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[11] **1**: $a = 964.8(2)$, $b = 1079.9(2)$, $c = 1271.7(3)$ pm, $\alpha = 76.69(3)$, $\beta = 75.67(3)$, $\gamma = 64.67(3)^\circ$, $V = 1148.6(4) \times 10^6$ pm^3; triclinic, space group $P\bar{1}$, $Z = 1$, $\rho_{calcd} = 1.547$ gcm^{-1}, $\mu = 3.258$ mm^{-1}, STOE IPDS2, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 200$ K, $2\theta_{max} = 52^\circ$; 5297 reflections measured, 3692 independent reflections ($R_{int} = 0.0312$), 3690 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-square techniques against F^2, 286 parameters (Pt, P, S, O, C refined anisotropically, H atoms were calculated at ideal positions); $R1 = 0.0401$; $wR2 = 0.1058$ (all data); GOF = 1.058; max. residual electron density 1.032 e Å^{-3}. CCDC 169386 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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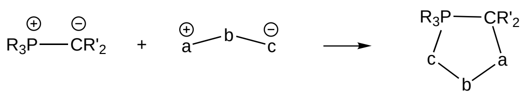
Intramolecular [3+2] Cycloaddition of a Nitrilium Phosphane Ylide Complex to the *P*-Phenyl Group of a Wittig Ylide[**]

Nils Hoffmann, Peter G. Jones, and Rainer Streubel[*]

Dedicated to Professor Masaaki Yoshifuji
on the occasion of his 60th birthday

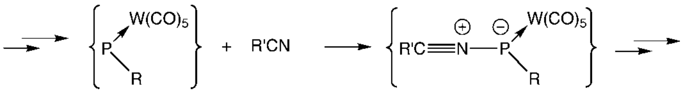
Wittig ylides[1, 2] of the general type $R_3PCR'_2$ **I** are some of the most widely used and thus most extensively investigated phosphorus compounds in organic synthesis; cycloaddition reactions such as those of **I** with 1,3-dipoles **II** belong to the classical repertoire of heterocyclic chemistry. Such reactions, which exploit the P,C-ylide function, generally proceed smoothly and lead to the five-membered phosphorus(v) heterocycles **III** (Scheme 1).[1] Until now, cycloadditions to a *P*-bonded phenyl group of Wittig ylides, involving the former as a 2π-cycloaddition component, were unknown (as indeed were similar reactions involving any other benzene derivatives[3]). Cyclometalations of *P*-phenyl Wittig ylide derivatives are known, but are rare; they have been observed, for example, in reactions with zirconium[4] and platinum[5] complexes.



I **II** **III**

Scheme 1. Cycloaddition of Wittig ylides with 1,3-dipoles (R, R′ = arbitrary organic substituents; a, b, c denote organoelement fragments).

Nitrilium phosphane ylide complexes **VI**, whose existence as intermediates we were able to demonstrate by trapping reactions,[6] now represent a new and well-established 1,3-dipole system in heterocyclic chemistry.[7–9] We recently discovered the 1,1-addition of electrophilic terminal phosphanediyl complexes **IV** to nitriles **V**, providing an independent access to **VI** (Scheme 2), so that the synthetic potential of **VI** could be extended further by the use of 7-phosphanorbornadiene complexes.[10, 11]



IV **V** **VI**

Scheme 2. Formation of nitrilium phosphane ylide complexes by 1,1-addition of electrophilic terminal phosphanediyl complexes with nitriles (R, R′ = arbitrary organic substituents).

For some time we have been investigating the possibility of obtaining kinetically stabilized nitrilium phosphane ylide complexes, in order to study their properties. Promising candidates in this respect are, for example, Wittig ylide derivatives that contain a nitrile function at the ylide carbon atom. Because of their variable stereoelectronic properties, these are potential reaction partners for 1,1-additions to **IV**. Surprisingly, however, heating the 2*H*-azaphosphirene complex **1**[12] in toluene in the presence of the Wittig ylide derivative **2**[13] led diastereoselectively to the new tricycle **5**, whose formation we explain by a [3+2] cycloaddition of the intermediate 1,3-dipole **4** to a phenyl group of **2** (Scheme 3). Monitoring the reaction by ^{31}P NMR spectroscopy indeed revealed the appearance and disappearance of a further product ($\delta = 22.3$ (d, J(P,P) = 10.8, ^1J(W,P) = 243.9 Hz) and -0.7 (d)), which however could not be more precisely characterized because it was a minor component of the product mixture. A previous study using other, sterically more demanding, ylide-*C*-substituted triorganosilyl derivatives of **2** provided support for our interpretation via 1,1-addition as a primary step, in that here also the same tricyclic ring systems were formed as in **5**.[14] The results presented here are also interesting in view of recently reported first examples of reactions of other benzene derivatives with μ^1- and μ^2-phosphanediyl complexes. In the first case a [5]metacyclophane[15] reacted as a 4π-cycloaddition component,[16] whereas the second example involved the phenyl group of benzonitrile

