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Synthesis of the first 1,2,3,4-azatriphospholene complex†

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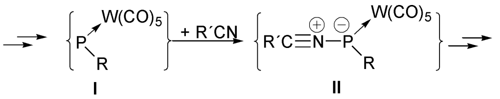
Synthesis of the first 1,2,3,4-azatriphospholene complex was achieved by heating a solution of a *P*-phenyl-substituted 7-phosphanorbornadiene tungsten complex and triphenylphosphonio cyanomethylide, whereby CH-insertion products were formed in a competing reaction; these results also provide first evidence for the ability of electrophilic terminal phosphanediyl complexes to react at the ylide carbon atom and at the carbonitrile nitrogen atom of Wittig-ylides having a nitrile functional group; the structures of both complexes were established through X-ray single-crystal diffraction studies.

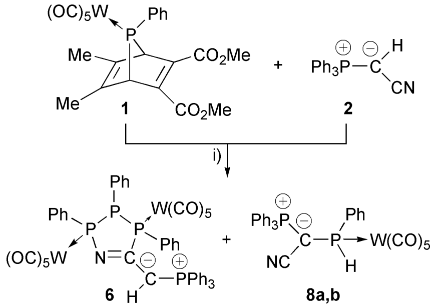
The transition-metal-promoted synthesis of P-heterocycles is of current interest because of the frequently outstanding reaction selectivities and product yields.[1] Recently, we presented a new concept in phosphorus-heterocycle synthesis, which relies on trapping reactions[2–5] of short-lived nitrilium phosphanylide complexes **II**, a new 1,3-dipole system, with alkynes or nitriles. Apart from ring opening of 2*H*-azaphosphirene complexes,[2] we demonstrated that the formation of **II** can be achieved *via* 1,1-addition of thermally generated electrophilic terminal phosphanediyl complexes **I** to carbonitriles (Scheme 1), using two different precursor systems of **I**, 2*H*-azaphosphirene complexes[6] and 7-phosphanorbornadiene complexes.[7] According to theoretical calculations[8] such 1,1-addition reactions are weakly exothermic.

Because of our interest in exploiting the synthetic potential of reactive intermediates of type **II** having small substituents at phosphorus, we started a preliminary investigation on the reactivity of a *P*-phenyl-substituted 7-phosphanorbornadiene complex towards carbonitriles with Wittig-ylide substituents *in the absence* of alkynes. Here we report the synthesis of the first 1,2,3,4-azatriphospholene complex and atropisomeric CH-insertion products. The compounds were obtained in pure form by column chromatography and fully characterized by various means; both complexes were characterized additionally by X-ray diffraction studies.

Heating 1,2-dichlorobenzene solutions of *P*-phenyl-substituted 7-phosphanorbornadiene tungsten complex **1**[9] and triphenylphosphonium cyanomethylide **2**[10] for 2 h afforded the 1,2,3,4-azatriphospholene complex **6** and the PH-substituted complexes **8a**,**b** (**6**:**8a** ratio 3:5) (Scheme 2); only small amounts of **8b** were formed (*ca.* 10% of **8a**), as observed by ^{31}P NMR spectroscopy. The complexes **6** and **8a** were confirmed by elemental analyses, NMR spectroscopy and mass spectrometry.‡ The formation of **6** can be explained by assuming a [3 + 2] cycloaddition of two transiently formed species, the nitrilium phosphanylide complex **4**, as the 1,1-addition product of the carbonitrile **2** and the terminal phosphanediyl complex **3**, and the diphosphene tungsten complex **5**, *cf.* ref. 11. In contrast, the formation of the atropisomers **8a** and **8b** as CH-insertion products points to an initial attack of the phosphorus atom of **3** at the ylide carbon atom of the Wittig-ylide **2**, thus forming transiently complex **7** that rearranges to furnish **8a**,**b** (Scheme 3). Altogether, this reaction provides first evidence for the ability of electrophilic terminal phosphanediyl complexes to react at the ylide carbon atom and at the carbonitrile nitrogen atom of Wittig-ylides.

