P–P Insertions

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Metal-Assisted, Reversible Phosphinyl Phosphination of the Carbon–Nitrogen Triple Bond in a Nitrile

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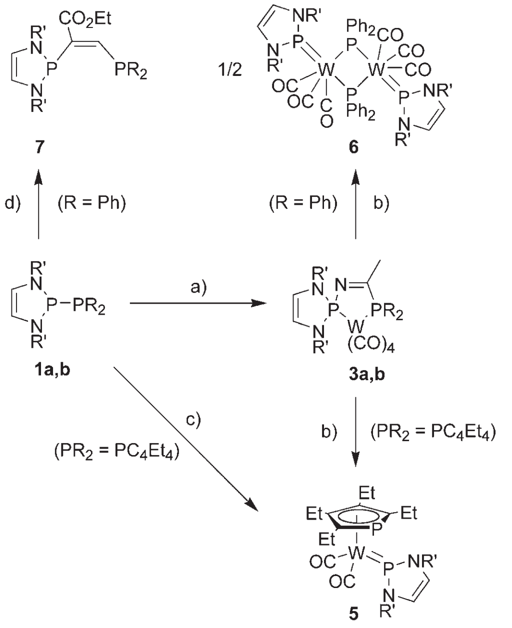
Bidentate ligands have a long standing in organometallic chemistry, coordination chemistry, and catalysis. For their synthesis, additions to alkenes that allow simultaneous introduction of two donor groups to an organic backbone have recently gained attention. The largest progress has been made in the field of O,O and N,N ligands, for which protocols for stereo- and even enantioselective dihydroxylation[1] or diamination of olefins[2] have been worked out. Viable approaches to P,P-donor ligands, which are likewise of great significance, by diphosphination of organic precursors have been found in the double metathesis of 1,2-disubstituted olefins,[3] or in the addition of the P–P bonds of diphosphines to alkenes[4] or alkynes.[5,6]

We have recently described the N-heterocyclic phosphines **1**[4] (Scheme 1), which are distinguished by exceptionally reactive P–P bonds and undergo phosphinyl phosphination of alkenes to yield hybrid bisphosphines that have two donor sites with different electronic properties. Specimen of this type have received great interest as ligands in catalysis.[7] We have now discovered an unprecedented metal-assisted addition of **1** to the triple bond of a nitrile, which offers a surprisingly simple access to complexes of hybrid 1,2-bisphosphines. Quite interestingly, the addition is reversible and permits controlled conversion of the formed complexes into species that arise formally from metal insertion into the P–P bond of **1**.

While exploring the coordination properties of **1a**, we treated an acetonitrile solution of the diphosphine with the tungsten complex **2**. A color change from orange to green indicated the formation of a new product, which was isolated by crystallization and identified as a bisphosphine complex by observation of an AX pattern with ^{183}W satellites on both signals in the $^{31}P\{^1H\}$ NMR spectrum (see the Experimental Section). The anticipated presence of a chelate complex of **1** was, however, ruled out as the ^1H and ^{13}C NMR spectra gave evidence for a CH_3C fragment that could not be accounted for. Unambiguous structural assignment was finally feasible from a single-crystal X-ray diffraction study,[8] which showed the presence of the chelate complex **3a**, which features a hybrid 1,2-bisphosphine ligand arising from addition of the P–P bond of **1a** to the triple bond of acetonitrile (Scheme 1).



Scheme 1. PR_2 = 2,3,4,5-tetraethylphospholyl, R′ = Mes (**1a**, **3a**, **5**); R = Ph, R′ = 2,6-$Me_2C_6H_3$ (**1b**, **3b**, **6**, **7**). Reagents and conditions: a) 1 equiv $[W(CO)_4(cod)]$ (**2**), MeCN, 20 °C (for **1a**) or 50 °C (for **1b**); b) 185 °C; c) 1 equiv $[W(CO)_3(MeCN)_3]$ (**4**), 20 °C, toluene; d) 1 equiv ethyl propiolate, toluene, 0–20 °C; cod = cycloocta-1,5-diene, Mes = 2,4,6-$Me_3C_6H_2$.

