F_2 cocondensation reaction apparently proceeds through a pentavalent activated complex, which rearranges and relaxes to diaxial PH_3F_2 or decomposes to give the PHF_2 and PH_2F products on the condensing sample surface. Apparently HF elimination is the more favorable decomposition pathway as PH_2F absorptions are stronger than PHF_2 bands. In contrast, the NH_3 and F_2 cocondensation reaction produced only a coaxial NH_3--F_2 complex, which required photolysis to give the NH_2F--HF product.[4] The greater reactivity of the second-row hydride and expanded valence capability are manifested in these fluorine matrix reactions.

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Reactivity of Phosphonitriles with Low-Coordinated Phosphorus Double-Bonded Compounds

Jürgen Böske,[†] Edgar Niecke,*[,†] Martin Nieger,[†] Edgar Ocando,[‡] Jean-Pierre Majoral,*[,‡] and Guy Bertrand*[,§]

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Several trapping reactions of photochemically generated phosphonitriles (>P≡N) by iminophosphanes (–P=N–) are reported. Depending on the nature of the substituents of both reaction partners, quite different products are obtained. Irradiation of bis(diisopropylamino)azidophosphine (**1a**) in the presence of (2,2,6,6-tetramethylpiperidino)((trimethylsilyl)imino)phosphane (**2a**) led to the iminophosphorane–iminophosphane **3**. In contrast, photolysis of **1a**, in the presence of [bis(trimethylsilyl)amino]-[(trimethylsilyl)imino]phosphane (**2c**) afforded the 1,3,2λ^3,4λ^5-diazadiphosphetidine **6**, which can be converted to the corresponding imino- and thiodiazadiphosphetidines **7** and **8** by using tosyl azide and sulfur, respectively. Similarly, irradiation of **1a** with the (trimethylsilyl)[bis(trimethylsilyl)amino]phosphaalkene **2d** led to the 2,4-bis(diisopropylamino)-4-[(trimethylsilyl)imino]-1,2λ^3,4λ^5-azadiphosphetidine **9**. Compound **9** reacted with sulfur, affording the corresponding thioazadiphosphetidine **10**. Addition of carbon tetrachloride to the 1,3,2λ^3,4λ^3-diazadiphosphetidine **15** gave [((diisopropylamino)chloro((trimethylsilyl)imino)-phosphoranyl)imino](diisopropylamino)phosphane (**16**), characterized at low temperature. **16** dimerized at room temperature to the diazadiphosphetidine **17**, while addition of carbon tetrachloride, at –40 °C, led to the corresponding adduct **18**. Addition of carbon tetrachloride to the 2,4-bis(diisopropylamino)-1,3,2λ^3,4λ^3-diazadiphosphetidine **19** afforded the iminophosphorane–iminophosphane **20**, which rearranged into 2-[bis(trimethylsilyl)amino]-1,3-bis(trimethylsilyl)-4-chloro-4-[(trimethylsilyl)imino]-1,3,2λ^3,4λ^5-diazadiphosphetidine (**21**). The crystal and molecular structure of $C_{24}H_{55}N_5P_2Si$ (**3**) has been determined by X-ray crystallography. The crystals of **3** are triclinic and belong to the space group *P*1 with a = 10.361 (3) Å, b = 12.308 (7) Å, c = 12.759 (6) Å, α = 89.65 (4)°, β = 82.89 (3)°, γ = 80.03 (4)°, and Z = 2. The constitution of **3** disproves the mechanism of a (2 + 2) cycloaddition in this case. A new type of rearrangement could be observed in this example: the valence isomerization of two phosphorus atoms in β positions via the 1,3-shift of an amino group.

Introduction

It has already been shown that phosphonitriles are formed in the photolysis of phosphine azides (I).[1] In the absence of trapping agents, depending on the nature of the phosphorus substituents, these phosphorus nitrogen species dimerize, trimerize, or polymerize, giving cyclodi-, cyclotri-, or cyclopolyphosphazenes,[2] or even undergo 1 → 3 migration leading to tricoordinated, pentavalent phosphorus derivatives.[3] Up to now, the study of the reactivity of phosphonitriles was rather limited: [1, 2] additions with methanol, dimethylamine, or alkylchlorosilanes; [2 + 2] cycloadditions with phenyl isocyanate or dimethyl sulfoxide; [2 + 3] cycloadditions with trimethylsilyl azide.[1,2] The reactivity of phosphonitriles (>P≡N, II) with dicoordinated phosphorus compounds (–P=X, III) was of interest since both of the reagents are potentially extremely versatile. All the reactions of phosphonitriles, previously described, involved phosphorus–nitrogen multiple-bonded character (>P^+=N^-). However, since these species can also be formulated as phosphinonitrenes (>P—N), nitrene-type reactivity could be expected. On the other hand, iminophosphanes (–P=N–) and phosphaalkenes (–^{1}>=C<) are known to react either via the phosphorus lone pair or through the (p–p)π double bond.[4] Thus, four possible reactions could be expected: (i) a [2 + 2] cycloaddition of the π systems of both species giving mono unsaturated four-membered rings; (ii) a [2 + 1] cycloaddition involving the phosphorus–nitrogen multiple bond of II and the phosphorus lone pair of III leading to 3,1λ^5,2λ^5-azadiphosphirines; (iii) a [1 + 2] cycloaddition of the nitrene on the (p–p)* double bond of III, affording saturated three-membered rings; (iv) a [1 + 1] addition of the nitrene on the phosphorus lone pair of III giving a tricoordinated, pentavalent phosphorus derivative.

Indeed, examples of each of reactions i–iv are observed in this work.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker WM250 or a Bruker WP80 spectrometer. ^{1}H chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer at 32.43 MHz and a Varian FT80A spectrometer at 32.203 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. ^{13}C NMR spectra were recorded on a Bruker AC80 spectrometer at 20.15 MHz or a Varian FT80A spectrometer at 20.00 MHz. ^{29}Si NMR spectra were obtained on a Bruker AM300

[†] Universitat Bonn.
[‡] UA 454, Université Paul Sabatier.
[§] UA 477, Université Paul Sabatier.

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spectrometer. ^{29}Si chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{15}N NMR spectra were recorded on a Bruker AM300 spectrometer (nitromethane as external standard). Infrared spectra were recorded on a Beckman IR10 spectrometer and a Perkin-Elmer lattice spectrometer (Mol 598), using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument or a Varian MAT 311A instrument.

Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor or with a TQ150 high-pressure mercury vapor lamp.