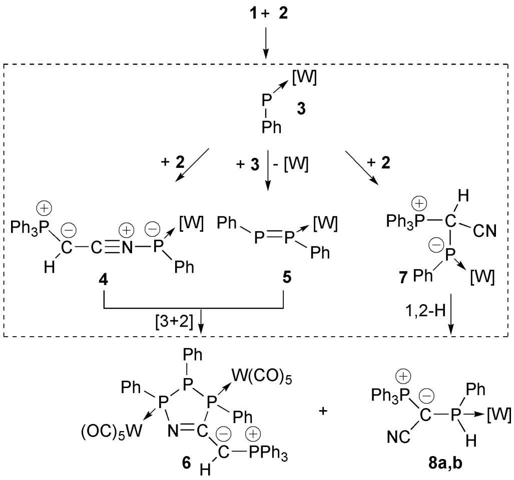


Scheme 1 Generation of nitrilium phosphanylide tungsten complexes **II** using 1,1-addition reactions of carbonitriles and electrophilic terminal phosphanediyl tungsten complexes **I** (R, R′ = organic substituents).



Scheme 2 *Reagents and conditions*: i) 0.60 g (0.9 mmol) of complex **1** and 0.28 g (0.9 mmol) of carbonitrile **2**, 5.5 mL 1,2-dichlorobenzene, 125 °C, 2 h; column chromatography (SiO$_2$, −5 °C, *n*-pentane/diethyl ether 50:50); **6**: yellow solid, yield: 17 %, mp 179 °C (decomp.); **8a**: brown solid, yield: 15%, mp 65 °C (decomp.).

The ^{31}P{^{1}H} NMR spectra of complexes **6** and **8a**,**b** showed the expected pattern of such spin systems, *e.g.* the spectrum of **6** involves four distinctly different resonances for the four inequivalent phosphorus nuclei. Therefore, they could be interpreted as first-order spectra (for **6** see footnotes). The AB-spin system of **8a** displayed resonances at δ 26.0 and −28.6 ($|^2J(\mathrm{PP})|$ 11.7 Hz (**8b**: δ 27.0 and –30.2, $|^2J(\mathrm{PP})|$ 8.9 Hz), which could be assigned unambiguously because of the phosphorus–hydrogen and tungsten–phosphorus coupling constants (**8a:** δ



Scheme 3 Proposed reaction course for the formation of complexes **6** and **8a**,**b** (enclosed with dotted lines; [W] = W(CO)$_5$).

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† This work is dedicated to Professor O. Scherer.

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-28.6 ($|^1J(\mathrm{PH})|$ 355.5 Hz and $|^1J(\mathrm{WP})|$ 231.7 Hz; **8b**: δ -30.2 ($|^1J(\mathrm{PH})|$ 357.5 Hz and $|^1J(\mathrm{WP})|$ 233.4 Hz). Because of the close resemblance of the NMR parameters of complexes **8a**,**b** we assume that they are atropisomers, which could originate from a hindered rotation of the P(H)PhW(CO)$_5$-moiety around the P–C bond of the ylide carbon atom. The nature of complexes **6** and **8a** was also unambiguously confirmed by ^{13}C{^{1}H} NMR spectroscopy. For example, complex **6** displayed the structurally important imino carbon atom resonance at δ 177.2 as a non-resolved multiplet (pseudo-triplet, $\Sigma|J(\mathrm{P,C})|$ 19.8 Hz). For complex **8a** the carbon resonance at δ 9.0 ppm provides the key information on the atom connectivity of the PCP-moiety (dd, $|^1J(\mathrm{PC})|$ 106.6 Hz and $|^1J(\mathrm{PC})|$ 47.7 Hz). The molecular structures of complexes **6** (Fig. 1) and **8a** (Fig. 2), as established for the solid state by X-ray crystallography,§ show, *e.g.* for **6** an envelope-type conformation of the 1,2,3,4-azatriphospholene ring, whereby (P(4) lies outside the plane (P(1)–N–C(12)–P(3)-moiety torsion angle: 4.8(3)°), an approximately planar N–C(12)–C(13)–P(2)-moiety (torsion angle: $-8.6(4)$°) and a rather short C(13)–C(12) distance of 1.384(4) Å, thus implying some π-electronic delocalization within this moiety; the bond angle sum at C(13) is 360°. The two W(CO)$_5$-moieties are in *cis*-position at the five-membered ring. The molecular structure of complex **8a** shows the tricoordinated C(12) atom with a bond angle sum of 359° and a significantly widened C$_{\mathrm{sp}^2}$-angle P(2)–C(12)–P(1) of 124.19(10)°, which indicates some steric repulsion between the two bulky substituents. The P(1)–C(12) distance 1.7792(16) represents a shortened P–C single bond; the average value for P$_{\mathrm{sp}^2}$–C$_{\mathrm{sp}^2}$ is 1.855 Å.[12] The coordination environment of the P(1) atom is tetrahedral with a P(1)–C(6) distance of 1.8295(16) Å, a P(1)–H(1) distance of 1.29(2) Å and a P(1)–W distance of 2.5122(5) Å.