The crystals of **3a** (Figure 1) contain discrete complexes with a distorted octahedral coordination at the tungsten atom that results mainly from the small bite angle of the chelate ligand (P2-W1-P1 79.33(4)°). The bond lengths in the diazaphospholene and phosphole rings differ by less than 0.02 Å from those in free **1a**.[4] The chelate ring is nearly planar (deviations from mean plane less than 0.07 Å). The bonds W1–P2 (2.450(1) Å) and W1–P1 (2.459(1) Å) are very similar and shorter than known bond lengths in {bis(phosphine)$W(CO)_4$} complexes ((2.50 ± 0.02) Å[9]), regardless of the different environment of the donor atoms (N_3 vs. C_3 substituent pattern). The bonds N1–P1 (1.766(4) Å) and C1–P2 (1.888(5) Å) are notably longer than the P–N and P–C bonds in the diazaphospholene and phosphole rings. All these features point to the strengthening of the W–P bonds by substantial metal-to-ligand back donation, which occurs at the expense of weakening of the N1–P1 and C1–P2 bonds by hyperconjugation.

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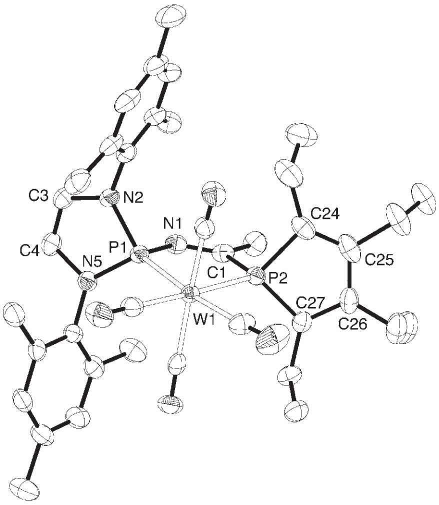

Figure 1. Molecular structure of **3a** in the solid state (H atoms omitted; 50% probability thermal ellipsoids). Selected bond lengths [Å] and angle [°]: W1-P2 2.450(1), W1-P1 2.459(1), N1-C1 1.270(6), N1-P1 1.766(4), C1-P2 1.888(5), P1-N5 1.688(4), P1-N2 1.692(4), N2-C3 1.418(6), C3-C4 1.327(7), C4-N5 1.417(6), P2-C24 1.803(5), P2-C27 1.807(5), C24-C25 1.354(7), C25-C26 1.466(7), C26-C27 1.365(6); P2-W1-P1 79.33(4).

Solid **3a** is moderately air- and moisture-stable and was found to melt above 185 °C under specific conversion into the dark-red phosphenium–phospholide complex **5**. This species was likewise accessible from **1a** and a dilute solution of [W(CO)$_3$(MeCN)$_3$] (**4**) and was identified by analytical and spectroscopic data and a single-crystal X-ray diffraction study (Figure 2).[8] The η^5-bound phospholyl ligand in this half-sandwich complex exhibits intraligand and metal–ligand bond lengths that are similar to those of the only known comparable complex, [η^5-(Me$_2$C$_4$H$_2$P)W(CO)$_3$I].[10] The planar geometry at the P1 atom (sum of bond angles 359.7(3)°) and the very short P1−W1 bond (2.218(1) Å) are typical for phosphenium complexes; the value of the latter is close to the shortest bond lengths in known tungsten phosphenium complexes (2.18–2.34 Å)[11] and suggests a high degree of phosphorus–metal π bonding.

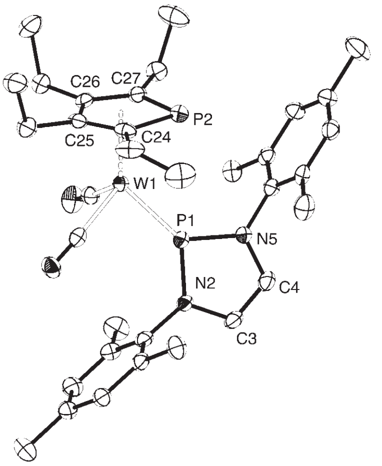

Figure 2. Molecular structure of **5** in the solid state (H atoms omitted; 50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: W1-P1 2.218(1), W1-C25 2.362(4), W1-C26 2.371(3), W1-C24 2.381(4), W1-C27 2.398(3), W1-P2 2.560(1), W1-centroid(C$_4$P) 2.014(2), P1-N5 1.681(3), P1-N2 1.684(3), N2-C3 1.405(4), C3-C4 1.333(4), C4-N5 1.391(4); N5-P1-N2 88.7(1), N5-P1-W1 134.0(1), N2-P1-W1 137.0(1).

