n, e.g., 2, 5(adenine),[3] and greater) rather than from mere bonding aspects. This property is in turn closely coupled with the question of chemical evolution.[4, 5]

Hydrogen isocyanide (HNC), which has only recently been discovered in interstellar clouds, is also connected with prebiotic organic synthesis.[6] We discovered the marked tendency of this acid to form hydrogen bonds during an attempted preparation of $[Cr(CO)_5CNH]$ in THF, when instead the sublimable (!) etherate **1** was obtained. On the strength of this finding we carried out directed syntheses of further adducts with cyclic ethers (e.g. **2**) and crown ethers (**3**, **4**), which selectively take up one or two hydrogen isocyanide complex molecules, respectively.[7] In the case of **2** we determined X-ray crystallographically an N(H)···O distance of 2.877(11) Å,[8] whose very small difference from the sum of the van-der-Waals radii of nitrogen and oxygen (2.93 Å) is indicative of only a weak H bond. Due to the low quality of the intensity data, however, this value should be regarded with some reservation.

We expected to find stronger hydrogen bonding in adducts of the (at least formally) symmetric type $AHA^{\ominus}$ **5** ($A^{\ominus} = [Cr(CN)(CO)_5]^{\ominus}$), which should be formed from pentacarbonyl(hydrogen isocyanide)chromium and its conjugate base. It has long been known that such structural units are present in the crystal lattice of "cyanometallic acids" and determine their coordination polymeric structure.[9] The N(H)···N distances in this type of bridge are very short; the shortest distance measured so far is that in the highly symmetric, three-dimensionally H-cross-linked $H_3[Co(CN)_6]$ (2.582(4) Å).[10] In this connection, the prediction of a surprisingly high stability for $[NCHCN]^{\ominus}$[2c] warrants attention, which might even be surpassed by the stability of the "iso form" $[CNHNC]^{\ominus}$.[11]



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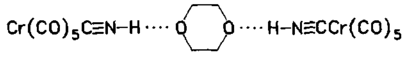

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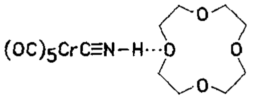

3

$[\{Cr(CO)_5C{\equiv}N{-}H\cdots\}_2([18]crown{-}6)]$

4

$[(OC)_5Cr\{C{\equiv}N{-}H{-}N{\equiv}C\}Cr(CO)_5]^{\ominus}$

5

Indeed, yellow (**5a**, $ER_4 = NEt_4$) or colorless (**5b**, $ER_4 = AsPh_4$) products having all the properties required of the *metal-stabilized hydrogen bisisocyanide ion* **5** crystallize from ether-layered CH_2Cl_2-solutions of equimolar amounts of $[Cr(CO)_5CNH]$ and $(ER_4)[Cr(CN)(CO)_5]$. In the first place, the ν(NH) absorption bands are broadened and shifted to long wavelengths such as to develop an absorption continuum which superimposes the IR region from about 1800 to 300 cm^{-1}. Also the downfield shifts of the ^1H-NMR signals of the hydrogen bridge protons ($\delta = 11.2$ (**5a**), 11.9 (**5b**)), which are larger than those of the NH···O adducts **1**–**4** by a good 2 ppm, point to strong hydrogen bonding. That the hydrogen bonds, moreover, are symmetrical, is indicated by the appearance of only one set of ^{13}C-NMR res-