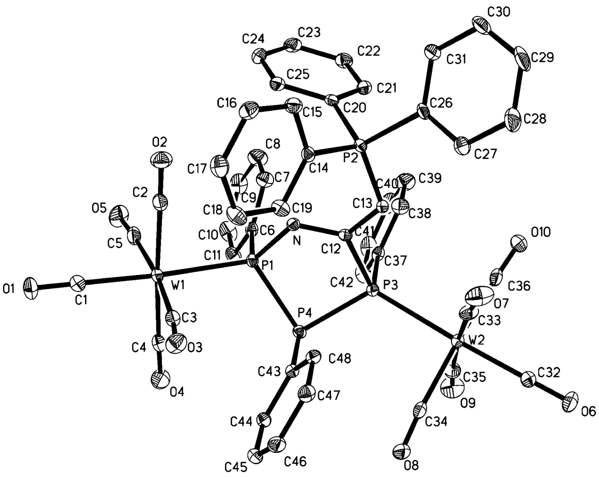

Fig. 1 Molecular structure of **6** in the crystal (ellipsoids represent 50% probability levels). Selected bond lengths [Å] and angles [°]: W(1)–P(1) 2.5154(8), W(2)–P(3) 2.5361(7), P(1)–C(6) 1.827(3), P(3)–C(37) 1.845(3), P(4)–C(43) 1.833(3), P(1)–N 1.665(2), P(3)–C(12) 1.903(3), N–C(12) 1.320(3), P(2)–C(13) 1.732(3), C(12)–C(13) 1.384(4); N–P(1)–P(4) 102.83(8), P(3)–P(4)–P(1) 90.84(4), C(12)–P(3)–P(4) 97.52(9), N–C(12)–P(3) 119.43(19), C(12)–N–P(1) 122.37(19), N–C(12)–C(13) 123.5(2), C(13)–C(12)–P(3) 117.1(2), C(12)–C(13)–P(2) 118.7(2), P(1)–N–C(12)–C(13–176.1(2), N–C(12)–C(13)–P(2)–8.6(4), P(1)–N–C(12)–P(3) 4.8(3), N–P(1)–P(4)–P(3)–22.11(9), C(12)–P(3)–P(4)–P(1) 21.94(9).

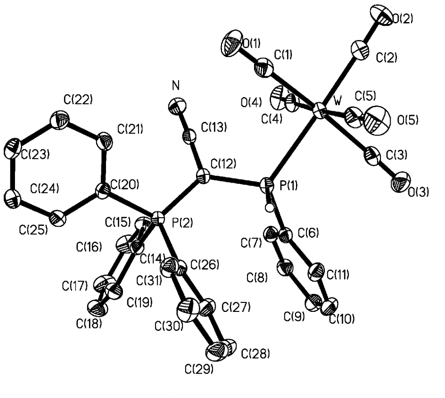

Fig. 2 Molecular structure of **8a** in the crystal (ellipsoids represent 50% probability levels; hydrogen atoms except H(1) are omitted for clarity). Selected bond lengths [Å] and angles [°]: P(1)–W 2.5122(5), P(1)–H(1) 1.2903(0.0232), P(1)–C(6) 1.8295(16), P(1)–C(12) 1.7792(16), C(12)–C(13) 1.415(2), C(13)–N 1.154(2), C(12)–P(2) 1.7283(17); P(2)–C(12)–P(1) 124.19(10), C(13)–C(12)–P(1) 119.06(13), C(13)–C(12)–P(2) 115.92(12), W–P(1)–H(1) 112.97(97), C(6)–P(1)–H(1) 99.42(0.96), C(12)–P(1)–H(1) 104.04(0.98).

