Heteroatom Chemistry
Volume 13, Number 1, 2002

Reactions of Transiently Formed Nitrilium Phosphanylide Chromium, Molybdenum, and Tungsten Complexes with Heterocumulenes

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Received 27 April 2001; revised 25 June 2001

ABSTRACT: *Thermal decomposition of the 2H-azaphosphirene metal complexes* **1a–c** *in the presence of 1-piperidinecarbonitrile and heterocumulene derivatives* **3, 4**, *and* **5** *yielded the* Δ^3*-1,3,2-oxazaphospholene complexes* **6c** *and the* Δ^3*-1,3,2-thiazaphospholene complexes* **7a–c** *as isolable products; the latter represent the first complexes of this ring system. It is remarkable that these trapping reactions of the nitrilium phosphanylide complexes* **2a–c**, *which were formed as reactive intermediates, proceeded with high regio- and substrate selectivities. The complexes were isolated by column chromatography and characterized by elemental analysis, NMR spectroscopy and mass spectrometry.* © 2002 John Wiley & Sons, Inc. Heteroatom Chem 13:72–76, 2002; DOI 10.1002/hc.1108

INTRODUCTION

Nitrilium ylides, such as nitrile oxides [1], nitrile sulfides [2], and nitrile imines [1,3], are versatile building blocks in heterocyclic chemistry. Recently, we provided the first evidence for the intermediate formation of nitrilium phosphanylide complexes **II** during thermal ring-opening of 2*H*-azaphosphirene complexes **I** in toluene in the presence of dimethyl acetylenedicarboxylate (DMAD) [4]. Further studies showed that, by employing nitriles having good electron-donating substituents such as in dialkyl cyanamides, formal nitrile/nitrile exchange reactions (*transylidations*) were achieved, thus leading to new transiently formed nitrilium phosphanylide complexes **III** [5]. Trapping of complexes **III** with alkynes [5], nitriles [5], and phosphaalkynes [6] resulted in the formation of heterophosphole complexes **IV–VI** (Scheme 1).

In order to exploit our new synthetic concept, we started [7] to investigate heterocumulene systems such as phenyl isocyanate, phenyl isothiocyanate [7], and bis(trimethylsilyl)thioketene [8] as trapping reagents for transiently formed nitrilium phosphanylide complexes; first results were reported in a short communication.

RESULTS AND DISCUSSION

Thermal ring-opening of the 2*H*-azaphosphirene complexes **1a** [9] and **1b,c** [10] in the presence of two equivalents of 1-piperidinecarbonitrile and two equivalents of phenyl isocyanate (**3**) and phenyl isothiocyanate (**4**), respectively, furnished selectively the Δ^3-1,3,2-oxazaphospholene complexes **6a–c** and the Δ^3-1,3,2-thiazaphospholene complexes **7a–c** as the sole phosphorus-containing products. Although complexes **6a,b** were formed also, only complexes **6c** and **7a–c** could be isolated by column chromatography. Complexes **6c** and **7a–c** were characterized by elemental analysis, NMR spectroscopy (Table 1),

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Dedicated to Prof. Heinz Heimgartner on the occasion of his 60th birthday.