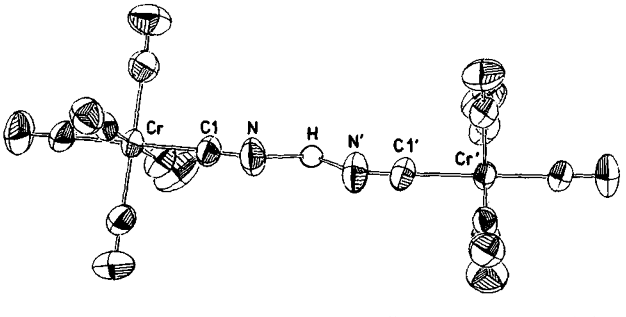

Fig. 1. Structure of **5** in crystals of **5b** (ORTEP, ellipsoids at the 50% probability level). Space group *P2/n*, $a = 11.295(2)$, $b = 6.817(1)$, $c = 24.476(6)$ Å, $\beta = 100.85(1)°$, $V = 1850.9$ Å^3, $Z = 2$; 2824 measured reflections, 2552 observed ($I > 2\sigma(I)$), 271 refined parameters, $R = 0.056$ ($R_w = 0.054$). Selected bond lengths [Å] and angles [°]: Cr–C(O)$_{trans}$ 1.847(6), Cr–C(O)$_{cis}$ (average value) 1.894, Cr–C1 2.012(6), C1–N 1.167(8), N···N' 2.569(7); Cr–C1–N 178.8(5). The H position taken from the difference Fourier synthesis and refined (*y* coordinate) is associated with a high temperature factor and is therefore not reliable (cf. text).

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onance signals ($\delta = 157.4$ s (CN), 216.5 CO_{cis}), 219.1 (CO_{trans}) and by the band-deficient IR and Raman spectra.

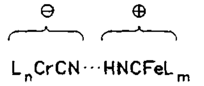
The X-ray structure analysis of **5b** (Fig. 1)[12] confirms the strong bridge bond: the N(H)···N distance of 2.569(7) Å is even less than that in $H_3[Co(CN)_6]$. Since the bridge H-atom could not be localized with certainty, however, the question of its symmetrical arrangement had to remain open for the time being. In any case, no decision can be made as to whether the bridge H atom moves in a single or a double minimum potential, because of the crystallographic symmetry element (C_2) coinciding with the bridge midpoint.[13, 10b]

The method of choice for obtaining detailed information about proton motions in NH···N hydrogen bridges is currently high-resolution solid-state ^{15}N-CPMAS-NMR spectroscopy (^{1}H cross polarization (CP), sample rotation about the magic angle (MAS)) with ^{1}H decoupling.[14] The spectra[15] of the reference compounds $[Cr(CO)_5C^{15}NH]$ and $NnPr_4$ $[Cr(C^{15}N)(CO)_5]$ measured at 25 °C each show one singlet, at $\delta \approx 135$ and 273, respectively. In contrast, the two nitrogen atoms of ^{15}N-labeled **5b** (= **5b'**) give rise to only *one* line at $\delta = 193$ ($\nu_{1/2} = 38.5$ Hz), i.e. they are (as to be expected from the X-ray structure analysis of **5b**) chemically equivalent. The value of $\delta = 193$ is reconcilable both with a symmetrical double minimum potential with small energy barrier as well as with a single minimum potential for the proton motion. Surprisingly, however, two signals are observed at $\delta = 209$ ($\nu_{1/2} = 50.2$ Hz) and 178 ($\nu_{1/2} = 53.5$ Hz) in the case of **5a'** (= ^{15}N-labeled **5a**). This means that the established chemical equivalence of the two nitrogen atoms in **5b'** does not apply here due to interactions between the ions; the average distances between the bridge H-atom and the two nitrogen atoms are no longer identical. Measurements at several temperatures showed that the signal splitting observed in the case of **5a'**, in contrast to that of other NH···N hydrogen bridges perturbed by intermolecular interactions, is temperature independent. We regard this as a first indication that the proton motion in **5a** is a result of an unsymmetrical single minimum potential.