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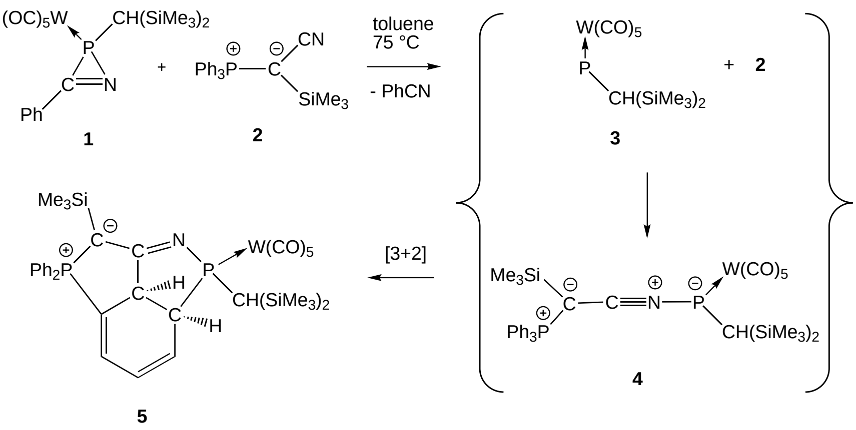


Scheme 3. Suggested reaction sequence for the formation of complex **5**.

in a complicated reaction sequence of C–H activation and cyclization[17]—the aromatic 6π-electron system, however, remained intact.

The constitution of complex **5** was established from NMR and MS data[18] and confirmed (Figure 1) by X-ray structure analysis.[19] The presence in solution of the tricycle **5** (rather than the isomeric nitrilium phosphane ylide complex **4**) is

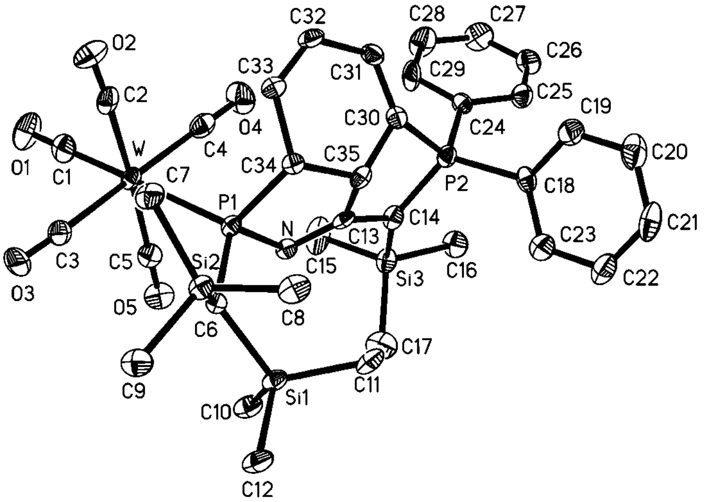
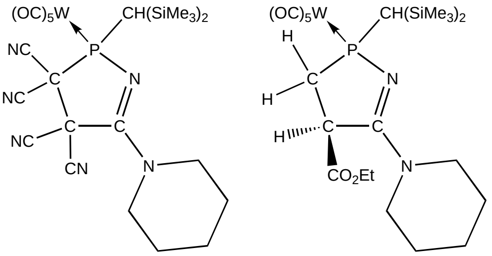


Figure 1. Molecular structure of complex **5** in the crystal (ellipsoids represent 50 % probabilities; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: W-P1 2.5172(15), P1-C6 1.846(6), P1-N 1.693(4), P1-C34 1.903(6), C13-N 1.299(7), C13-C14 1.433(2), P2-C14 1.721(7), P2-C30 1.802(6), C30-C35 1.498(8), C35-C13 1.541(8), C35-C34 1.536(7), C34-C33 1.498(8); N-P1-C34 95.8(2), P1-C34-C35 103.0(4), C34-C35-C13 108.5(5), C35-C13-N 117.8(5), C13-N-P1 113.2(4), P2-C14-Si3 128.5(3), C13-C14-P2 107.3(4), C13-C14-Si3 123.1(5).