Synthesis of [((Diisopropylamino)(2,2,6,6-tetramethylpiperidino)-((trimethylsilyl)imino)phosphoranyl)imino](diisopropylamino)phosphane (3). A solution of bis(diisopropylamino)azidophosphine (**1a**)[5] (3.96 g, 14.5 mmol) in 50 mL of *n*-hexane was irradiated at 12 °C in the presence of (2,2,6,6-tetramethylpiperidino)[(trimethylsilyl)imino]phosphane (**2a**)[6] (3.75 g, 14.5 mmol), at 254 nm, for 20 h. After removal of the solvent the resulting viscous orange liquid was dissolved in methylene chloride and crystallized at −30 °C as pale yellow crystals of **3**: mp 105–110 °C; yield 3.5 g (48%). ^{31}P NMR (C_6D_6): 314.4 (d), −1.5 (d), $^2J_{PP}$ = 100.6 Hz). ^1H NMR ($CDCl_3$): 0.0 (s, 9 H, $Si(CH_3)$); 1.20 (m, 12 H, CH_3); 1.40 (m, 24 H, CH_3); 1.54 (s, 6 H, CH_3); 3.74 (m, 4 H, $NCH<$). ^{13}C NMR (C_6D_6): 4.55 (dd, $^3J_{CP^V}$ = 3.9 Hz, $^5J_{CP^{III}}$ = 2.5 Hz, SiC); 16.98 (s, $CH_2CH_2CH_2$); 21.57 (s, $CHCH_3$); 22.18 (d, $^3J_{CP}$ = 6.0 Hz, $CHCH_3$); 22.33 (d, $^3J_{CP}$ = 5.8 Hz, $CHCH_3$); 22.9 (d, $^3J_{CP}$ = 2.9 Hz, $CHCH_3$); 27.49 (d, $^3J_{CP}$ = 3.4 Hz, $CH_2CH_2CH_2$); 28.17 (d, $^3J_{CP}$ = 2.8 Hz, $CH_2CH_2CH_2$); 31.94 (s, $>CCH_3$); 32.97 (br s, $>CCH_3$); 42.09 (d, $^3J_{CP}$ = 7.0 Hz, $NCH<$); 46.47 (d, $^2J_{CP}$ = 6.3 Hz, $NCH<$, 3 C); 56.15 (d, $^2J_{CP}$ = 3.5 Hz, $NC<$). Mass spectrum: *m/e* 503 (M^+). Anal. Calcd for $C_{24}H_{55}N_5P_2Si$: C, 57.22; H, 11.00; N, 13.90. Found: C, 56.93; H, 10.79; N, 14.02.

Synthesis of [((Diisopropylamino)(*tert*-butyl)(*tert*-butylimino)-phosphoranyl)imino](diisopropylamino)phosphane (5). A solution of the phosphine azide **1a** (0.61 g, 2.2 mmol) and 3-(*tert*-butylimino)-1,2,3-tri-*tert*-butyl-1,2λ^3,3λ^5-azadiphosphirane (**4**)[7] (0.36 g, 1.1 mmol) in 4 mL of hexane was irradiated for 6 h, at 0 °C. Compound **5** was obtained among polymers in 70–80% yield (spectroscopically). Due to the high thermolability of **5**, no fractional distillation was possible and attempted crystallization of **5** failed. ^{31}P NMR (hexane): 298.5 (d), 1.1 (d, $^2J_{PP}$ = 59.4 Hz).

Synthesis of 2,4-Bis(diisopropylamino)-4-[(trimethylsilyl)imino]-1,3-bis(trimethylsilyl)-1,3,2λ^3,4λ^5-diazadiphosphetidine (6). Bis(diisopropylamino)azidophosphine (**1a**) (2.32 g, 8.49 mmol) and [bis(trimethylsilyl)amino][(trimethylsilyl)imino]phosphane (**2c**)[8] (2.37 g, 8.53 mmol), in 15 mL of benzene, were irradiated at 300 nm for 12 h at room temperature. After evaporation of the solvent, **6** remained as a brown oil that crystallized when washed with acetonitrile as a white powder: mp 76–78 °C; yield 3.34 g (75%). ^{31}P NMR (C_6D_6): 84.06 (d), −17.96 (d), $^2J_{PP}$ = 25.4 Hz. ^1H NMR (C_6D_6): 0.25 (s, 9 H, N—$Si(CH_3)$); 0.30 (s, 18 H, N—$Si(CH_3)$); 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CCH_3); 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CCH_3); 2.85 (m, 4 H, CH). ^{13}C NMR (C_6D_6): 2.16 (dd, $^3J_{CP^{III}}$ = 4.0 Hz, $^3J_{CP^{IV}}$ = 2.2 Hz, N—$Si(CH_3)$); 4.61 (dd, $^3J_{CP}$ = 3.6 Hz, $^5J_{CP}$ = 1.4 Hz, P=N—$Si(CH_3)$); 23.41 (d, $^3J_{CP^{IV}}$ = 1.4 Hz, $NCH(CH_3)_2$); 24.69 (d, $^3J_{CP^{III}}$ = 9.1 Hz, $NCH(CH_3)_2$); 44.13 (d, $^2J_{CP^{III}}$ = 12.3 Hz, NCH); 47.09 (d, $^2J_{CP^{IV}}$ = 7.3 Hz, NCH). ^{29}Si NMR (C_6D_6): −1.80 (d, J_{SiP} = 11.2 Hz, $>NSiMe_3$); −21.10 (d, J_{SiP} = 30.1 Hz, =N—$SiMe_3$). ^{15}N (C_6D_6): −281.25 (dd, $J_{NP^{III}}$ = 48.1 Hz, $J_{NP^{IV}}$ = 6.0 Hz, $>N—SiMe_3$); −282.41 (d, $J_{NP^{III}}$ = 104.1 Hz, $P^{III}—N(iPr)_2$); −286.09 (dd, $^1J_{NP}$ = 24.8 Hz, $^3J_{NP}$ = 3 Hz, $P^{IV}—N(iPr)_2$); −311.12 (d, $^1J_{NP}$ = 20.56 Hz, P=N—$SiMe_3$). Mass spectrum: *m/e* 523 (M^+). Anal. Calcd for $C_{21}H_{55}N_5P_2Si_3$: C, 48.14; H, 10.58; N, 13.37. Found: C, 47.99; H, 10.45; N, 13.28.

Synthesis of 2,4-Bis(Diisopropylamino)-2-(tosylimino)-4-((trimethylsilyl)imino)-1,3-bis(trimethylsilyl)-1,3,2λ^5,4λ^5-diazadiphosphetidine (7). A solution of **6** in toluene was stirred at room temperature for 6 h in the presence of a stoichiometric amount of tosyl azide. Evaporation of the solvent gave **7** as a pale yellow powder (80% yield). ^{31}P NMR (toluene-d_8): −14.80 (d), −40.43 (d), J_{PP} = 6.1 Hz. ^1H NMR (toluene-d_8): 0.61 (s, 18 H, N—$Si(CH_3)$), 0.67 (s, 9 H, =N—$Si(CH_3)$, 1.13 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $CHCH_3$), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CHCH_3$); 2.09 (s, 3 H, $CH_3(C_6H_4)$); 3.6 (m, 4 H, CH); 6.9 (m, C_6H_4). ^{13}C NMR (toluene-d_8): 1.89 (t-like, J_{CP} = 2 Hz, >N—$Si(CH_3)$); 5.43 (d, J_{CP} = 2.6 Hz, =N—$Si(CH_3)_3$); 18.87, 19.82, 20.77, 21.42, 21.51, 21.73, 22.68, 23.64, 24.24 (s, CH_3); 47.39 (br s, CH); 129 (m, C_6H_4). Mass spectrum: *m/e* 693 (M^+). Anal. Calcd for $C_{28}H_{62}N_6O_2P_2Si_3S$: C, 48.52; H, 9.02; N, 12.13. Found: C, 48.24; H, 8.97; N, 12.04.