The handicap of an enforced crystal symmetry (see **5b**) does not apply in the heterodinuclear *neutral* adduct **6** (diphos = bis(diphenylphosphino)ethane, for which one naturally does not expect an ideally symmetrical H-bridge either. Nevertheless, it is surprising at first sight, how asymmetrically the unequivocally established bridge H-atom here is located between the very close cyano N atoms (Fig. 2).[12] In view of the charge separation, which should effect a shift of the bridge H-atom in the direction of the iron atom (see **7**), the structural variety of the hydrogen bisisocyanide **6** contrary to **5** does not, however, seem unlikely. Both the asymmetry and the strength of this NH···N bond are also reflected in the IR and NMR spectra of **6**, which show markedly separated ν(CN) bands [(Nujol): $\tilde{\nu} = 2122$ s, 2070 w cm^{-1}] and CN signals [$\delta(^{13}C) = 156.9$ (s, CrCN), 161.7 (t, $J = 30.5$ Hz, FeCN)] besides the characteristic NHN absorption continuum ($\tilde{\nu} = 1300-300$ cm^{-1}) and downfield shift ($\delta(^1H) = 11.4$).

$$\left[(OC)_5Cr\left\{C{\equiv}N{-}H\cdots N{\equiv}C\right\}FeCp(diphos)\right]$$

6



$$\overset{\ominus}{\overbrace{L_nCrCN}}\cdots\overset{\oplus}{\overbrace{HNCFeL_m}}$$

7

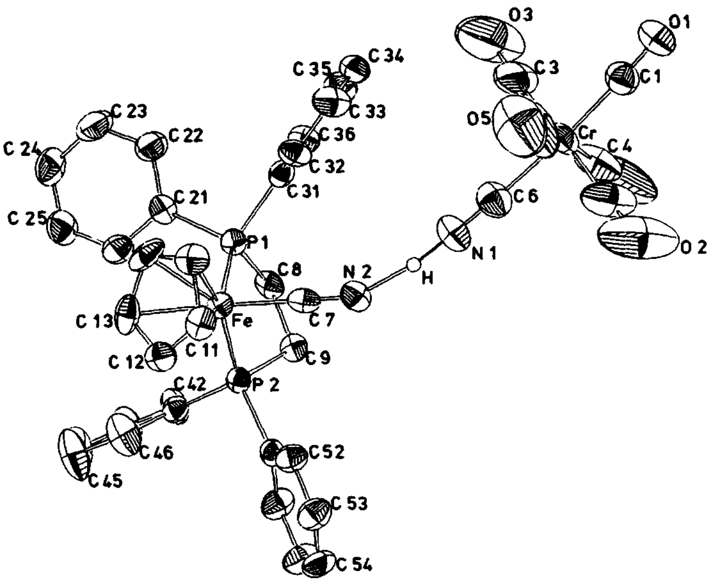


Fig. 2. Molecular structure of **6** (ORTEP), ellipsoids at the 50% probability level). Space group $P\bar{1}$, $a = 8.919(2)$, $b = 15.617(4)$, $c = 15.809(5)$ Å, $\alpha = 111.68(2)$, $\beta = 101.88(2)$, $\gamma = 96.49(2)°$, $V = 1958.65$ Å^3, $Z = 2$; 4950 measured reflections, 4188 observed ($I > 2\sigma(I)$), 593 refined parameters, $R = 0.062$ ($R_w = 0.064$). Selected bond lengths [Å] and angles [°]: Cr–C1 1.846(11), Cr–$C(O)_{cis}$ (mean value) 1.854, Cr–C6 2.025(12), C6-N1 1.155(15), N1-H 1.17(14), H-N2 1.40(14), N1···N2 2.557(12), N2-C7 1.164(11), C7-Fe 1.855(9); Fe-C7-N2 177.9(6), C7-N2-H 157(4), N2-H-N1 171(9), H-N1-C6 178(5), N1-C6-Cr 178.5(8).

Experimental Procedure

3: Freshly sublimed $[Cr(CO)_5CNH]$ [17] (0.22 g, 1.00 mmol) was dissolved in ca. 5 mL of [12]crown-4, the excess ether removed in a vacuum, and the residue reprecipitated from CH_2Cl_2/*n*-hexane at − 20 °C. There remained 265 mg (67%) of colorless crystals which melt without decomposition at 50 °C. IR-(polyoil): $\tilde{\nu}$ [cm^{-1}] = 3200−2400 s, br. (NH···O) 2123, 2077 m, 2053 m−s, 1946 vs, br. (ν(CN) + ν(CO)); Raman (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2094 m,sh,p, 2088 s,p, 2036 s,p, 1993 s,dp, 1943 m,br.,dp (ν(CN) + ν(CO)); 270-MHz ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 9.2$ (s, br., NH···O), 3.6 (s, 16 H, CH_2). sh = shoulder, p = polarized, dp = depolarized.