unambiguously shown by the observation of two resonance signals from both four-coordinate carbon atoms of the former phenyl ring at $\delta = 54.2$ and 50.5. The identification of the signals was facilitated by significant differences in the magnitudes of the coupling constants, for example 75.7 and 13.2 Hz for the carbon atom bonded to the 1,2-azaphosphole phosphorus. The $^{13}C\{^1H\}$ NMR data of the 1,2-azaphosphole moiety of complex **5** are generally similar to values of related compounds, for example, the 3,3′,4,4′-tetracyano-1,2-azaphospholene-tungsten complex **6a**[20] (Figure 2); the marked deshielding of the imino carbon atom in complex **5** ($\delta = 183.6$, cf. $\delta = 144.9$ in **6a**) is thus unexpected. A comparison of the ^{31}P NMR data of **5** and **6a** is also interesting; the resonance signal of the 1,2-azaphosphole phosphorus atom in **5** ($\delta = 159.8$) is very close to that of **6a** ($\delta = 158.5$), which is surprising in view of the differing substitution patterns at the sp^3 carbon atoms of the 1,2-azaphosphole moieties.

The molecular structure of complex **5** confirms the assumption of a cisoid linkage of the terminal atoms of the 1,3-dipole with the C_2 element of the phenyl group, and shows a marked cyclohexa-1,3-diene structure for the ring (C33–C32 1.319(8), C32–C31 1.452(8), C31–C30 1.333(8) Å). Otherwise, most dimensions of the 1,2-azaphosphole moiety are as expected and correspond closely to those of the 1,2-azaphosphole-tungsten complex[21] **6b** (Figure 2), except for the P1–C34 distance in **5** of 1.903(6) Å (1.851(5) Å in **6b**). The former value indicates a significantly lengthened single bond (the standard value of a C_{sp^3}–P^{III} single bond is 1.855 Å).[22] The tricyclic ring system in **5** displays the approximate shape of a flattened dish, in which the atom C35 marks the lowest point of the ring framework, lying 0.5 Å from the plane C13-C30-C34. The pentacarbonyltungsten group is *endo* at P1.



6a **6b**

Figure 2. Complexes **6a** and **6b**.

Experimental Section

5: A solution of complex **1** (0.62 g, 1 mmol) and the Wittig ylide **2** (0.38 g, 1 mmol) in toluene (6 mL) was heated with constant stirring to 75 °C for about 2 h; the end of the reaction was determined by ^{31}P NMR spectroscopy. The solution was evaporated to dryness in vacuo (ca. 0.1 mbar) and the residue was separated by column chromatography (SiO_2, –15 °C, petroleum ether/diethyl ether 2:1). Removal of the solvent and recrystallization from diethyl ether at –20 °C gave **5** as yellow crystals. Yield: 0.48 g (51 %), m.p. 61 °C (decomp); ^1H NMR (200.0 MHz, $CDCl_3$, 25 °C, ext. TMS): $\delta = 0.01$ (s, 9H; $SiMe_3$), 0.19 (s, 9H; $SiMe_3$), 0.26 (s, 9H; $SiMe_3$), 1.73 (d, $^2J(P,H) = 10.0$ Hz, 1H; C*H*($SiMe_3$)$_2$), 3.37 (m, 1H; CH), 3.60 (dd, $^2J(P,H) = 17.0$ Hz, $^4J(P,H) = 6.4$ Hz, 1H; CH), 6.10 (m, 2H; sp^2-CH), 6.34 (m, 1H; sp^2-CH), 7.35 (m, 4H; Ph), 7.60 (m, 4H; Ph), 7.86 (m, 2H; Ph); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C, ext. TMS): $\delta = 0.9$ (d, $J(P,C) = 2.4$ Hz; $SiMe_3$), 2.4 (d, $J(P,C) = 2.6$ Hz; $SiMe_3$), 2.5 (s; $SiMe_3$), 30.3 (d, $^1J(P,C) = 13.3$ Hz; *C*H($SiMe_3$)$_2$), 39.7 (m br; P*C*CN), 50.5 (dd, $J(P,C) = 22.1$ Hz, $J(P,C) = 15.3$ Hz; CHP), 54.2 (dd, $J(P,C) = 75.7$ Hz, $J(P,C) = 18.5$ Hz; CHP), 120.2 (dd, $J(P,C) = 12.8$ Hz, $J(P,C) = 8.5$ Hz; sp^2-CH), 124.1 (pt, $J(P,C) = 4.3$ Hz; sp^2-CH), 125.1 (dd, $^1J(P,C) = 86.5$ Hz, $^3J(P,C) = 4.9$ Hz; sp^2-CP), 125.3 (d, $^1J(P,C) = 88.8$ Hz; *ipso*-Ph), 126.2 (d, $^1J(P,C) = 80.4$ Hz; *ipso*-Ph), 128.9 (d, $^3J(P,C) = 12.8$ Hz; *m*-Ph), 129.2 (d, $^3J(P,C) = 12.0$ Hz; *m*-Ph), 130.1 (pt, $J(P,C) = 3.6$ Hz; sp^2-*C*H), 132.5 (d, $^2J(P,C) = 10.6$ Hz; *o*-Ph), 132.6 (d, $^4J(P,C) = 4.4$ Hz; *p*-Ph), 133.2 (d, $^4J(P,C) =$