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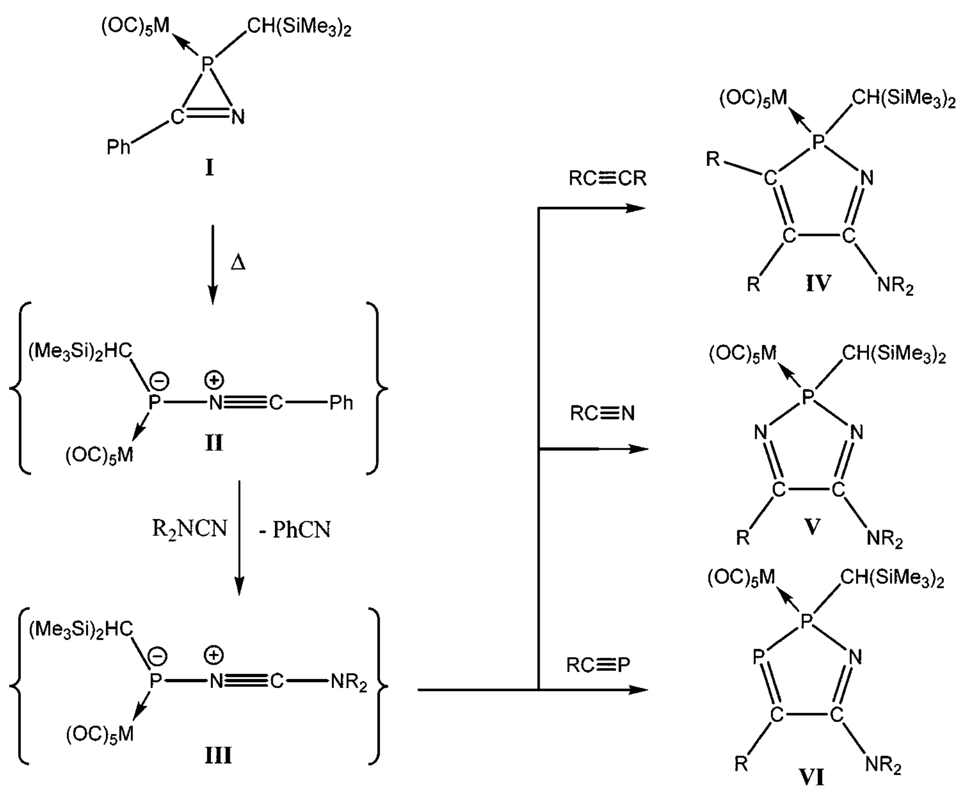
Contract grant sponsor: Deutsche Forschungsgemeinschaft.
Contract grant sponsor: Fonds der Chemischen Industrie.



SCHEME 1 Thermal ring opening and transylidation reactions of 2*H*-azaphosphirene complexes.

and mass spectrometry. Although the refinement was unsatisfactory due to heavily disordered substituents of the five-membered ring system [7], the connectivity of the heterocyclic ring atoms of the Δ^3-1,3,2-thiazaphospholene complex **7c** was established by X-ray crystal structure analysis.

Remarkable was the observation that no regioisomers of complexes **6a–c** and **7a–c** were formed and that the nitrilium phosphanylide complexes **2a–c** did not react with the C–N π-system of the heterocumulenes **3** and **4**. The product formation is explained via ring opening of the 2*H*-azaphosphirene complexes **1a–c** and transylidation to give transiently the nitrilium phosphanylide complexes **2a–c**, which then undergo [3 + 2]-cycloaddition reactions with the C–X π-system (X = O, S) of **3** and **4** to afford the final products (Scheme 2).

