

removed or transformed into a variety of functional groups as amply demonstrated by Barton.^[13] Since radical precursors are generated through a hydroboration step, this procedure could take advantage of the chemo- and regioselectivity of the hydroboration and offers a very simple and efficient method for the preparation of highly functionalized systems through inter- and intramolecular radical addition. Applications of this approach to cascade reactions starting from a polyene are currently under investigation. Finally, preparation of optically active materials through enantioselective hydroboration of prochiral alkenes should represent valuable entries into the synthesis of enantiomerically enriched compounds.

Experimental Section

Sulfur inclusion into *B*-Alkylcatecholboranes: Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at 0 °C to a solution of the olefin (3.0 mmol) and *N,N*-dimethylacetamide (28.0 µL, 0.3 mmol) in CH₂Cl₂ (2.0 mL). The mixture was heated under reflux for 3 h. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C and the mixture was stirred for 15 min at room temperature. The CH₂Cl₂ was evaporated under vacuum with strict exclusion of O₂.^[14] A yellow solution of PTOC-OMe (9.0 mmol), freshly prepared by stirring for 1 h in the dark the sodium salt of *N*-hydroxypyridine-2-thione (1.41 g, 9.45 mmol) and methyl chloroformate (0.7 mL, 9.0 mmol) in benzene (15 mL), was added to the *B*-alkylcatecholborane followed by 1,3-dimethyl hexahydro-2-pyrimidone (DMPU; 0.36 mL, 3.0 mmol). The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp for about 14 h, and treated with 1N NaOH (20 mL). The aqueous layer was extracted with CH₂Cl₂ and the combined organic phases were washed with a saturated NaCl solution (30 mL), dried with MgSO₄, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/EtOAc).

Conjugate addition: Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at 0 °C to a solution of the olefin (3.0 mmol) and *N,N*-dimethylacetamide (28.0 µL, 0.3 mmol) in CH₂Cl₂ (2.0 mL). The reaction mixture was heated under reflux for 3 h. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C and the mixture was stirred for 15 min at room temperature. A yellow solution of PTOC-OMe (9.0 mmol), freshly prepared as previously described, was added to the *B*-alkylcatecholborane followed by the activated alkene (15 mmol) in benzene (15 mL) and DMPU (0.36 mL, 3.0 mmol). In the case of dimethyl fumarate as the alkene, CH₂Cl₂ (15 mL) was used instead of benzene. The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp for about 14 h, and treated with 1N NaOH (20 mL). The aqueous layer was extracted with CH₂Cl₂ and the combined organic phases were washed with a saturated NaCl solution (30 mL), dried with MgSO₄, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/EtOAc).

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“Naked” Phosphorus as a Bent Bridging Ligand**

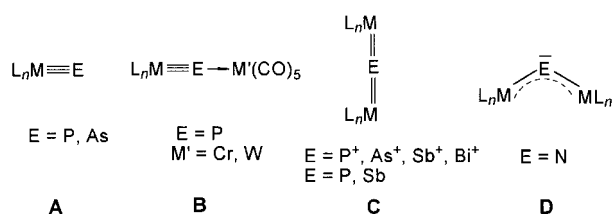
Peter Kramkowski and Manfred Scheer*

*Dedicated to Professor Dirk Walther
on the occasion of his 60th birthday*

Only a small number of the complexes containing pnico-genido (E^{3−}) ligands of the heavier Group 15 elements (E = P, As, Sb, Bi)^[1] are known in which the ligands display low coordination numbers 1 and 2. Only in 1995 were the first complexes of type **A**,^[6] with terminal ligands and coordination number 1, synthesized and structurally characterized with the compounds [(Ar'RN)₃Mo≡P] (Ar' = 3,5-C₆H₃Me₂, R = C(CD₃)₂CH₃)^[2] and [(N₃N')M≡E] [N₃N' = N(CH₂CH₂NSiMe₃)₃; E = P, M = W, Mo;^[3] E = As, M = W,^[4] Mo^[5]]. We recently found the asymmetric linear coordination mode **B** with coordination number 2 in the complexes [(N₃N')M≡E → ML_m] (ML_m = GaCl₃,^[7] M(CO)₄, M = Cr, W^[5]) and [(RO)₃W≡P → M(CO)₅] (M = Cr, W; R = *t*Bu^[8], Ar (2,6-Me₂C₆H₃)^[9]). Symmetrical linearly bridged complexes of