Synthesis of 2,4-Bis(Diisopropylamino)-2-thio-4-[(trimethylsilyl)imino]-1,3-bis(trimethylsilyl)-1,3,2λ^5,4λ^5-diazadiphosphetidine (8). A solution of **6** in toluene was stirred at room temperature for 48 h in the presence of sulfur (20% excess). After filtration and evaporation of the solvent **8** was obtained as a pale yellow powder (85% yield). ^{31}P NMR (C_6D_6): 42.58 (br s), −30.04 (d, $^2J_{PP}$ = 1.2 Hz). ^1H NMR (C_6D_6): 0.35 (br s, 27 H, $Si(CH_3)_3$); 1.10 (d, $^3J_{HH}$ = 7 Hz, 12 H, $CHCH_3$); 1.15 (d, $^3J_{HH}$ = 7 Hz, 12 H, $CHCH_3$); 3.65 (m, 4 H, CH). ^{13}C NMR (C_6D_6): 2.28 (dd, $^3J_{CP=N}$ = 4.4 Hz, $^3J_{CP=S}$ = 2.2 Hz, $NSi(CH_3)$); 5.11 (d, J_{CP} = 3.0 Hz, $NSi(CH_3)$); 23.57 (m, CCH_3)); 47.70 (d, $^2J_{CP}$ = 7.2 Hz, $>CH$); 48.65 (d, $^2J_{CP}$ = 6.8 Hz, CH). Mass spectrum: *m/e* 555 (M^+). Anal. Calcd for $C_{21}H_{55}N_5P_2Si_3S$: C, 45.37; H, 9.97; N, 12.60. Found: C, 45.17; H, 10.03; N, 12.37.

Synthesis of 2,4-Bis(diisopropylamino)-4-[(trimethylsilyl)imino]-1,3-bis(trimethylsilyl)-1,2λ^3,4λ^5-azadiphosphetidine (9). A mixture of bis(diisopropylamino)azidophosphine (**1a**) (2.32 g, 8.49 mmol) and phosphaalkene **2d**[9] (2.33 g, 8.49 mmol) in 50 mL of toluene was irradiated for 36 h at room temperature. After evaporation of the solvent, the residue was recrystallized in acetonitrile, giving **9** as a white powder (70% yield). ^{31}P NMR ($CDCl_3$): 59.06 (d), −11.40 (d), $^2J_{PP}$ = 21.4 Hz. ^1H NMR ($CDCl_3$): 0.28 (s, 9 H, $SiMe_3$); 0.31 (s, 9 H, $SiMe_3$); 0.33 (s, 9 H, $SiMe_3$); 1.04 (d, J_{HH} = 6.75 Hz); 1.12 (d, J_{HH} = 6.72 Hz); 1.12 (d, J_{HH} = 6.72 Hz); 1.23 (d, J_{HH} = 6.93 Hz); 1.23 (d, J_{HH} = 6.78 Hz, 24 H, $NC(CH_3)_2$); 2.57 (d, $^2J_{PH}$ = 18 Hz, 1 H, $PCHP$); 3.47 (dh, $^2J_{PH}$ = 10.08 Hz, $^3J_{HH}$ = 6.72 Hz, 2 H, $CH(CH_3)_2$); 3.82 (dh, $^2J_{PH}$ = 15.84 Hz, J_{HH} = 6.84 Hz, 2 H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): 0.41 (dd, $^3J_{CP}$ = 3.8 Hz, $^3J_{CP}$ = 6.8 Hz, >N—$Si(CH_3)$); 1.7 (dd, $^3J_{PC}$ = 1.5 Hz, $^3J_{PC}$ = 3.8 Hz, $CSi(CH_3)$); 5.12 (d, $^3J_{PC}$ = 2.3 Hz, =N—$Si(CH_3)$); 23.63 (m, $NCH(CH_3)_2$); 24.65 (m, $NCH(CH_3)_2$); 43.29 (dd, $^1J_{CP}$ = 74.0 Hz, J_{CP} = 40.0 Hz, $^1J_{CH}$ = 117.9 Hz, $PCHP$); 45.64 (d, $^2J_{PC}$ = 10.6 Hz, NCH); 46.55 (d, $^2J_{PC}$ = 6.8 Hz, NCH). ^{29}Si NMR ($CDCl_3$): 2.53 (dd, $^2J_{PSi}$ = 11.6 Hz, $^2J_{PSi}$ = 1.5 Hz, $>CSiCH_3$); −2.57 (dd, $^2J_{PSi}$ = 24.15 Hz, $^2J_{PSi}$ = 4.7 Hz, $>NSiCH_3$); −21.23 (d, $^2J_{PSi}$ = 34.2 Hz, P=N—$SiCH_3$). Anal. Calcd for $C_{22}H_{56}N_4P_2Si_3$: C, 50.54; H, 10.80; N, 10.72. Found: C, 50.36; H, 10.74; N, 10.68.

Synthesis of 2,4-Bis(diisopropylamino)-2-thio-4-[(trimethylsilyl)imino]-1,3-bis(trimethylsilyl)-1,2λ^5,4λ^5-azadiphosphetidine (10). A solution of **9** in CH_2Cl_2 was stirred at room temperature for 5 h in the presence of sulfur (20% excess). After filtration and evaporation, **10** was recrystallized in acetonitrile (95% yield). ^{31}P NMR ($CDCl_3$): 50.62 (d), −19.42 (d), J_{PP} = 18.5 Hz. ^1H NMR ($CDCl_3$): 0.10 (s, 9 H, $Si(CH_3)$); 0.30 (s, 9 H, $Si(CH_3)$); 0.41 (s, 9 H, $Si(CH_3)$); 1.32 (m, 24 H, $CH(CH_3)_2$); 2.85 (t-like, J_{PH} = 18.67 Hz, 1 H, P—CH—P); 3.91 (m, 4 H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): 0.28 (m, N—$Si(CH_3)$); 2.14 (br s, $CSi(CH_3)$); 4.31 (d, $^3J_{PC}$ = 1.9 Hz, =N—$Si(CH_3)$); 23.4 (d, $^3J_{PC}$ = 3.4 Hz); 23.59 (d, $^3J_{PC}$ = 3.6 Hz); 24.06 (d, $^3J_{PC}$ = 2.8 Hz); 24.51 (d, $^3J_{PC}$ = 2.3 Hz, $NCH(CH_3)_2$); 46.45 (d, $^2J_{PC}$ = 7.2 Hz); 47.83 (d, $^2J_{PC}$ = 5.8 Hz, $CH(CH_3)_2$); 50.64 (dd, $^1J_{PC}$ = 71.5 Hz, $^1J_{PC}$ = 46.1 Hz, P—CH—P). ^{29}Si NMR ($CDCl_3$): 6.37 (s); −1.56 (dd, $^2J_{PSi}$ = 4.9 Hz, $^2J_{PSi}$ = 6.9 Hz); −18.09 (d, $^2J_{PSi}$ = 34.7 Hz, =N—$SiMe_3$)). Anal. Calcd for $C_{22}H_{56}N_4P_2Si_3S$: C, 47.61; H, 10.17; N, 10.10. Found: C, 47.39; H, 10.01; N, 10.17.

Synthesis of Phosphanyl Diiminophosphoranes 11 and 12. A 10% solution of [bis(trimethylsilyl)amino][bis(trimethylsilyl)methyl]azidophosphane (**1b**)[2c] in hexane and either the stoichiometric amount of [bis(trimethylsilyl)amino][(trimethylsilyl]imino)phosphane (**2c**)[8] or half the equivalent of 3-(*tert*-butylimino)-1,2,3-tri-*tert*-butyl-1,2,3-azadiphosphiridene (**4**)[7] was irradiated at −70 °C for 8 h. The reaction was monitored by ^{31}P NMR at −40 °C. Yields of **11** and **12** are more than 80%. Attempts to isolate **11** and **12** failed. ^{31}P NMR of **11** (hexane): 106.9 (d), 92.2 (d), $^2J_{PP}$ = 90.0 Hz. ^{31}P NMR of **12** (hexane): 100.40 (d), 66.80 (d), $^2J_{PP}$ = 186.0 Hz.