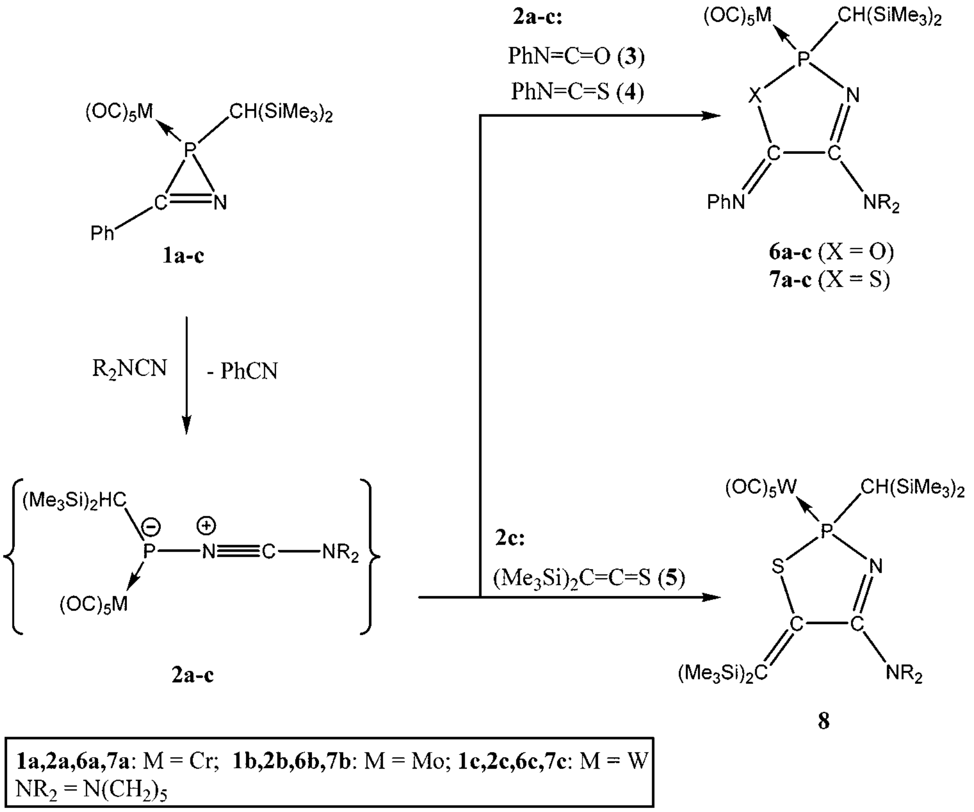
TABLE 1 Selected NMR Data of **6a–c, 7a–c,** and **8** (δ [ppm], *J* [Hz])

Compound	$\delta^{31}P$ ($\lvert ^1J_{P,W}\rvert$)	$\delta^{13}C^4$ ($\lvert ^{(2+3)}J_{C,P}\rvert$)	$\delta^{13}C^5$ ($\lvert ^{(2+3)}J_{C,P}\rvert$)
6a	234.4	[a]	[a]
6b	210.7	[a]	[a]
6c	181.9 (306.5)	153.8 (4.6)	147.4[b]
7a	169.4	156.7 (12.8)	161.1 (9.2)
7b	134.5	157.2 (12.8)	160.7 (9.2)
7c	105.6 (287.1)	157.7 (12.8)	160.9 (9.2)
8	104.4 (281.7)	[a]	[a]

[a] Not recorded.
[b] Not resolved.

In a preliminary investigation, we examined bis(trimethylsilyl)thioketene (**5**) as a trapping reagent of complex **2c**. The analogous reaction of complex **1c**, 1-piperidinecarbonitrile with **5**, the Δ^3-1,3,2-thiazaphospholene tungsten complex, furnished **8**, albeit with <20% yield. Although the isolation of **8** failed (decomposition during column chromatography), the observed phosphorus resonance at δ 104.4 and the phosphorus–tungsten coupling constant of 281.7 Hz are in accord with **8**; these NMR data are also almost identical with those of complex **7c**.

A comparison of the ^{31}P NMR data of the tungsten complexes **6c** and **7c** showed a highfield shift of 75 ppm of the latter and also a decrease in the phosphorus–tungsten coupling constant of ca. 20 Hz; this apparently results from the formal exchange of oxygen by sulfur in these rings. The ^{31}P NMR spectroscopic data of the Δ^3-1,3,2-oxazaphospholene complex **6c** are comparable to other derivatives of this ring system such as {[2-bis(trimethylsilyl)methyl-5-cyano-5-ethoxy-4(1-piperidino)-Δ^3-1,3,2-oxazaphospholene-κ*P*]pentacarbonyltungsten(0)} (**9**) [5]



SCHEME 2 [3 + 2] cycloaddition reactions of the complexes **2a–c** with the heterocumulenes **3** and **4** and of complex **2c** with **5**.

