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Reaction of a Diphosphene Complex with Dimethylcyanamide

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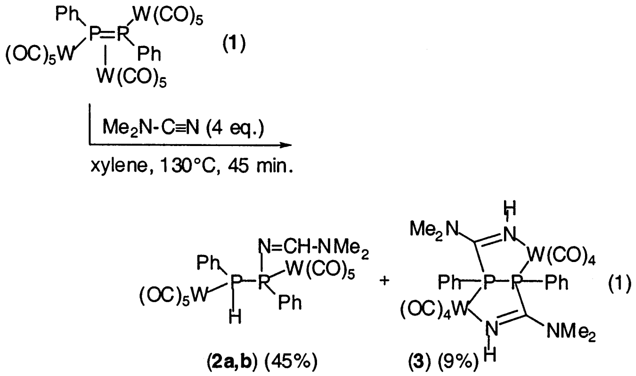
*Summary: The reaction of the diphenyldiphosphene-$[W(CO)_5]_3$ complex **1** with N,N-dimethylcyanamide affords complex **2**, resulting from the formal addition of one H and one N═CH−NMe_2 unit onto the P═P double bond of **1** as the major product. A bicyclic complex (**3**) probably resulting from an initial substitution of one cis-CO of each [P−$W(CO)_5$] group by the cyanamide is also formed. Both **2** and **3** have been characterized by X-ray crystal structure analysis.*

Introduction

Only a few [2+2] cycloaddition reactions have been described with diphosphenes or their complexes.[1] These include the reaction of a metalladiphosphene with electron-poor alkenes,[2] the condensation of a diphosphene complex with alkynes,[3] and the reaction of a metalladiphosphene with an aminophosphaalkyne.[4] In the context of the phosphorus−nitrogen vs phosphorus−carbon analogies,[5] it was interesting to transpose the last reaction with the nitrogen analogues of aminophosphaalkynes.

Results and Discussion

We decided to investigate the reaction of the diphosphene complex **1**[3] with *N*,*N*-dimethylcyanamide. Heating **1** with a 4-fold excess of cyanamide in reflexing xylene led to two products (eq 1).



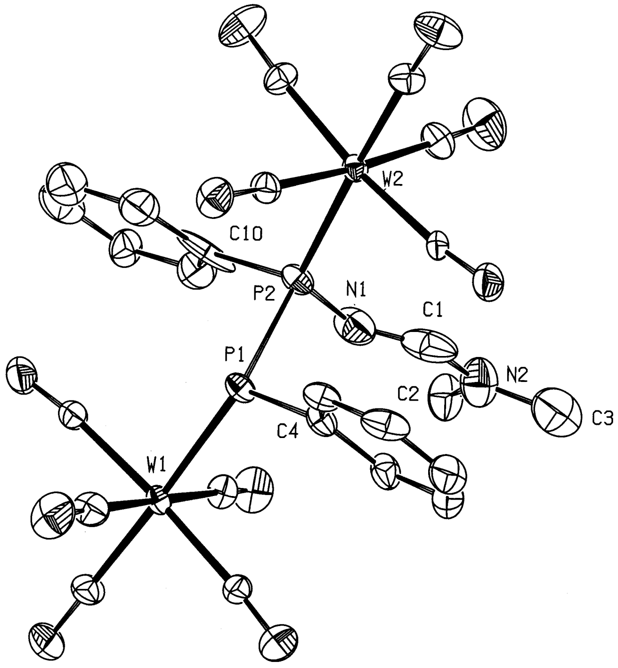


Figure 1. ORTEP drawing of one molecule of **2a**. Selected bond lengths (Å) and angles (deg): P(1)−W(1) 2.519(2), P(1)−C(4) 1.813(8), P(1)−P(2) 2.258(3), P(2)−C(10) 1.86(1), P(2)−N(1) 1.64(1), P(2)−W(2) 2.512(2), N(1)−C(1) 1.27(2), N(2)−C(1) 1.38(1), N(2)−C(2) 1.43(1), N(2)−C(3) 1.40(1); C(4)−P(1)−W(1) 117.2(2), C(4)−P(1)−H 97(4), C(4)−P(1)−P(2) 103.6(3), P(2)−P(1)−W(1) 123.2(1), N(1)−P(2)−C(10) 100.4(5), N(1)−P(2)−P(1) 101.7(3), C(10)−P(2)−P(1) 97.4(3), N(1)−P(2)−W(2) 122.1(3), C(10)−P(2)−W(2) 115.7(3), P(1)−P(2)−W(2) 115.6(1), C(1)−N(1)−P(2) 119.7(8), C(1)−N(2)−C(3) 118(1), C(1)−N(2)−C(2) 119(1), C(3)−N(2)−C(2) 122(1).