By analogy to **1a**, reaction of diphosphine **1b** with **2** in acetonitrile at 50 °C afforded the spectroscopically detectable complex **3b**, as well as by-products arising from hydrolysis of **1b**.[4] Thermolysis of the crude product mixture resulted again in elimination of acetonitrile from **3b** and formation of the phosphido–phosphenium complex **6**, which was isolated by crystallization. The presence of a dinuclear complex followed from the AA′XX′-type splitting of the ^{31}P NMR signals and was confirmed by a single-crystal X-ray diffraction study,[8] which revealed the presence of a centrosymmetric dimer with *mer* arrangement of CO ligands and mutual *trans* orientation of μ$_2$-phosphido and phosphenium ligands at each metal center (Figure 3). The deviation from regular octahedral coordination owes chiefly to angle distortions in the W$_2$P$_2$ ring (P2-W1-P2′ 76.9(2), P1-W1-P2 107.3(2)°) that are presumably caused by steric interference of the phosphido and phosphenium ligands. The terminal P1−W1 bonds (2.251 Å) are longer than those in **3b**, but are comparable to the bonds in other tungsten phosphenium complexes (2.18–2.34 Å).[11] The bridging W1−P2/2′ bonds (2.577(2)/2.596(2) Å) match those in [{Ph$_2$PW(CO)$_4$}$_2$]$^{2-}$,[12] and the large difference in bond lengths between terminal and bridging phosphorus atoms is in accord with the presence of formal single and double bonds.

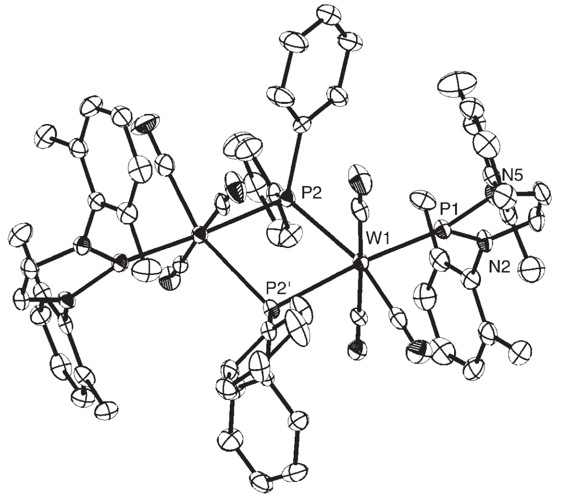

Figure 3. Molecular structure of **6** in the solid state (H atoms omitted; 50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: W1-P1 2.251(2), W1-P2′ 2.577(2), W1-P2 2.596(2), P1-N2 1.684(5), P1-N5 1.692(5), N2-C3 1.386(7), C3-C4 1.327(9), C4-N5 1.392(7); P2′-W1-P2 76.9(1), N2-P1-N5 88.5(2), N2-P1-W1 134.4(2), N5-P1-W1 135.7(2), W1′-P2-W1 101.7(1).

Although the presence of singly and doubly bonded R$_2$P ligands at one metal atom has precedence,[13] the deviation of bond lengths between these types of ligands in **6** is unsurpassed and points to a special bonding situation which can be described by considering the ligand properties of the R_2P groups. In previously known complexes, both singly and doubly bonded ligands are electron-rich phosphido species that act as simple σ-donor or σ/π-donor ligands to a metal center in high oxidation state. In **6**, the bridging R_2P moieties behave as pure σ donors, but the terminal phosphenium units represent σ-donor/π-acceptor ligands that interact with a metal center in low oxidation state, thus creating a similar bonding situation as in a Fischer-type carbene complex.

Investigations of mechanistic details in the formation of **3a** showed that **1a** and acetonitrile did not react in the absence of complex **2**, and **1a** and **2** did not react in inert solvents in the absence of acetonitrile. These findings lead us to conclude that the formation of **3a** is initiated by replacement of the diolefin ligand in **2** by nitriles. Since metal coordination of a nitrile facilitates addition of nucleophiles,[14] the next step is presumably formation of a carbon–phosphorus bond between the R_2P moiety of **1a** and the nitrile carbon atom. The completion of the reaction must then involve migration of the phosphenium moiety to the nitrogen atom by P–P bond cleavage and formation of two new phosphorus–metal bonds. This sequence is obviously facilitated by a higher degree of P–P bond weakening in **1a**. The formation of **5** from **1a** and **4** may either involve **3a** as an intermediate or proceed by direct "nonoxidative" addition of the P–P bond to the metal center; analogous insertions into P–C bonds have precedence for phosphenium–carbene adducts.[15]

In view of the reactivity of **1a**,**b** one would expect that these compounds also undergo phosphinyl phosphination of electron-poor alkynes.[6] We found this to be true for **1b**, which reacted with ethyl propiolate at room temperature even in the absence of an activating metal in a regio- and *Z*-stereoselective addition to afford the bisphosphine **7** (see the Supporting Information). Surprisingly, no such reaction was observed for **1a**, and it is still unclear if this lack of reaction can be attributed to the lower nucleophilicity of a phospholyl substituent as compared to a Ph_2P substituent or to an increased degree of steric hindrance.