(δ205.0, ${}^1J_{P,W} = 304.8$ Hz) or {[2-bis(trimethylsilyl)-methyl-5-cyano-5-phenyl-4-dimethylamino-Δ^3-1,3,2-oxazaphospholene-κ *P*]-pentacarbonyltungsten(0)} (**10**) [5] (δ 203.5, ${}^1J_{P,W} = 310.6$ Hz. The heterocyclic ring in **6c** shows a carbon resonance of the imino carbon at δ 153.8, which is similar to the values of **9** and **10**, but the C^5 resonance at δ 147.4 is significantly lowfield shifted by 50 ppm as compared to δ 96.3 (**9**) and δ 82.0 (**10**). This difference points to a strong electronic influence of the exocyclic imino substituent. The Δ^3-1,3,2-thiazaphospholene complexes **7a–c**, which are the first examples of P-coordinated derivatives, show phosphorus resonances in the range of 100–160 ppm, which are similar to the value of 2-(4-methoxyphenyl)-4,5-diphenyl-5*H*-1,3,2-thiazaphosphole-2-sulfide (**11**) [11] (δ 80.8). The ^{13}C resonances of the ring carbon atoms of the complexes **7a–c** show only little dependence of the pentacarbonylmetal fragment (Table 1). Comparing the resonances of the ring carbon atoms C^4 in complexes **7c** (δ 157) and **7c** (δ 153.8), they show only a slight downfield shift of the latter. Because of the exocyclic imino group the resonance of the C^5-carbon atom is at much lower field than that of the corresponding carbon atom in **11**.

As shown in Table 1, the phosphorus–carbon coupling constant magnitudes of the Δ^3-1,3,2-oxazaphospholene and Δ^3-1,3,2-thiazaphospholene ring atoms exhibit relatively small values, in general, which seems to be a characteristic phenomenon for such heterocyclic ring-systems, although the coupling constants increase upon changing sulfur by oxygen.

EXPERIMENTAL

General Procedures

All reactions were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware. Solvents were dried according to standard procedures. NMR-spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) using [D]chloroform and [D$_6$]benzene as standards. Shifts are given relative to ext. tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnigan Mat 8430 (70 eV); apart from the *m*/*z*-values of the molecule ions, only *m*/*z*-values having intensities more than

20% are given. Infrared spectra were recorded on a Biorad FT 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were obtained using a Carlo Erba analytical gas chromatograph. The κ*P*-notation in the nomenclature is intended to differentiate between *P*- and *N*-coordination of the appropriate heterocycle to the metal.

General Reaction Procedure

One millimole of the appropriate 2*H*-azaphosphirene complexes **1a–c** were dissolved in 4 ml of toluene, and 2 mmol of 1-piperidinecarbonitrile and 2 mmol of the heterocumulene were added. The reaction mixture was heated at 75°C for 2 h with stirring. After evaporation of the solvent (ca. 0.01 mbar), low-temperature column chromatography (−20°C, on silica gel, with petrol ether/diethyl ether 97.5/2.5) as eluent and recrystallisation from *n*-pentane furnished the products as pale-yellow to yellow solids.