The major product (**2**) is a mixture of two diastereomers and incorporates a P−P and a P−H bond as shown by its ^{31}P NMR spectrum. **2a** (65%): δ^{31}P ($CDCl_3$) −7.7, $^1J_{PP}$ = 114.6 Hz, $^1J_{PH}$ = 320 Hz (PH); +69.2 (P−N). **2b** (35%): δ^{31}P −1.8, $^1J_{P-P}$ = 145 Hz, $^1J_{P-H}$ = 322 Hz (PH); +65.7 (P−N). The major isomer was crystallized in CH_2Cl_2. The X-ray crystal structure analysis (Figure 1) demonstrates that **2** results from the formal addition of the diphosphene to the cyanamide +2H. Noteworthy are the planarity of the NMe_2 nitrogen and the delocalization of the N═CH−NMe_2 unit. The most likely mechanism for the formation of **2** implies the initial formation of a zwitterionic adduct (**4**) by nucleophilic attack of the C≡N nitrogen onto the P═P double bond. It is interesting to note that a similar adduct has been

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(1) Review: Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

(2) Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

(3) Tran Huy, N. H.; Inubushi, Y.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 2506.

(4) Grobe, J.; Le Van, D.; Pohlmeyer, T.; Krebs, B.; Conrad, O.; Dobbert, E.; Weber, L. *Organometallics* **1998**, *17*, 3383.

(5) Reviews: Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998. Mathey, F. *Angew. Chem., Int. Ed.*, in press.

10.1021/om021016w CCC: $25.00

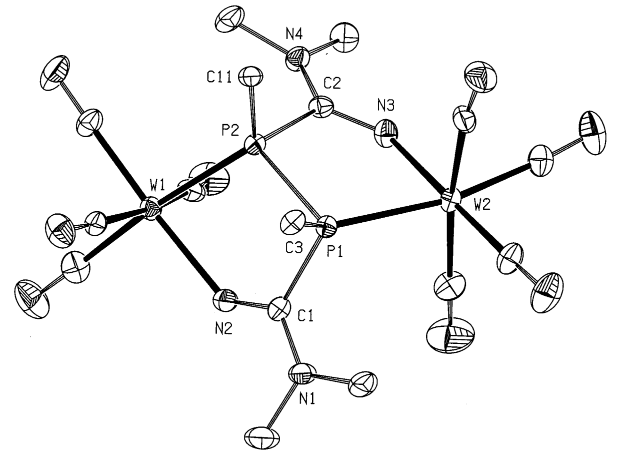
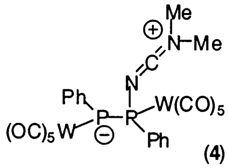
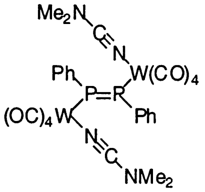


Figure 2. ORTEP drawing of one molecule of **3**. Phenyls are omitted for clarity. Selected bond lengths (Å) and angles (deg): W(1)−N(2) 2.250(4), N(2)−C(1) 1.303(7), C(1)−N(1) 1.341(6), C(1)−P(1) 1.872(6), P(1)−C(3) 1.820(6), P(1)−P(2) 2.245(2), P(1)−W(2) 2.480(2), P(2)−W(1) 2.469(2), P(2)−C(2) 1.863(6), P(2)−C(11) 1.816(5), C(2)−N(4) 1.342(6), C(2)−N(3) 1.299(7), N(3)−W(2) 2.235(4); P(2)−W(1)−N(2) 79.1(1), W(1)−N(2)−C(1) 133.9(4), N(2)−C(1)−P(1) 118.1(4), C(1)−P(1)−P(2) 98.2(2), P(1)−P(2)−W(1) 107.01(6), C(1)−P(1)−C(3) 101.0(3), C(3)−P(1)−P(2) 99.8(2).

postulated in the reaction of $^{i}Pr_2N-C{\equiv}P$ with a metalladiphosphene.[4]



(4)



(5)

However in our case, the zwitterion does not cyclize but abstracts 2H from the solvent. The formation of the secondary product (**3**) has a completely different origin. It is known that cyanamides are good ligands via their C≡N nitrogen.[6] Substitution of one *cis*-CO on both W(CO)$_5$ groups yields the intermediate complex **5**, which can cyclize to give **3** upon abstraction of hydrogen from the solvent. The structure of **3** has been unambiguously established by X-ray analysis (Figure 2). Once again, the NMe$_2$ nitrogen is planar and the delocalization of the N=C−N unit appears even more effective than in the case of **2a**. When comparing the reactions of $R_2N-C{\equiv}P$[4] and $R_2N-C{\equiv}N$ with a P=P unit, it is striking to see that the final products are quite different, whereas the postulated intermediates are similar. Two parameters might explain this difference: (1) the cyanamide is a much better donor than the phosphaalkyne; (2) the P=P substrate is apolar in the first case and highly polarized in the second case. More work would be needed to understand the outcome of these reactions.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4 (^{31}P). Elemental analyses were performed by the Service de microanalyse du CNRS, Gif-sur-Yvette, France

Diphosphine Complexes (2a,b). A solution of the diphosphene complex **1** (350 mg, 3×10^{-4} mol) and *N*,*N*-dimethylcyanamide (0.1 mL, 12×10^{-4} mol) in xylene (3 mL) was heated at 130 °C for 45 min. After evaporation of the solvent, the residue was chromatographed on silica gel with 4:1 hexane/CH$_2$Cl$_2$ as the eluent. Complex **2** was isolated as white crystals (125 mg, 45%).