Synthesis of Phosphanyl Diiminophosphoranes 13 and 14. Irradiation of **1c**[2c] with (2,2,6,6-tetramethylpiperidino)[(trimethylsilyl)imino]phosphane (**2a**)[6] was performed in hexane with vigorous stirring, at 12 °C for 24 h, with a TNN 15 low-pressure mercury lamp (λ = 254 nm). A 20% solution of [bis(trimethylsilyl)methyl](2,2,6,6-tetramethylpiperidino)-azidophosphane (**1c**), in hexane, with the stoichiometric amount of [bis(trimethylsilyl)amino][(trimethylsilyl)imino]phosphane **2c**[8] was irradiated at 0 °C for 15 h with a 150 TQ high-pressure mercury lamp. Both reactions were monitored by ^{31}P NMR. Yields of **13** and **14** were higher than 80%. Attempts to isolate them failed. ^{31}P NMR for **13**

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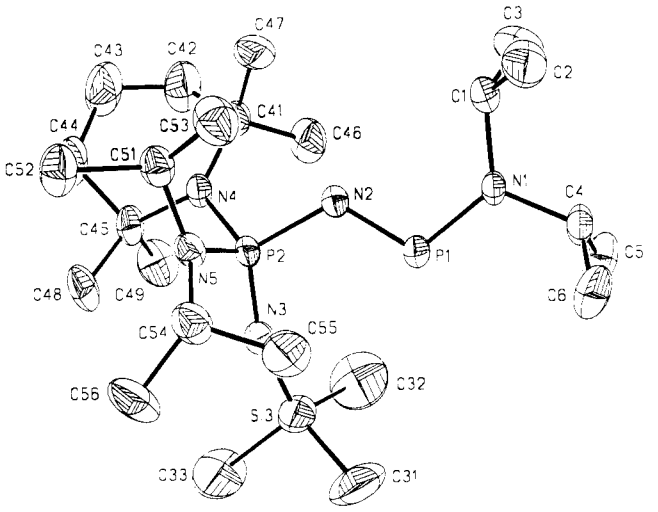


Figure 1. ORTEP plot of **3** (30% probability thermal ellipsoids; torsion angle N(1)–P(1)–N(2)–P(2) = 174.0 (1)°).

(hexane): 88.9 (d), 58.9 (d), $^2J_{PP}$ = 184.2 Hz. ^{31}P NMR for **14** (hexane): 93.80 (d), 63.00 (d), $^2J_{PP}$ = 186.7 Hz.

Characterization of [((Diisopropylamino)chloro((trimethylsilyl)imino)phosphoranyl)imino](diisopropylamino)phosphane (16). A solution of the diazadiphosphetidine **15**[10] (4.4 g, 10 mmol) in 40 mL of toluene was cooled to −60 °C. CCl_4 (1 mL, 10 mmol) was added dropwise with a syringe. ^{31}P NMR studies at low temperature allowed us to characterize compound **16** between −60 and −40 °C. ^{31}P NMR for **16** (toluene): 303.7 (d), −8.5 (d), J_{PP} = 103.5 Hz.

Dimerization of **16** started at −20 °C as indicated by an AA'XX' system in the ^{31}P NMR spectrum. The reaction mixture was slowly warmed up to room temperature. After evaporation of the solvent, the crude product **17** was recrystallized from a small amount of *n*-pentane (64% yield) and obtained as a 50/50 mixture of two diastereoisomers according to ^{31}P NMR at 121.5 MHz; this mixture could not be differentiated in ^{1}H and ^{13}C NMR. ^{31}P NMR: 104.2 (t), −20.1 (t), $^2J_{PP}$ = 39.7 Hz/104.1 (t), −20.1 (t), $^2J_{PP}$ = 39.7 Hz. ^{1}H NMR: 0.54 (s, 18 H, Me_3Si); 1.40/1.50 (s/s, 48 H, $CH(CH_3)_2$); 3.9 (m, br, 8 H, $CH(CH_3)_2$). Mass spectrum: *m/e* 796 (M^+).

Compound **16** can be also trapped by CCl_4 in excess, at −40 °C, giving rise to the adduct **18** (60% yield) as an 80/20 mixture of two diastereoisomers. ^{31}P NMR: −5.78 (d), −25.38 (d), J_{PP} = 33.0 Hz/−5.32 (d), −23.98 (d), J_{PP} = 35.6 Hz. ^{1}H NMR: 0.35/0.34 (s, 9 H, Me_3Si); 1.29/1.29 (m, 24 H, $CH(CH_3)_2$); 3.6/3.6 (m, 4 H, $CH(CH_3)_2$). ^{13}C NMR: 3.99 (d, J_{PC} = 5.0 Hz)/4.20 (d, J_{PC} = 5.6 Hz, Me_3Si); 22.52/22.52 (m, $(CH_3)_2CH$); 47.55 (d, $^2J_{PC}$ = 3 Hz)/47.56 (d, $^2J_{PC}$ = 3 Hz, $CH(CH_3)_2$); 51.19 (d, $^3J_{PC}$ = 2 Hz)/51.00 (d, $^2J_{PC}$ = 2 Hz, $CH(CH_3)_2$). Mass spectrum: *m/e* 550 (M^+).

Synthesis of 2-(Bis(trimethylsilyl)amino)-1,3-bis(trimethylsilyl)-4-chloro-4-[(trimethylsilyl)imino]-1,3,2λ^3,4λ^5-diazadiphosphetidine (21). Carbon tetrachloride (0.85 g, 5.52 mmol) was added dropwise to a toluene solution of 2,4-bis[(trimethylsilyl)amino]-1,3-bis(trimethylsilyl)-1,3,2λ^3,4λ^3-diazadiphosphetidine (**19**)[11] (2.41 g, 5.52 mmol) maintained at −60 °C. The reaction monitored by ^{31}P NMR showed the quantitative formation of the iminophosphane–iminophosphorane **20** (^{31}P NMR: 341.1, −10.6, J_{PP} = 79.9 Hz) at −60 °C. After warmup and evaporation of the solvent under reduced pressure, the remaining solid was recrystallized from dichloromethane at −40 °C: yield 1.09 (42%); one isomer. ^{31}P NMR (C_6D_6): 102.5 (d), −28.9 (d), J_{PP} = 46.5 Hz, ^{1}H NMR (−35 °C): 0.02 (d, J_{PH} = 0.6 Hz, 9 H, =N—$SiMe_3$); 0.20 (t, J_{PH} < 0.2 Hz, 18 H, >N—$SiMe_3$); 0.26 (d, J_{PH} = 4.4 Hz, 9 H, –$NSiMe_3$); 0.38 (s, 9 H, N—$SiMe_3$). ^{13}C NMR (−40 °C): 0.06 (t, J_{CP} = 3.0 Hz, >N—$SiMe_3$); 2.52 (d, J_{PC} = 5.3 Hz, =N—$SiMe_3$); 4.97 (d, J_{PC} = 21.6 Hz, –$NSiMe_3$); 4.83 (s, –$NSiMe_3$). ^{29}Si NMR (room temperature): −10.3 (d, J_{SiP} = 20.7 Hz, =N—Si); 6.4 (d, J_{SiP} = 13.1 Hz, $N(SiMe_3)_2$); 8.4 (br s, >N—$SiMe_3$). Mass spectrum: *m/e* 503 ($M^+ - CH_3$).