{[2-Bis(trimethylsilyl)methyl-4-N-phenylimino-5-N-piperidino-Δ^3*-1,3,2-oxazaphospholene-κP]pentacarbonyltungsten(0)}* (**6c**). Pale yellow crystals (35%, m.p. 108°C); IR (KBr): $\nu_{\mathrm{CO}} = 1920.8$ (vs), 1945.9 (s), 2070.8 (w) cm^{-1}; MS (70 eV, EI, ^{184}W) $m/z = 743$ [M$^+$ (45)], 659 [(M-3CO)$^+$ (100)], 603 [(M-5CO)$^+$ (70)]; ^{1}H NMR: $\delta = 0.02$ (s, 9H, SiMe$_3$), 0.25 (s, 9H, SiMe$_3$), 1.53 (d, $^2J_{\mathrm{P,H}} = 3.2$ Hz, PC*H*), 1.70 (m, 6H, $\mathrm{NCH_2C}H_2\mathrm{C}H_2$), 3.83 (m, 2H, $\mathrm{NC}H_2$), 4.58 (m, 2H, $\mathrm{NC}H_2$), 7.31 (m, 5H, Ph); ^{13}C{^{1}H} NMR: $\delta = 2.1$ (d, $^3J_{\mathrm{C,P}} = 2.1$ Hz, SiMe$_3$), 2.4 (d, $^3J_{\mathrm{C,P}} = 2.3$ Hz, SiMe$_3$), 24.6 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 26.6 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 27.1 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 36.0 (d, $^1J_{\mathrm{C,P}} = 6.6$ Hz, P*C*H), 48.2 (s, $\mathrm{N}C\mathrm{H_2}$), 49.6 (s, $\mathrm{N}C\mathrm{H_2}$), 122.9 (*o*-Ph), 125.4 (s, *p*-Ph), 128.6 (s, *m*-Ph), 144.7 (s, *i*-Ph), 147.4 (d, PO*C*), 153.8 (d, $^{(2+3)}J_{\mathrm{C,P}} = 4.6$ Hz, PN*C*), 196.7 (d, $^2J_{\mathrm{C,P}} = 8.6$ Hz, *cis*-*C*O), 199.9 (d, $^2J_{\mathrm{C,P}} = 31.5$ Hz, *trans*-CO); ^{31}P{^{1}H} NMR: $\delta = 181.9$ ($^1J_{\mathrm{P,W}} = 306.5$ Hz). Anal. Calcd. for $\mathrm{C_{25}H_{34}N_3O_6PSi_2W}$: C, 40.38%; H, 4.61%; N, 5.65%. Found: C, 40.32%; H, 4.68%; N, 5.61%.

{[2-Bis(trimethylsilyl)methyl-4-N-phenylimino-5-N-piperidino-Δ^3*-1,3,2-thiazaphospholene-κP]pentacarbonylchromium(0)}* (**7a**). Yellow crystals (31%, m.p. 68°C); IR (KBr): $\nu_{\mathrm{CO}} = 1914.9$ (vs), 1947.9 (vs), 1983.7 (sh), 2060.8 (s) cm^{-1}; MS (70 eV, EI, ^{52}Cr) $m/z = 627$ [(M)$^+$ (5)], 599 [(M-1CO)$^+$ (30)], 543 [(M-3CO)$^+$ (30)], 487 [(M-5CO)$^+$ (100)], 73 [SiMe$_3^+$ (60)]; $\delta = 0.06$ (s, 9H, SiMe$_3$), 0.21 (s, 9H, SiMe$_3$), 1.56 (d, $^2J_{\mathrm{P,H}} = 3.1$ Hz, PC*H*), 1.69 (m, 6H, $\mathrm{NCH_2C}H_2\mathrm{C}H_2$), 4.04 (m, 4H, $\mathrm{NC}H_2$), 7.29 (m, 5H, Ph); ^{13}C{^{1}H} NMR: $\delta = 2.5$ (d, $^3J_{\mathrm{C,P}} = 3.4$ Hz, SiMe$_3$), 2,7 (d, $^3J_{\mathrm{C,P}} = 1.8$ Hz, SiMe$_3$), 24.7 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 26.4 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 33.1 (d, $^1J_{\mathrm{C,P}} = 11.1$ Hz, P*C*H), 50.2 (s, $\mathrm{N}C\mathrm{H_2}$), 125.7 (s, *o*-Ph), 127.3 (s, *p*-Ph), 129.6 (s, *m*-Ph), 151.0 (s, *i*-Ph), 156.7 (d, $^{(2+3)}J_{\mathrm{C,P}} = 12.8$ Hz, PN*C*), 161.1 (d, $^{(2+3)}J_{\mathrm{C,P}} = 9.2$ Hz, PS*C*), 216.1 (d, $^2J_{\mathrm{C,P}} = 15.0$ Hz, *cis*-CO), 221.6 (d, $^2J_{\mathrm{C,P}} = 5.9$ Hz, *trans*-CO); ^{31}P{^{1}H} NMR: $\delta = 161.6$ (s).