Complex 2a. ^{1}H NMR (CDCl$_3$): δ 3.13 (s, Me), 3.23 (s, Me), 6.17 (dd, $^1J_{H-P} = 320$ Hz, $^2J_{H-P} = 14$ Hz, PH), 7.68 (d, $^3J_{H-P} = 21.9$ Hz, CH=N). ^{13}C NMR (CDCl$_3$): δ 34.24 (s, Me), 39.92 (s, Me), 163.43 (dd, $^2J_{CP} = 22.3$ Hz, $^3J_{CP} = 5.4$ Hz, CH=N). Anal. Calcd for $C_{25}H_{18}O_{10}N_2P_2W_2$: C, 32.08; H,1.94. Found: C, 32.06; H, 2.04.

Complex 2b. ^{1}H NMR (CDCl$_3$): δ 3.09 (s, Me), 3.15 (s, Me), 5.95 (dd, $^1J_{H-P} = 322$ Hz, $^2J_{H-P} = 14$ Hz, PH), 7.80 (d, $^3J_{H-P} = 22.3$ Hz, CH=N). ^{13}C NMR (CDCl$_3$): δ 33.92 (s, Me), 39.89 (s, Me), 162.00 (dd, $^2J_{CP} = 19.5$ Hz, $^3J_{CP} = 4.8$ Hz, CH=N).

Complex 3. The chromatographic purification was carried out with 2:1 hexane/CH$_2$Cl$_2$ as the eluent. Complex **3** was isolated as yellow crystals (25 mg, 9%). ^{31}P NMR (CDCl$_3$): δ 34.0 (dd, $^1J_{P-W} = 161.5$ Hz, $^2J_{P-W} = 67.2$ Hz). ^{1}H NMR (CDCl$_3$): δ 2.98 (s, NMe$_2$), 6.39 (pseudo t, NH). ^{13}C NMR (CDCl$_3$): δ 53.9 (s, NMe$_2$), 177.6 (m, C=N).

Crystallographic data for 2a: $C_{25}H_{18}N_2O_{10}P_2W_2$; M = 936.05 g/mol; triclinic; space group $P\bar{1}$; $a = 9.847(1)$ Å, $b = 10.539(1)$ Å, $c = 14.951(1)$ Å, $\alpha = 89.360(1)°$, $\beta = 76.650(1)°$, $\gamma = 78.000(1)°$, $V = 1475.6(2)$ Å^3; $Z = 2$; $D = 2.107$ g cm^{-3}; $\mu = 7.954$ cm^{-1}; $F(000) = 880$. Crystal dimensions $0.20 \times 0.12 \times 0.06$ mm. Total reflections collected 11 828 and 7167 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.047; $R(I>2\sigma(I)) = 0.0473$, wR2 = 0.1217(all data); maximum/minimum residual density 2.894(0.235)/−3.141(0.235) e Å^{-3}.

Crystallographic data for 3: $C_{27}H_{25}Cl_3N_4O_8P_2W_2$; M = 1069.50 g/mol; monoclinic; space group $P2_1/c$; $a = 9.867(5)$ Å, $b = 11.807(5)$ Å, $c = 30.100(5)$ Å, $\beta = 98.580(5)°$, $V = 3467(2)$ Å^3; $Z = 4$; $D = 2.049$ g cm^{-3}; $\mu = 7.005$ cm^{-1}; $F(000) = 2032$. Crystal dimensions $0.20 \times 0.12 \times 0.06$ mm. Total reflections collected 17 494 and 8036 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.101; $R(I>2\sigma(I)) = 0.0421$, wR2 = 0.1131(all data); maximum/minimum residual density 3.730(0.223)/−3.947(0.223) e Å^{-3}.

Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation ($\lambda = 0.71073$ Å).

Supporting Information Available: Full details of the crystallographic analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) See for example: Desjardins, P.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1999**, *38*, 5901. Ferreira, C. M. P.; da Silva, M. F. C. G.; da Silva, J. J. R. F.; Pombeiro, A. J. L.; Kukushkin, V. Y.; Michelin, R. A. *Inorg. Chem.* **2001**, *40*, 1134. Fairlie, D. P.; Jackson, W. G.; Skelton, B. W.; Wen, H.; White, A. H.; Wickramasinghe, W. A.; Woon, T. C.; Taube, H. *Inorg. Chem.* **1997**, *36*, 1020.