Crystal and Molecular Structure of 3. Crystal data: $C_{24}H_{55}N_5P_2Si$, M_r = 503.7, yellow prisms crystallized from CH_2Cl_2, crystal dimensions 0.3 × 0.5 × 0.5 mm^3, triclinic, space group *P*1, *a* = 10.361 (3) Å, *b* = 12.308 (7) Å, *c* = 12.759 (6) Å, α = 89.65 (4)°, β = 82.89 (3)°, γ = 80.03 (4)°, *V* = 1590 Å^3, *Z* = 2, d_{calc} = 1.05 g cm^{-3}, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 0.19 mm^{-1}, 8786 reflections measured on a Nicolet R3m diffractometer at room temperature ($2\theta_{max}$ = 45°), 4141 symmetry-independent reflections (R_{merge} = 0.053), 3293 reflections with $|F| > 4\sigma(F)$ used for structure solution (direct methods) and refinement (334 parameters), non-hydrogen atoms refined anisotropically, H atoms localized by difference electron density determination and refined by using a "riding" model, R = 0.054 (R_w = 0.058, $w^{-1} = \sigma^2(F) + 0.0002F^2$), structure solved with SHELX-86 and refined with SHELXTL.

Table I. Selected Bond Lengths (Å) and Angles (deg)

P(1)–N(1)	1.646 (3)	P(2)–N(2)	1.671 (3)
P(1)–N(2)	1.558 (3)	P(2)–N(3)	1.526 (3)
N(1)–C(1)	1.472 (4)	P(2)–N(4)	1.686 (2)
N(1)–C(4)	1.494 (4)	P(2)–N(5)	1.670 (2)
		N(3)–Si(3)	1.660 (3)
N(1)–P(1)–N(2)	107.2 (1)	N(2)–P(2)–N(3)	114.6 (1)
P(1)–N(2)–P(2)	118.2 (2)	N(2)–P(2)–N(4)	104.5 (1)
P(1)–N(1)–C(1)	125.3 (2)	N(2)–P(2)–N(5)	105.2 (1)
P(1)–N(1)–C(4)	116.9 (2)	N(3)–P(2)–N(4)	117.0 (1)
C(1)–N(1)–C(4)	117.8 (3)	N(3)–P(2)–N(5)	109.7 (1)
P(2)–N(3)–Si(3)	160.7 (2)	N(4)–P(2)–N(5)	104.7 (1)

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

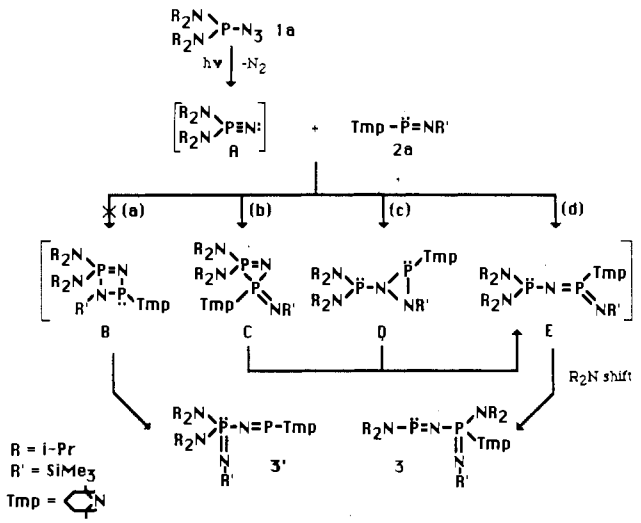
	x	*y*	*z*	*U*[a]
P(1)	7738 (1)	2124 (1)	4295 (1)	53 (1)
P(2)	7309 (1)	2823 (1)	2279 (1)	45 (1)
Si(3)	5917 (2)	746 (1)	2510 (1)	94 (1)
C(31)	4682 (7)	808 (5)	3698 (5)	160 (4)
C(32)	7288 (9)	−397 (4)	2726 (7)	177 (4)
C(33)	5053 (8)	393 (5)	1399 (5)	193 (5)
N(1)	8557 (3)	2418 (2)	5251 (2)	48 (1)
C(1)	9495 (4)	3195 (2)	5178 (3)	58 (1)
C(2)	9114 (5)	4101 (3)	6017 (4)	90 (2)
C(3)	10908 (4)	2599 (4)	5180 (4)	102 (2)
C(4)	8301 (4)	1862 (3)	6282 (3)	63 (1)
C(5)	8661 (5)	630 (3)	6190 (4)	98 (2)
C(6)	6910 (4)	2200 (4)	6789 (3)	93 (2)
N(2)	8107 (3)	2849 (2)	3336 (2)	48 (1)
N(3)	6441 (3)	1938 (2)	2298 (2)	62 (1)
N(4)	8491 (3)	2798 (2)	1240 (2)	48 (1)
C(41)	9956 (3)	2617 (3)	1336 (3)	60 (1)
C(42)	10780 (4)	2503 (4)	242 (4)	115 (2)
C(43)	10282 (5)	3156 (5)	−586 (4)	138 (3)
C(44)	8881 (4)	3183 (4)	−674 (3)	97 (2)
C(45)	8119 (4)	2545 (3)	154 (3)	64 (1)
C(46)	10426 (4)	1527 (3)	1895 (4)	88 (2)
C(47)	10313 (4)	3568 (3)	1939 (4)	85 (2)
C(48)	6649 (4)	2961 (3)	58 (3)	80 (2)
C(49)	8376 (5)	1300 (3)	−87 (4)	98 (2)
N(5)	6376 (2)	4071 (2)	2252 (2)	49 (1)
C(51)	7009 (3)	5054 (2)	2084 (3)	58 (1)
C(52)	6317 (5)	5881 (3)	1324 (4)	87 (2)
C(53)	7153 (5)	5639 (3)	3102 (4)	82 (2)
C(54)	4978 (4)	4316 (3)	2774 (3)	70 (1)
C(55)	4762 (4)	3909 (4)	3893 (3)	91 (2)
C(56)	4010 (4)	3984 (4)	2085 (4)	102 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The ORTEP view of **3** is illustrated in Figure 1 along with the atom-numbering scheme. A summary of pertinent metric parameters is given in Tables I and II. The bond lengths in compound **3** are in good agreement with our expectation. For example, both phosphorus–nitrogen distances P(1)–N(2) and P(2)–N(3) of 1.56 and 1.53 Å clearly prove the two double-bond systems. The smaller value is due to the higher oxidation number of the phosphorus atom P(2). The comparison of the crystal structure data of the two well-known aminoiminophosphanes $(Me_3Si)_2N—P=NSiMe_3$ (**2c**)[8] and $(tBu)(Me_3Si)N—P=N(tBu)$[12] with those of **3** shows only slight differences as well for P–N single bonds and P–N double bonds as well as for the valence angles N–P–N at the low-coordinated phosphorus atoms. In contrast the valence angle P(1)–N(2)–P(2) of 118.20° is significantly reduced compared with that of the

(10) Böske, J.; Ocando-Mavarez, E.; Niecke, E.; Majoral, J. P.; Bertrand, G. *J. Am. Chem. Soc.* **1987**, *109*, 2822.
(11) Niecke, E.; Flick, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 309.
(12) (a) Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 687. (b) Pohl, S. *Z. Naturforsch.* **1977**, *32B*, 1344.