3.1 Hz; *p*-Ph), 134.0 (d, ^3J(P,C) = 11.2 Hz; *o*-Ph), 183.6 (dd, ^2J(P,C) = 16.4 Hz, ^2J(P,C) = 10.7 Hz; PC*C*N), 198.9 (d, ^2J(P,C) = 7.9 Hz; *cis*-CO), 202.5 (d, ^2J(P,C) = 23.4 Hz; *trans*-CO); ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 25 °C, ext. 85 % H_3PO_4): $\delta = 46.4$ (d, ^4J(P,P) = 5.1 Hz; PPh_2), 159.8 (d, ^1J(W,P) = 260.9 Hz; PW).

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[18] **5**: MS (positive-ion FAB (nitrobenzyl alcohol), ^{184}W): m/z (%) 888 (20) $[M+H]^+$, the isotope pattern is in agreement with calculation.

[19] Crystal structure of complex **5** ($C_{35}H_{43}NO_5P_2Si_3W$): triclinic, space group $P\bar{1}$, $a = 10.9277(12)$, $b = 13.3245(16)$, $c = 13.7618(16)$ Å, $\alpha = 90.325(6)$, $\beta = 91.388(6)$, $\gamma = 103.281(6)°$, $V = 1934.9$ Å^3, $Z = 2$, $\mu = 5.0$ mm^{-1}, $T = -140$ °C. A yellow tablet with dimensions of about 0.1 × 0.1 × 0.03 mm was mounted in perfluoropolyether oil on a Bruker SMART 1000 CCD diffractometer. Intensity data were registered to $2\theta_{max.} = 52°$ ($Mo_{K\alpha}$). Of a total of 24130 reflections, 7889 were independent ($R_{int} = 0.073$). After a semiempirical absorption correction (SADABS), the structure was solved with the heavy-atom method and refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen. Hydrogen atoms were included by using a riding model or as rigid methyl groups. Final $wR2$ (all data) = 0.0808, conventional $R1 = 0.042$, 433 parameters; $S = 0.922$; max. $\Delta\rho = 1.861/-1.953$ e Å^{-3}. CCDC-173084 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Self-Assembly of ZnO: From Nanodots to Nanorods**

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Horst Weller*

Bottom-up techniques for the fabrication of small particles, which mostly arise from colloid chemistry, are integral components in nanotechnology and materials manufacturing. Control of particle size, shape, and crystalline structure represent some of the key issues in this area. Classical models describe the genesis of particles by the formation of tiny crystalline nuclei in a supersaturated medium followed by crystal growth. The latter process is controlled by mass transport and by the surface equilibrium of addition and removal of individual monomers, that is atoms, ions, or molecules. Hereby, the driving force for monomer removal (dissolution) increases with decreasing particle size. Thus, within an ensemble of particles with slightly different sizes the large particles will grow at the cost of the small ones. This mechanism is called Ostwald ripening and is generally believed to be the main path of crystal growth.

A different view of crystal growth is emerging from recent experiments by Penn and Banfield.[1–3] They observed that anatase and iron oxide nanoparticles with sizes of a few nm can coalesce under hydrothermal conditions in a way they call "oriented attachment". In the so formed aggregates, the crystalline lattice planes may be almost perfectly aligned or dislocations at the contact areas between the adjacent particles lead to defects in the finally formed bulk crystals. They presented strong evidence that this type of crystal growth plays an important role in earth history during mineral formation. Oriented attachment was also proposed by other authors during crystal growth of TiO_2[4] and for micrometer-sized ZnO particles during the formation of rodlike ZnO microcystals.[5] The latter experiments give, however, only indirect evidence.

Self-assembly of colloidal particles into larger aggregates is not principally new. The formation of secondary particles with typical sizes in the micrometer regime is a well-known phenomenon in classic colloid chemistry.[6] Kinetic models for this type of growth have been developed which do, however, not consider the process on an atomic level nor give attention to crystallographic orientation of the aggregated particles. Indeed, the X-ray diffraction (XRD) pattern of those secondary particles usually indicate polycrystalline morphology.

Recently, self-assembly of ligand-stabilized nanoparticles with sizes of a few nanometer into two- and three-dimen-

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