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Notes and references

‡ Satisfactory elemental analysis were obtained for complex **6** and **8a**. NMR data were recorded in CDCl$_3$ solutions (295 K) at 50.3 MHz (^{13}C) and 81.0 MHz (^{31}P), using TMS and 85% H$_3$PO$_4$ as standard references; *J*/Hz. *Selected spectroscopic data* for **6** and **8a**,**b**: **6**: ^{31}P{^{1}H} NMR: δ -38.9 [dd, ^1J(PP) 285.2, ^1J(PP) 241.8 Hz, P*P*(Ph)P], 13.9 [d, ^4J(PP) 50.5 Hz, PPh$_3$], 59.2 [ddd, ^1J(PW) 284.1, ^1J(PP) 285.2, ^4J(PP) 50.5, ^3J(PP) 10.9 Hz, N*P*P]; 107.1 [dd, ^1J(PW) 279.2, ^1J(PP) 241.8, ^3J(PP) 10.9 Hz, C*P*P]. **8a**: ^{13}C{^{1}H} NMR: δ 9.0 [dd, ^1J(PC) 106.6, ^1J(PC) 47.7 Hz, PCP], 123.6 [d, ^1J(PC) 90.9 Hz, *i*-PPh$_3$], 126.3 [dd, ^2J(PC) 17.9, ^2J(PC) 8.8 Hz, CN], 128.2 [d, ^2J(PC) 9.7 Hz, *o*-PPh], 129.2 [d, ^3J(PC) 12.5 Hz, *m*-Ph$_3$], 129.6 [d, ^3J(PC) 12.6 Hz, *m*-PPh], 133.4 [d, ^4J(PC) 3.0 Hz, *p*-PPh$_3$], 133.5 [d, ^2J(PC) 10.1 Hz, *o*-PPh$_3$], 134.0 [d, ^4J(PC) 3.0 Hz, *p*-PPh], 139.9 [d, ^1J(PC) 39.8 Hz, *i*-PPh)], 196.7 [d, ^2J(PC) 7.0, ^1J(WC) 126.1 Hz, *cis*-CO], 200.4 [dd, ^2J(PC) 21.2, ^4J(PC) 1.5 Hz, *trans*-CO].

§ *Crystal structure determination* of **6**: C$_{52}$H$_{42}$NO$_{11}$P$_4$W$_2$. *Crystal data*: triclinic, space group $P\bar{1}$, a = 13.5051(8), b = 14.5592(11), c = 14.8611(11) Å, α = 85.462(3), β = 79.491(3), γ = 63.886(3)°, U = 2579.7(3) Å^3, Z = 2, T = -140 °C. *Data collection*: a yellow crystal *ca.* 0.32 × 0.12 × 0.07 mm was used to record 54053 intensities on a Bruker SMART 1000 CCD diffractometer (Mo-Kα radiation, $2\theta_{\max}$ = 60°). Absorption corrections were applied using SADABS. *Structure refinement*: the structure was refined anisotropically on F^2 (program SHELXL-97, G.M. Sheldrick, Univ. of Göttingen) to $wR2$ = 0.0594, $R1$ = 0.0266 for 631 parameters, 125 restraints (to light atom displacement factor components and local ring symmetry) and 15022 unique reflections; S = 0.95, max. $\Delta\rho$ 2.5 and -1.1 e Å^{-3}. The hydrogens were refined using a riding model. *Crystal structure determination* of **8a**: C$_{31}$H$_{21}$NO$_5$P$_2$W. *Crystal data*: monoclinic, space group $P2_1/n$, a = 12.6819(8), b = 17.0312(10), c = 13.7777(8) Å, β = 106.733(3), U = 2849.8(3) Å^3, Z = 4, T = -140 °C. *Data collection*: a brown crystal *ca.* 0.29 × 0.25 × 0.09 mm was used to record 44915 intensities as above. *Structure refinement*: the structure was refined to $wR2$ = 0.0495, $R1$ = 0.0181 for 365 parameters, 56 restraints (to light atom displacement factor components) and 8327 unique reflections; S = 1.04, max. $\Delta\rho$ 1.2 and –1.0 e Å^{-3}. The P-hydrogen was refined freely, others using a riding model.

CCDC reference numbers 175758 and 175759. See http://www.rsc.org/suppdata/cc/b1/b110803b/ for crystallographic data in CIF or other electronic format.

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