In summary, we have demonstrated the first transition-metal-assisted addition of diphosphines to a nitrile, which gives direct access to complexes of hybrid 1,2-bisphosphines. Retroaddition at high temperature or direct "nonoxidative" addition[15] of a diphosphine to a metal center yielded complexes featuring a combination of phospholide-donor and phosphenium-acceptor ligands which offer interesting prospects for further reactions. The extension of this chemistry to the synthesis of complexes of other metals and new ligands for catalysis is currently under investigation.

Experimental Section

3a: Comlpex **2** (0.81 g, 2 mmol) in MeCN (30 mL) was added dropwise to **1a** (1.36 g, 2 mmol) in MeCN (30 mL). The mixture was stirred for 4 h and volatiles were evaporated in vacuum. The residue was dissolved in hexane (20 mL) and filtered. Crystallization at −20 °C afforded green crystals, which were collected by filtration and dried in vacuum to yield 1.23 g (63 %) of **3a**. M.p. 186 °C; $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K, 101.2 MHz): $\delta = 149.5$ (d, $^2J_{PP} = 32.5$ Hz, $^1J_{PW} = 315$ Hz), 93.6 ppm (d, $^2J_{PP} = 32.5$ Hz, $^1J_{PW} = 240$ Hz).

5: a) Milligram amounts were prepared by heating **3a** for 1 min to 186 °C. b) Complex **4** (0.76 g, 2 mmol) in toluene (70 mL) was added dropwise to a solution of **1a** (1.36 g, 2 mmol) in toluene (30 mL). The mixture was stirred for 4 h and volatiles were evaporated in vacuum. The residue was dissolved in hexane (20 mL) and filtered. Crystallization at −20 °C afforded orange crystals, which were collected by filtration and dried in vacuum to yield 1.15 g (76 %) of **5**. M.p. 143 °C; $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K, 101.2 MHz): $\delta = 182.9$ (d, $^2J_{PP} = 11.4$ Hz, $^1J_{PW} = 728$ Hz), −17.8 ppm (d, $^2J_{PP} = 11.4$ Hz, $^1J_{PW} = 7.6$ Hz).

6: A solution of **1b** (0.48 g, 1 mmol) and **2** (0.41 g, 1 mmol) in MeCN (25 mL) was stirred for 6 h at 50 °C. Volatiles were evaporated in vacuum. A ^{31}P NMR measurement revealed formation of **3b** ($\delta = 151.2$ (d, $^2J_{PP} = 42.5$ Hz, $^1J_{PW} = 312$ Hz), 86.4 ppm (d, $^2J_{PP} = 42.5$ Hz, $^1J_{PW} = 256$ Hz)) as well as products arising from the hydrolysis of **1b**. A portion of the crude product (409 mg) was melted in vacuum until gas evolution ceased. The solid was allowed to cool to room temperature and extracted with hexane (5 mL). Recrystallization of the residue at 4 °C from THF/toluene afforded red crystals, which were filtered off and dried in vacuum to give 295 mg (88 %) of **6**. M.p. 348 °C; $^{31}P\{^1H\}$ NMR (C_6D_6, 303 K, 101.2 MHz): $\delta = 166.3$, −98.6 ppm (AA′XX′ pattern, $J_{AA'} = 80$ Hz, $J_{XX'} = 15$ Hz, $J_{AX} = 100$ Hz, $J_{AX'} = -19$ Hz).

Comprehensive anatytical and spectroscopic data of **3a** and **5**–**7** are available in the Supporting Information.

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[1] H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483; K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2126; *Angew. Chem. Int. Ed.* **2002**, *41*, 2024.

[2] K. Muñiz, *New J. Chem.* **2005**, *29*, 1371.

[3] J. Holz, A. Monsees, H. Jiao, J. You, I. V. Komarov, C. Fischer, K. Drauz, A. Börner, *J. Org. Chem.* **2003**, *68*, 1701; J. Holz, O. Zayas, H. Jiao, W. Baumann, A. Spannenberg, A. Monsees, T. H. Riermeier, J. Almena, R. Kadyrov, A. Börner, *Chem. Eur. J.* **2006**, *12*, 5001.

[4] S. Burck, D. Gudat, M. Nieger, *Angew. Chem.* **2004**, *116*, 4905; *Angew. Chem. Int. Ed.* **2004**, *43*, 4801.