Scheme I



silyl derivative **2c** (129.9°) or the *tert*-butyl derivative (124.4°), showing the dependence of this angle on the sterical bulk of the substituent at the low-coordinated nitrogen. Finally the corresponding valence angle P(2)–N(3)–Si (160.7°) should be mentioned; it is remarkably widened. Perhaps this is an explanation for the great value of the coupling constant $^5J_{CP}$ from silyl carbons to phosphorus(III) (see ^{13}C NMR data).

Results

A clean reaction occurred when bis(diisopropylamino)phosphine azide (**1a**)[5] was irradiated, at −20 °C, in the presence of a stoichiometric amount of iminophosphane **2a**,[6] leading to the iminophosphorane–iminophosphane **3** (48% yield), which was characterized by an X-ray crystal structure analysis. Similarly, iminophosphane–iminophosphorane **5** (70% yield) was obtained in the photolysis of phosphine azide **1a** and 1,2λ³,3λ⁵-azadiphosphiridene **4**,[7] which is a well-known precursor of iminophosphane **2b**.

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[-20\ °C]{h\nu} \mathbf{3}$$

$$\mathbf{1a} + \mathbf{4} \xrightarrow[0\ °C]{h\nu} \mathbf{5}$$

In contrast, photolysis of phosphine azide **1a**, in the presence of the fully silylated iminophosphane **2c**,[8] afforded the 1,3,2λ³,4λ⁵-diazadiphosphetidine **6**. The exact formulation of

$$\mathbf{1a} + \mathbf{2c} \xrightarrow[\text{room temp}]{h\nu} \mathbf{6} \xrightarrow[\text{room temp}]{\text{TosN}_3} \mathbf{7}\ (\text{S}_8 \rightarrow \mathbf{8})$$

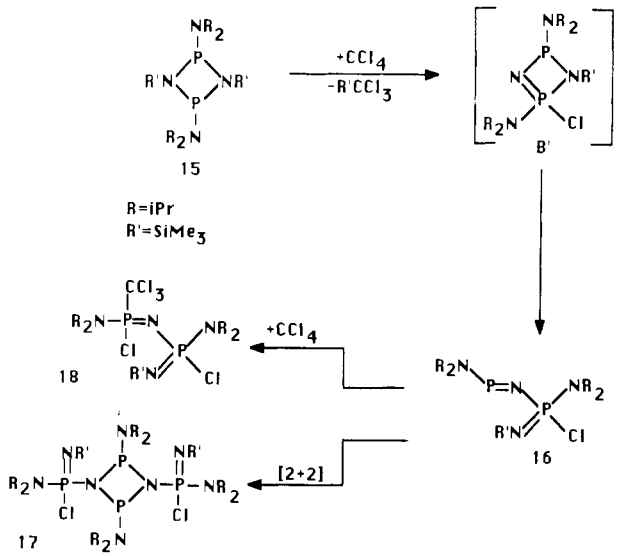
6 has been established by mass spectroscopy and ^1H, ^{13}C, ^{15}N, ^{29}Si, and ^{31}P NMR. In particular, ^1H and ^{13}C NMR spectra confirm the presence of two different diisopropylamino groups while the ^{31}P chemical shifts are in perfect agreement with such a structure (two doublets centered at 84.06 and −17.96 ppm, J_{PP} = 25.43 Hz). Addition of tosyl azide or sulfur to **6** led to the formation of the corresponding 1,3,2λ⁵,4λ⁵-diazadiphosphetidines **7** and **8**.

Similarly, irradiation of phosphine azide **1a** in the presence of the phosphaalkene **2d**,[9] in toluene, for 36 h at room temperature, gave rise to the azadiphosphetidine **9**, fully characterized by its spectroscopic data as well as by its reaction with elemental sulfur, which led to the corresponding thioazadiphosphetidine **10**.

$$\mathbf{1a} + \mathbf{2d} \xrightarrow[\text{room temp}]{h\nu} \mathbf{9} \xrightarrow[\text{room temp}]{S_8} \mathbf{10}$$

Four reactions have been done involving two other phosphine azides, [bis(trimethylsilyl)amino][bis(trimethylsilyl)methyl]-phosphine azide (**1b**)[2c] and (tetramethylpiperidino)[bis(trimethylsilyl)methyl]phosphine azide (**1c**),[2c] and three different iminophosphanes, (tetramethylpiperidino)[(trimethylsilyl)imino]phosphane (**2a**),[6] *tert*-butyl(*tert*-butylimino)phosphane (**2b**,

Scheme II



generated by photolysis of 3-(*tert*-butylimino)-1,2,3-tri-*tert*-butyl-1,2λ³,3λ⁵-azadiphosphiridene (**4**)[7]), and [bis(trimethylsilyl)-amino][(trimethylsilyl)imino]phosphane (**2c**).[8] According to ^{31}P NMR, all of these reactions led to the corresponding bis(imino)phosphoranes **11**–**14**, in good yield. However, due to their thermal instability, attempted isolation failed.

$$\mathbf{1b} + \mathbf{4} \xrightarrow[-70\ °C]{h\nu} \mathbf{11}$$

$$\mathbf{1b} + \mathbf{2c} \xrightarrow[-70\ °C]{h\nu} \mathbf{12}$$

$$\mathbf{1c} + \mathbf{2a} \xrightarrow[12\ °C]{h\nu} \mathbf{13}$$

$$\mathbf{1c} + \mathbf{2c} \xrightarrow[0\ °C]{h\nu} \mathbf{14}$$

Further experiments have been carried out in order to clarify the mechanism of the previous reactions. Addition of CCl_4, at −60 °C, to the 1,3,2λ³,4λ³-diazadiphosphetidine **15**[10] afforded the iminophosphane–iminophosphorane **16**, characterized, at low

$$\mathbf{15} + CCl_4 \xrightarrow[-60\ °C]{-Me_3SiCCl_3} \mathbf{16} \begin{cases} \xrightarrow[-20\ °C]{} \mathbf{17} \\ \xrightarrow[-40\ °C]{CCl_4} \mathbf{16} \end{cases}$$

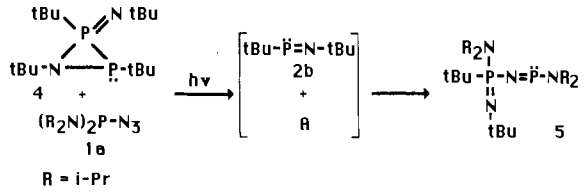
$$\mathbf{19} + CCl_4 \xrightarrow[-60\ °C]{-Me_3SiCCl_3} \mathbf{20} \xrightarrow[\text{room temp}]{} \mathbf{21}$$

temperature, by ^{31}P NMR. In the absence of any trapping agent, **16** dimerized to the diazadiphosphetidine **17**, while addition of CCl_4 led to the expected adduct **18**. In the same way, when the aminosilylated diazadiphosphetidine **19**[11] (trans isomer) was treated with a stoichiometric amount of CCl_4 at −60 °C, the iminophosphane–iminophosphorane **20** ($\delta(^{31}P)$ 341.1 and −10.6 ppm, J_{PP} = 79.9 Hz) was quantitatively formed. However, instead of dimerizing upon warmup, **20** rearranged into the 1,3,2λ³,4λ⁵-diazadiphosphetidine **21** (cis isomer).