5b: A solution of $AsPh_4[Cr(CN)(CO)_5]$ (0.60 g, 1.00 mmol) in CH_2Cl_2 (20 mL) was filtered through a cellulose filter and added dropwise to a solution of freshly sublimed $[Cr(CO)_5CNH]$ (0.22 g, 1.00 mL) in CH_2Cl_2 (20 mL). The reaction solution was then carefully layered with ca. 30 mL of diethyl ether and cooled to −78 °C. A pale yellow solid was formed (0.45 g, 55% yield; m.p. 103 °C (decomp.)), which was collected on a glass frit and dried in a stream of argon.

6: A solution of $[Cr(CO)_5CNH]$ (220 mg, 1.00 mmol) and [Fe(CN)(Cp)diphos] [18] (545 mg, 1.00 mmol) in CH_2Cl_2 (20 mL) was layered with petroleum ether (40−60 °C). On cooling to − 20 °C orange-red crystals were formed in about 80% yield. M.p. 150 °C (decomp.).

All the new compounds gave correct elemental analyses.

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CAS Registry numbers:
2, 131130-23-9; **3**, 131105-42-5; **5a**, 131105-43-6; **5b**, 131105-45-8; **6**, 131105-44-7; $[Cr(CO)_5CNH]$, 15040-33-2; $NEt_4[Cr(CN)(CO)_5]$, 82675-16-9; $AsPh_4[Cr(CN)(CO)_5]$, 131105-46-9; [Fe(CN)(Cp)diphos], 70460-15-0; [12]crown-4, 294-93-9.

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[1] Cf., e.g. a) J. Emsley, D. J. Jones, J. Lucas, *Rev. Inorg. Chem. 3* (1981) 105; b) B. S. Ault, *Acc. Chem. Res. 15* (1982) 103; c) D. Mootz, K. Bartmann, *Angew. Chem. 100* (1988) 424; *Angew. Chem. Int. Ed. Engl. 27* (1988) 391; d) H. J. Berthold, W. Preibsch, E. Vonholdt, *ibid. 100* (1988) 1581 and *27* (1988) 1527.

[2] a) M. Meot-Ner, *J. Am. Chem. Soc. 100* (1978) 4694; b) G. L. Johnson, L. Andrews, *ibid. 105* (1983) 163; c) J. W. Larson, T. B. McMahon, *Inorg. Chem. 23* (1984) 2029.

[3] F. Seel, M. von Blon, A. Dessauer, *Z. Naturforsch. B37* (1982) 820.

[4] K. Dose, H. Rauchfuss: *Chemische Evolution und der Ursprung lebender Systeme*, Wissenschaftliche Verlagsgesellschaft, Stuttgart 1975, p. 105f.

[5] J. P. Ferris, W. J. Hagan, Jr., *Tetrahedron 40* (1984) 1093.

[6] a) G. Winnewisser, *Top. Curr. Chem. 99* (1981) 39; b) D. W. McPherson, M. L. McKee, P. B. Shevlin, *J. Am. Chem. Soc. 105* (1983) 6493.

[7] Diverse $[Cr(CO)_5CNH]$ adducts with acyclic diethers are reported in a patent: R. E. Maginn, US Pat. 3136798 (1964), Ethyl Corporation, New York, NY.