[5] W. R. Cullen, D. S. Dawson, *Can. J. Chem.* **1967**, *45*, 2887; A. Sato, H. Yorimitsu, K. Oshima, *Angew. Chem.* **2005**, *117*, 1722; *Angew. Chem. Int. Ed.* **2005**, *44*, 1694.

[6] During writing of this article, the addition of diphosphines to electron-poor alkynes was reported: D. L. Dodds, M. F. Haddow, A. G. Orpen, P. G. Pringle, G. Woodward, *Organometallics* **2006**, *25*, 5937.

[7] Selected references: N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033; K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc.* **1997**, *119*, 4413; Y. Yan, X. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 7198.

[8] Crystal structures: Nonius Kappa-CCD diffractometer, $T = 123(2)$ K, $Mo_{K\alpha}$ radiation, empirical absorption correction, SHELX97[16] for structure solution (Patterson methods (**3a**) and direct methods (**5**, **6**)) and refinement (full matrix, least squares refined against F^2). The positions of the hydrogen atoms were refined with a riding model. Empirical absorption corrections were applied. **3a**: $C_{38}H_{47}N_3O_4P_2W$, $M_r = 855.6$, crystal size $0.50 \times 0.20 \times 0.15$ mm^3, orthorhombic, space group *Pbca* (No. 61), $a = 14.5762(1)$, $b = 20.5667(2)$, $c = 25.2197(3)$ Å, $V = 7560.5(1)$ Å^3, $Z = 8$, $\mu = 3.18$ mm^{-1}, $F(000) = 3456$, $\theta_{max} = 25°$, 99 751 reflexes, 6662 independent reflexes ($R_{int} = 0.068$), $R_1 = 0.031$ (for $I > 2\sigma(I)$), $wR_2 = 0.082$ (all data). **5**:

$C_{34}H_{44}N_2O_2P_2W{\cdot}C_6H_6$, $M_r = 836.6$, crystal size $0.15 \times 0.10 \times 0.05\,mm^3$, monoclinic, space group $C2/c$ (No. 15), $a = 29.3068(5)$, $b = 15.0260(3)$, $c = 18.9921(4)$ Å, $\beta = 113.689(2)°$, $V = 7658.7(3)$ Å^3, $Z = 8$, $\mu = 3.14\,mm^{-1}$, $F(000) = 3392$, $\theta_{max} = 27.5°$, 34046 reflexes, 8605 independent reflexes ($R_{int} = 0.056$), $R_1 = 0.030$ (for $I > 2\sigma(I)$), $wR_2 = 0.069$ (all data). **6**: $C_{66}H_{60}N_4O_6P_4W_2{\cdot}3\,C_7H_8$, $M_r = 1773.2$, crystal size $0.32 \times 0.16 \times 0.08\,mm^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 20.5351(5)$, $b = 16.0361(4)$, $c = 24.9648(4)$ Å, $\beta = 110.389(2)°$, $V = 7705.9(3)$ Å^3, $Z = 4$, $\mu = 3.12\,mm^{-1}$, $F(000) = 3560$, $\theta_{max} = 25°$, 44022 reflexes, 13557 independent reflexes ($R_{int} = 0.074$), $R_1 = 0.043$ (for $I > 2\sigma(I)$), $wR_2 = 0.091$ (all data). CCDC-632090 (**3a**), CCDC-632091 (**5**), and CCDC-632092 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] Result of a search in the CSD database for {(bisphosphine)W(CO)$_4$} complexes.

[10] S. Holand, F. Mathey, J. Fischer, *Polyhedron* **1986**, *5*, 1413.

[11] Result of a search in the CSD database for [L$_n$M=PR$_2$].

[12] S.-G. Shyu, M. Calligaris, G. Nardin, A. Wojcicki, *J. Am. Chem. Soc.* **1987**, *109*, 3617.

[13] R. T. Baker, P. J. Krusic, T. H. Tulip, J. C. Calabrese, S. S. Wreford, *J. Am. Chem. Soc.* **1983**, *105*, 6763; R. T. Baker, J. F. Whitney, S. S. Wreford, *Organometallics* **1983**, *2*, 1049; R. T. Baker, J. C. Calabrese, T. E. Glassman, *Organometallics* **1988**, *7*, 1889.

[14] V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771.

[15] N. J. Hardman, M. B. Abrams, M. A. Pribisko, T. M. Gilbert, R. L. Martin, G. J. Kubas, R. T. Baker, *Angew. Chem.* **2004**, *116*, 1989; *Angew. Chem. Int. Ed.* **2004**, *43*, 1955.

[16] G. M. Sheldrick, SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttignen, Germany, **1998**.