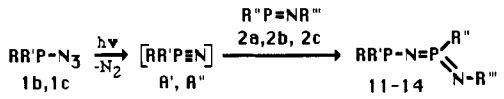
Discussion

Obtainment of the iminophosphorane–iminophosphane **3** in the cophotolysis of phosphine azide **1a** and iminophosphane **2a** allowed us to exclude a [2 + 2] cycloaddition of the phosphonitrile A with the phosphorus–nitrogen double bond of **2a** (route a, Scheme I). Such a mechanism would have led to the isomeric iminophosphorane–iminophosphane **3'** via ring opening of the first-formed 1,3,2λ³,4λ⁵-diazadiphosphete B. Indeed, the similar diazadiphosphete B', prepared by the action of CCl_4 on the 1,3,2λ³,4λ³-diazadiphosphetidine **15** gave rise to **16** without migration of the phosphorus substituent, as we have previously demonstrated (Scheme II).[10] To explain the formation of the observed product **3**, the bis(imino)phosphorane intermediate E

Scheme III



Scheme IV



1b, A' : R = $(Me_3Si)_2N$, R' = $(Me_3Si)_2CH$
1c, A": R = TMP, R' = $(Me_3Si)_2CH$
2a : R" = TMP, R'" = Me_3Si
2b : R" = R'" = t-Bu
2c : R" = $(Me_3Si)_2N$, R'" = Me_3Si
11 : R = $(Me_3Si)_2N$, R' = $(Me_3Si)_2CH$, R" = R'" = tBu
12 : R = R" = $(Me_3Si)_2N$, R' = $(Me_3Si)_2CH$, R'" = Me_3Si
13 : R = R" = TMP, R' = $(Me_3Si)_2CH$, R'" = Me_3Si
14 : R = TMP, R' = $(Me_3Si)_2CH$, R" = $(Me_3Si)_2N$, R'" = Me_3Si

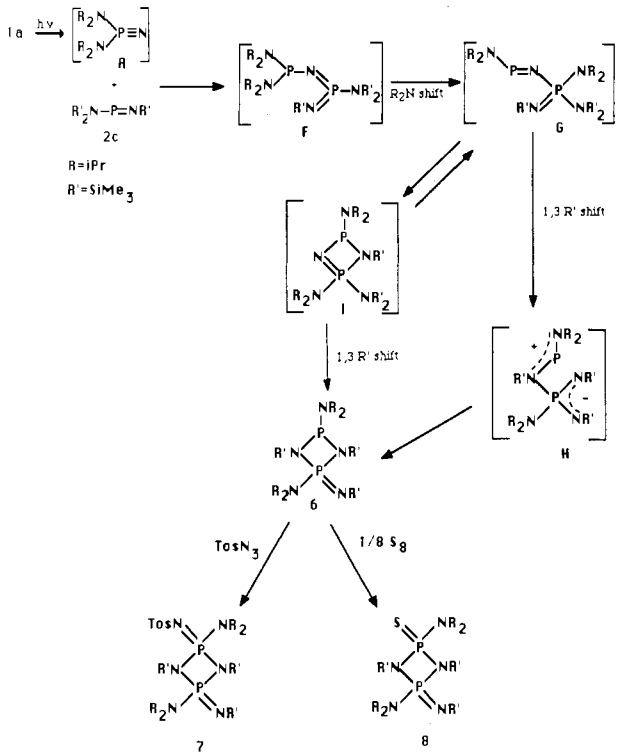
seems more likely. $\sigma^3\lambda^5$-Phosphorus atoms are strongly electrophilic, and this could well be the driving force of the diisopropylamino group migration. It seems difficult to explain such a 1 → 3 shift from intermediates C and D. However, we cannot totally exclude that E is formed by subsequent rearrangement of the first-formed C or D as indicated in Scheme I. Similar results were observed in the reaction of the phosphonitrile A with the iminophosphane **2b**, generated in situ by photolysis of the phosphine azide **1a** and the $1,2\lambda^3,3\lambda^5$-azadiphosphiridene **4**, respectively. Indeed, once more, a diisopropylamino migration occurred, leading to the iminophosphane–iminophosphorane **5** (Scheme III).

In order to prove the transient formation of the bis(imino)phosphorane of type E, it was of interest to replace the diisopropylamino groups by more sterically hindered and thus less easily migrating groups. The transient phosphonitrile A', generated by irradiation of the corresponding phosphine azide **1b**, reacted effectively with iminophosphanes **2b** and **2c**, affording the desired bis(imino)phosphoranes **11** and **12**. In the same way, the reaction of phosphonitrile A" with iminophosphanes **2a** and **2c** led to the tricoordinated, pentavalent species **13** and **14** (Scheme IV).

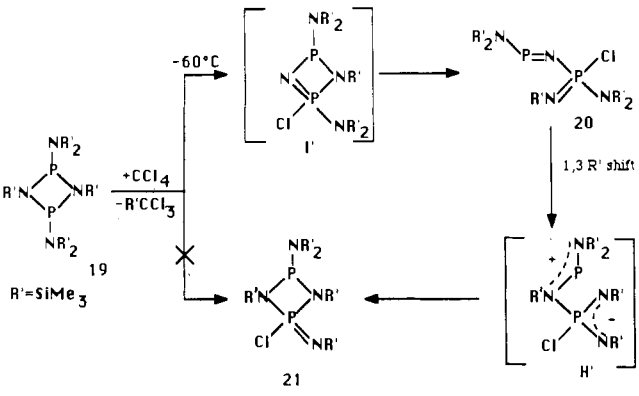
As we can prevent the rearrangement of the bis(imino)phosphorane E to the iminophosphane–iminophosphorane **3** using bulky substituents on the phosphonitrile, it is possible to favor further rearrangement using good migrating groups (Me_3Si) on the iminophosphane. Generation of the phosphonitrile A in the presence of the fully silylated iminophosphane **2c** afforded the $1,3,2\lambda^3,4\lambda^5$-diazadiphosphetidine **6** (Scheme V). Although the several-step mechanism reported in Scheme V seems complicated, it is quite likely. We have already demonstrated the first two steps in characterizing bis(imino)phosphoranes (**11**–**14**) of the same type as F and iminophosphorane–iminophosphanes (**3** and **5**) analogous to G. The transformation of the intermediate G to the isolated product **6** can be explained either by a 1 → 3 migration of a trimethylsilyl group with the transient generation of the zwitterionic form H followed by cyclization or by the existence of an equilibrium of the iminophosphane–iminophosphorane G with the diazadiphosphete I, followed by a 1 → 3 Me_3Si migration. These two possible mechanisms might have been involved when the aminosilylated diazadiphosphetidine **19** (trans isomer) was treated with a stoichiometric amount of CCl_4 at −60 °C. The iminophosphane–iminophosphorane **20** was quantitatively formed under these conditions. Instead of dimerizing upon warmup, **20** rearranged into the $1,3,2\lambda^3,4\lambda^5$-diazadiphosphetidine **21** (cis isomer) via H'. It is noteworthy that **21** does not result from a direct Me_3SiCCl_3 exocyclic elimination, because **20** is observed first (Scheme VI).

A similar mechanism is quite probably involved in the formation of the azadiphosphetidine **9** when the phosphine azide **1a** is irradiated in the presence of the phosphaalkene **2d**,[9] i.e. transient generation of J and then K, which undergoes a 1 → 3 trimethylsilyl migration, affording L (Scheme VII). The iminophosphane–iminophosphorane K can also be in equilibrium with the cyclic form M, which is converted in turn into **9**.