[8] Crystallographic data of **2**: STOE four-circle diffractometer, Cu_{K_α} radiation, nickel filter; monoclinic; space group $P2_1/n$; $a = 17.376(3)$, $b = 10.742(3)$, $c = 5.898(1)$ Å; $\beta = 94.54(2)°$; $\varrho_{calc} = 1.59$, $\varrho_{exp} = 1.58\ g\,cm^{-3}$; $Z = 2$. 1293 independent reflections, 1134 observed ($F > 2\sigma(F)$). For the refinement however, only reflections with odd l and the (specially scaled) equatorial reflections were used, since the crystal was twinned, and, for $l = 2n$, the h,k,l reflections of one twin coincided with the $h + l/2, -k, -l$ reflections of the other. $R = 0.075$.

[9] a) D. F. Evans, D. Jones, G. Wilkinson, *J. Chem. Soc. 1964*, 3164; W. Beck, H. Smedal, *Z. Naturforsch. B20* (1965) 109; c) H. U. Güdel, *J. Chem. Phys. 56* (1972) 4984.

[10] a) R. Haser, B. Bonnet, J. Roziere, *J. Mol. Struct. 40* (1977) 177; b) similarly short and even slightly shorter N(H)···N distances are found in the proton sponges. However, in this case they are *intra*molecular H-bridges: H. A. Staab, T. Saupe, *Angew. Chem. 100* (1988) 895; *Angew. Chem. Int. Ed. Engl. 27* (1988) 865; cf. also R. W. Alder, *Chem. Rev. 89* (1989) 1215.

[11] CNH is an essentially stronger proton donor than HCN: P. Kollman, J. McKelvey, A. Johansson, S. Rothenberg, *J. Am. Chem. Soc. 97* (1975) 955.

[12] **5b(6)**: STOE four-circle diffractometer, Cu_{K_α} (Mo_{K_α}) radiation, $5° \leq 2\theta \leq 120°$ ($4° \leq 2\theta \leq 50°$); ω scan; structure solutions by direct methods. Programs used: X-ray 76, Multan-77, ORTEP. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54867, the names of the authors, and the journal citation.

[13] Cf. A. Novak, *Struct. Bonding (Berlin) 18* (1974) 177.

[14] Cf. J. A. S. Smith, B. Wehrle, F. Aguilar-Parrilla, H.-H. Limbach, M. C. Foces-Foces, F. H. Cano, J. Elguero, A. Baldy, M. Pierrot, M. M. T. Khurshid, J. B. Larcombe-McDuall, *J. Am. Chem. Soc. 111* (1989) 7304, and references cited therein.

[15] The ^{15}N-CPMAS-NMR spectra were recorded with a Bruker CXP100 spectrometer (proton resonance frequency 90.02 MHz) and a CPMAS probe head manufactured by Doty-Scientific, Columbia, USA. Rotation frequency of the 7-mm rotor between 2.5 and 3.5 kHz. Spectra free of rotation sidebands were thus obtained. The chemical shifts of the ^{15}N nuclei are referred to external $^{15}NH_4Cl$.

[16] For example: H.-H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick, C. S. Yannoni, *J. Am. Chem. Soc. 109* (1987) 929; B. Wehrle, H. Zimmermann, H.-H. Limbach, *Ber. Bunsenges. Phys. Chem. 91* (1987) 941; B. Wehrle, H. Zimmermann, H.-H. Limbach, *J. Am. Chem. Soc. 110* (1988) 7014.

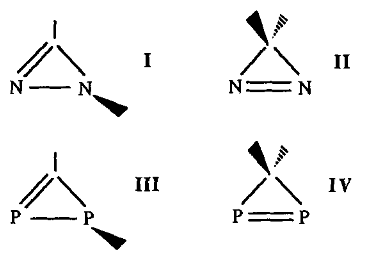
[17] W. P. Fehlhammer, W. A. Herrmann, K. Öfele in G. Brauer (Ed.): *Handbuch der Präparativen Anorganischen Chemie, Vol. III*, 3rd Edit., Ferdinand Enke Verlag, Stuttgart 1981.

[18] G. J. Baird, S. G. Davies, *J. Organomet. Chem. 262* (1984) 215.