{[2-Bis(trimethylsilyl)methyl-4-N-phenylimino-5-N-piperidino-Δ^3*-1,3,2-thiazaphospholene-κP]pentacarbonylmolybdenum(0)}* (**7b**). The product was obtained only as a mixture with phenyl isothiocyanate; all attempts to separate the starting material via column chromatography or crystallisation failed.

^{13}C{^{1}H} NMR: $\delta = 2.5$ (d, $^3J_{\mathrm{C,P}} = 3.4$ Hz, SiMe$_3$), 2,7 (d, $^3J_{\mathrm{C,P}} = 1.8$ Hz, SiMe$_3$), 24.7 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 26.4 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 33.1 (d, $^1J_{\mathrm{C,P}} = 11.1$ Hz, P*C*H), 50.2 (s, $\mathrm{N}C\mathrm{H_2}$), 125.7 (s, *o*-Ph), 127.3 (s, *p*-Ph), 129.6 (s, *m*-Ph), 151.0 (s, *i*-Ph), 157.2 (d, $^{(2+3)}J_{\mathrm{C,P}} = 12.8$ Hz, PN*C*) 160.7 (d, $^{(2+3)}J_{\mathrm{C,P}} = 9.2$ Hz, PS*C*), 203.5 (d, $^2J_{\mathrm{C,P}} = 7.9$ Hz, *cis*-CO), 205.4(d,$^2J_{\mathrm{C,P}} = 30.0$ Hz, *trans*-CO); ^{31}P{^{1}H} NMR: $\delta = 135.2$ (s).

{[2-Bis(trimethylsilyl)methyl-4-N-phenylimino-5-N-piperidino-Δ^3*-1,3,2-thiazaphospholene-κP]pentacarbonyltungsten(0)}* (**7c**). Yellow crystals (42%, m.p. 98°C); MS (70 eV, EI, ^{184}W) $m/z = 759$ [M$^+$ (5)], 731 [(M-1CO)$^+$ (30)], 675 [(M-3CO) $^+$(25)], 647 [(M-4CO)$^+$ (25)], [(M-5CO)$^+$ (100)], 73 [SiMe$_3^+$ (60)]; ^{13}C{^{1}H} NMR: $\delta = 2.5$ (d, $^3J_{\mathrm{C,P}} = 3.4$ Hz, SiMe$_3$), 2,7 (d,$^3J_{\mathrm{C,P}} = 1.8$ Hz, SiMe$_3$), 24.7 (s, $\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 26.4 (s, $\mathrm{NCH_2}C\mathrm{H_2}$), 33.1 (d, $^1J_{\mathrm{C,P}} = 11.1$ Hz, P*C*H), 50.2 (s, $\mathrm{N}C\mathrm{H_2}$), 125.7 (s, *o*-Ph), 127.3 (s, *p*-Ph), 129.6 (s, *m*-Ph), 151.0 (s, *i*-Ph), 157.7 (d, $^{(2+3)}J_{\mathrm{C,P}} = 12.8$ Hz, PN*C*), 160.9 (d, $^{(2+3)}J_{\mathrm{C,P}} = 9.2$ Hz, PS*C*), 197.5 (d, $^2J_{\mathrm{C,P}} = 7.9$ Hz, *cis*-*C*O), 200.9 (d, $^2J_{\mathrm{C,P}} = 30.0$ Hz, *trans*-CO); ^{31}P{^{1}H} NMR: $\delta = 105.8$ ($^1J_{\mathrm{P,W}} = 287.1$ Hz). Anal. Calcd. for $\mathrm{C_{25}H_{34}N_3O_5PSSi_2W}$: C, 39.53%; H, 4.51%; N, 5.53%; S, 4.22%. Found: C,39.24%; H, 4.77%; N, 5.35%; S, 4.35%.

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