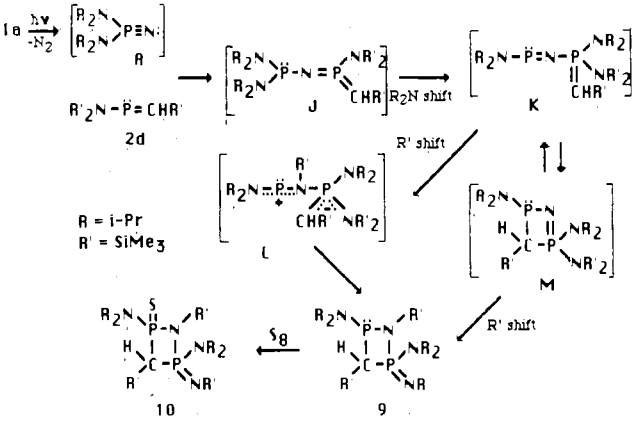
Scheme V



Scheme VI



Scheme VII



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Registry No. **1a**, 56183-64-3; **1b**, 102724-53-8; **1c**, 102699-27-4; **2a**, 72821-01-3; **2b**, 95552-76-4; **2c**, 50732-21-3; **2d**, 76173-65-4; **3**, 117874-61-0; **4**, 79933-17-8; **5**, 117874-62-1; **6**, 117874-63-2; **7**, 117874-64-3; **8**, 117874-65-4; **9**, 117874-66-5; **10**, 117874-67-6; **11**, 117874-68-7; **12**, 117874-69-8; **13**, 117874-70-1; **14**, 117874-71-2; **15**, 65160-85-2; **16**, 107769-94-8; **17** (diastereomer 1), 107769-96-0; **17** (diastereomer 2), 107869-72-7; **18** (diastereomer 1), 107769-95-9; **18** (diastereomer 2), 107798-25-4; **19**, 66435-40-3; **20**, 107770-00-3; **21**, 107770-01-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and additional bond distances and angles (3 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page. Inquiries for copies of these materials can also be directed to the corresponding authors.

Contribution from the Institut für anorganische Chemie der Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Spin Cluster Excitations of $Ti^{2+}Mn^{2+}$ and $Mn^{2+}Ti^{2+}Mn^{2+}$ in $MgCl_2$ Studied by Site-Selective Optical Spectroscopy

Markus Herren, Stuart M. Jacobsen, and Hans U. Güdel*

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The spin clusters Ti^{2+}–Mn^{2+} and Mn^{2+}–Ti^{2+}–Mn^{2+} were created by simultaneously doping Ti^{2+} and Mn^{2+} into single crystals of $MgCl_2$. They were studied by site-selective dye laser spectroscopy using $^4A_{1g}$, ^4E_g excitations on Mn^{2+}, and the luminescence transition observed was $^1E_g \rightarrow {}^3T_{1g}$ on Ti^{2+} (O_h single-ion notations). Exchange splittings in the electronic ground state were directly and accurately determined and the corresponding exchange parameters derived. Two types of trimers, structural isomers, could be clearly distinguished. Eleven ground-state spin levels are spectroscopically accessible, which were all observed for both trimers. The spin level structure in the trimers has the appearance of a ferromagnetic pattern. This is a direct result of the dominant antiferromagnetic Ti^{2+}–Mn^{2+} interaction, which leads to a ferromagnetic "alignment" of the Mn^{2+} spins in a classical picture. Deviations from the regular energy splitting pattern expected from a bilinear Ti^{2+}–Mn^{2+} (J) Heisenberg operator are small but significant in the spectroscopic data. They are quantitatively accounted for by including Mn^{2+}–Mn^{2+} interactions (J') as well as a biquadratic Ti^{2+}–Mn^{2+} term (j). The following parameter values were obtained: for the Ti^{2+}–Mn^{2+} dimers, $2J = -19.0$ cm^{-1} and $j = 0.5$ cm^{-1}; for the linear and bent Mn^{2+}–Ti^{2+}–Mn^{2+} trimers, $2J = -19.0$ cm^{-1}, $j = 0.5$ cm^{-1}, and $2J' = -0.1$ cm^{-1}; for triangular trimers, $2J = -19.0$ cm^{-1}, $j = 0.5$ cm^{-1}, $2J' = -2.2$ cm^{-1}, and $2J'_{exc}$ (in the ^1E_g excited state) $= -2.0$ cm^{-1}.

1. Introduction

Exchange-coupled clusters of transition-metal ions continue to fascinate the coordination chemists. There is a clear interest from the bioinorganic community, because an increasing number of active centers in metalloproteins are found to contain more than one metal atom.[1] In another area of research there is an intensive effort to design and understand new "molecular magnets", which is mainly directed toward the development of materials with novel properties.[2] Molecular systems with ferromagnetic or pseudoferromagnetic behavior appear to be of particular interest in the latter field. Antiferromagnetic pairing of electrons, on the other hand, plays an important part in some recent theoretical models developed for understanding the unusual behavior of the new family of high-T_c superconducting oxides.[3]

Dimers of magnetic ions in which the coupling is described by a Heisenberg Hamiltonian

$$\hat{H}_{ex} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2) \qquad (1)$$

show a regular spin level structure described by a Landé pattern. Trimers show a Landé splitting pattern only in a few special cases such as the equilateral triangles realized in complexes like $[Cr_3O(OAc)_6(H_2O)_3]^+$ and $[Fe_3O(SO_4)_6(H_2O)_3]^{5-}$.[4,5] In general the energy of the trimer spin states depends on two quantum numbers, and the spin-state structure is irregular. An example is provided by the linear Mn^{2+} trimers obtained by doping $CsMgBr_3$, the splitting pattern of which was recently determined.[6] Reference 6 also shows how the spin level structure evolves when the number of Mn^{2+} ions in the linear cluster increases. As expected in a semiclassical picture of nearest-neighbor antiferromagnetic coupling, the ground spin levels are $S = 0$ and $S = {}^5/_2$ for clusters with even and odd numbers of Mn^{2+} ions, respectively.

An interesting situation arises in a linear trimer ABA with dominant nearest-neighbor antiferromagnetic interaction. When A represents an ion with a large magnetic moment like Mn^{2+} ($S = {}^5/_2$) and B an ion with a smaller magnetic moment, this will lead to a pseudoferromagnetic coupling of the A spins with a resulting high-spin quantum number for the lowest energy level. The trinuclear species can then be considered as a molecular ferrimagnet. This situation has been discussed in some detail by Kahn and co-workers.[7] A molecular Mn^{2+}–Cu^{2+}–Mn^{2+} complex, as reported in ref 7, does indeed show the typical magnetic behavior of a ferromagnetically coupled complex, even though the Mn^{2+}–Cu^{2+} interactions are antiferromagnetic. The exchange energy splitting pattern is quite regular in such a situation, but not with Landé intervals. The spin levels are regularly spaced with an energy difference $\Delta E = -2J_{AB}$.

We have recently studied a very large spin cluster in which the same principles apply.[8] By doping Ti^{2+} into $MnCl_2$ we were able to determine the properties of a $Ti^{2+}(Mn^{2+})_6$ cluster, which are quite remarkable. The dominant antiferromagnetic Ti^{2+}–Mn^{2+} interaction leads to a pseudoferromagnetic coupling of all the six Mn^{2+} spins and thus very large spin quantum numbers of the lowest energy cluster levels. The ground level is $|S_a\, S\rangle = |15\ 14\rangle$, where S_a is the sum of all the Mn^{2+} spins and S the total cluster spin.

In the present study we report high-resolution spectroscopic results on Ti^{2+}–Mn^{2+} dimers and two types of Mn^{2+}–Ti^{2+}–Mn^{2+} trimers obtained by doping both Ti^{2+} and Mn^{2+} in $MgCl_2$. The

* To whom correspondence should be addressed.

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