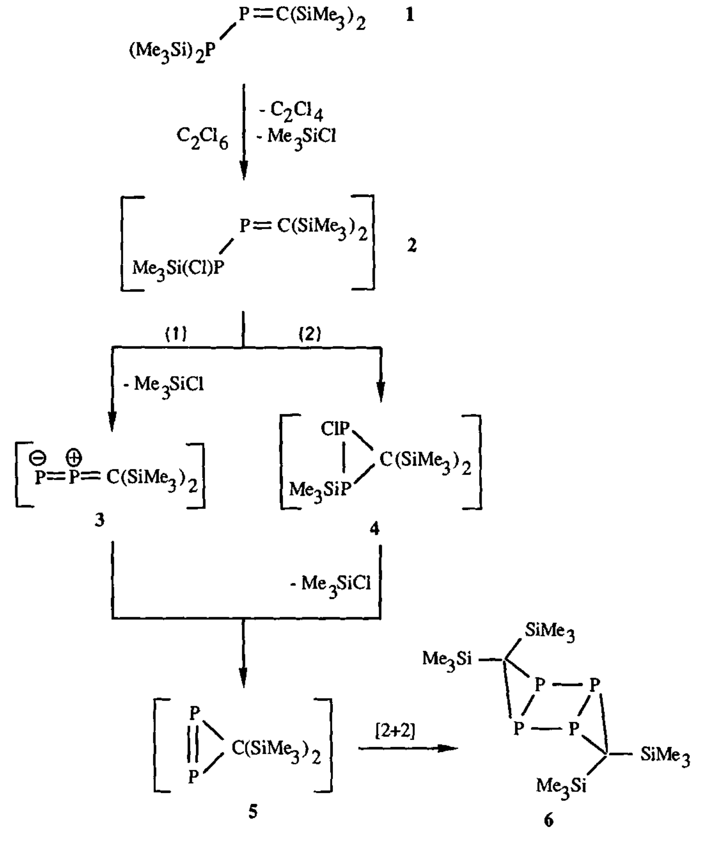
Formation of a *trans*-1,2,4,5-Tetraphosphatricyclo$[3.1.0.0^{2,4}]$hexane by [2+2] Cyclodimerization of a 3*H*-Diphosphirene**

By *Edgar Niecke,* Rainer Streubel,* and *Martin Nieger*

Diazirines exist only in the 3*H* form **II** [1,2] and are widely used as precursors of electrophilic carbenes.[2] On the other hand, only the 1*H* isomer **III**, which corresponds to **I** and was recently obtained by phosphanediyl transfer starting from a halogen(silyl)phosphane and a phosphaalkyne,[3] is known for the homologous phosphorus compounds. Our investigations in this area were motivated by the possibility of preparing a 3*H*-diphosphirene **IV**, isomeric to **III**, in a corresponding way from an α-bifunctional 1,2-diphospha-2-propene(halogen(silyl)phosphinomethylenephosphane).



Reaction of the persilylated 1,2-diphospha-2-propene **1**[4] with hexachloroethane under mild conditions[5] results in elimination of chlorotrimethylsilane and formation of a product having the analytical composition of diphosphirene **5** but twice its molecular mass. The spectroscopic data all indicate the formation of the tricyclic system **6**, a cyclodimer of **5**.



Two pathways are conceivable for the formation of the diphosphirene intermediate **5**: (1) an α elimination of chlorotrimethylsilane from the 1,2-diphospha-2-propene intermediate **2** to give **3**, the diphospha analogue of a diazaalkane, followed by cycloisomerization of **3** to afford **5**—an isomerization similar to the vinylcarbene/cyclopropene rearrangement;[6] (2) a 1,2-chloro shift accompanied by cyclization to give the β-functional diphosphirane **4**, which subsequently loses chlorotrimethylsilane to yield **5**. The recently observed diphospha-2-propene/diphosphirane isomerization[7] makes the second pathway equally plausible. The reaction step leading from **5** to **6** is typical of diphosphenes with *Z* configurations;[8] for cyclopropene, this process is thermodynamically favored and can be initiated by catalysts.[9]

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