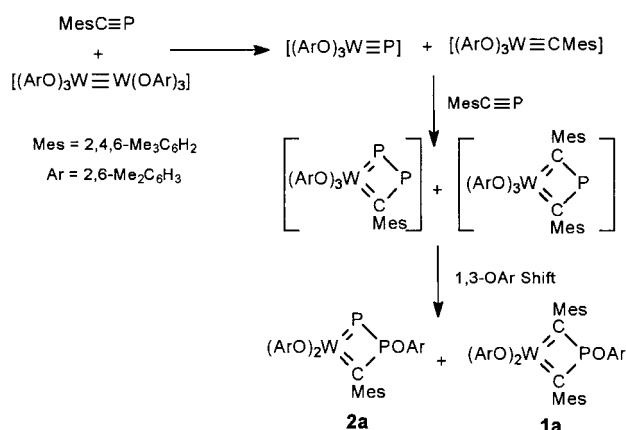
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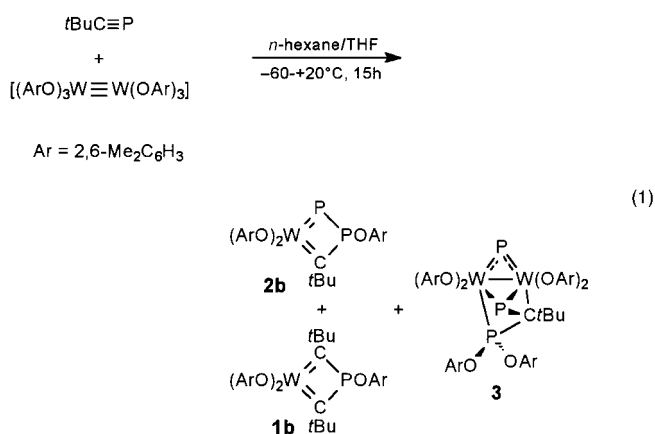
type **C** of the heavier Group 15 elements are so far exclusively known for cationic complexes, which were prepared by Huttner and co-workers.^[10] Neutral compounds of this type are only known for $E = P$ in the complexes $[(Cp_2Zr)_2(\mu-P)]$ and $[(R'RN)_3Mo)_2(\mu-P)]$ ($R = Ph$; $R' = tBu$), synthesized in the groups of Stephan^[11] and Cummins^[12], respectively. We recently synthesized the first neutral example for antimony in the complex $[(N_3N')W=Sb=W(N_3N')]$ (**C**) [$N_3N' = N(CH_2CH_2NCH_2tBu)_3$].^[13] The nonlinear bent bridging coordination mode **D** of the coordination number 2, however, has not yet been observed for the heavier Group 15 elements.^[11] So far this coordination mode has been found exclusively for nitrogen,^[14] for example, in complexes of vanadium^[15] and tantalum^[16]. We report here the synthesis, structure, and properties of the first complex with a bent bridging phosphorus ligand of coordination number 2.

In our studies on the synthesis of phosphido complexes of type **B** with the formula $[thf(ArO)_3W \equiv P \rightarrow M(CO)_5]$ using the three-component reaction between $[W_2(OAr)_6]$ ($Ar = 2,6-Me_2C_6H_3$)^[17] and $R'C \equiv P$ ($R' = tBu, Mes$; $Mes = 2,4,6-Me_3C_6H_2$) in the presence of $[M(CO)_5thf]$ ($M = Cr, W$),^[9] we have also investigated the corresponding two-component systems $[W_2(OAr)_6]/R'C \equiv P$.^[18] Whereas, for $MesC \equiv P$ only the four-membered ring derivatives **1a** and **2a** were obtained as a consequence of the reaction of the initially formed phosphido complex and alkylidyne complex, respectively, with further phosphalkyne and subsequent 1,3-OAr shift (Scheme 1), in the case of $tBuC \equiv P$ the complex **3** of type **D**



Scheme 1.

with a bent phosphorus ligand [Eq. (1)] is obtained in addition to the cyclic complexes **1b** and **2b**. The dark red crystalline complex **3** is extremely sensitive towards hydrolysis and is readily soluble in *n*-pentane, toluene, and THF. The molecular ion peak is observed in the mass spectrum of **3**.



The formation of **3** could occur by the dimerization of two phosphido complex units $[(ArO)_3W \equiv P]$ with simultaneous addition of a further phosphalkyne. This intermediate is stabilized by 1,3-ArO shifts from the W atoms to the P atom of the additionally attached phosphalkyne with formation of a tungsten–tungsten bond. The postulated dimerization of two $[(ArO)_3W \equiv P]$ intermediates is also observed for the isolable phosphido complex $[(ArO)_3W \equiv P \rightarrow W(CO)_5]$, leading to the planar four-membered ring derivative **4**.^[9]

The molecular structure of **3**^[19] (Figure 1) reveals a four-membered ring of the atoms W1, P1, W2, and P2, which is folded along the W1–W2 bond (2.8162(8) Å) (dihedral angle: 151.4°) and further coordinated by a *t*BuCP unit (C1 and P3). The atom C1 is connected to the tungsten atom W2 and to the phosphorus atoms P1 and P3

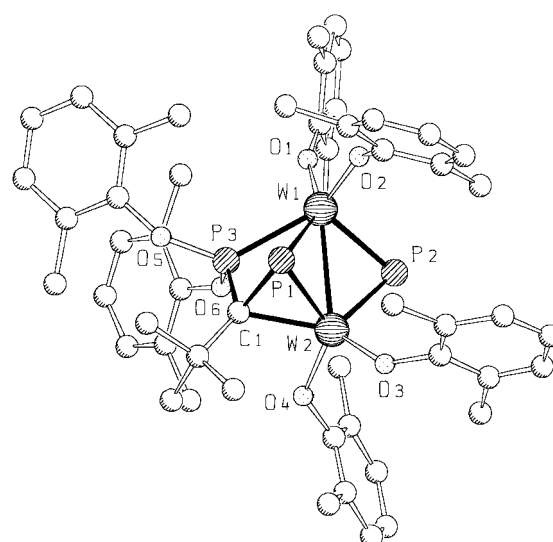
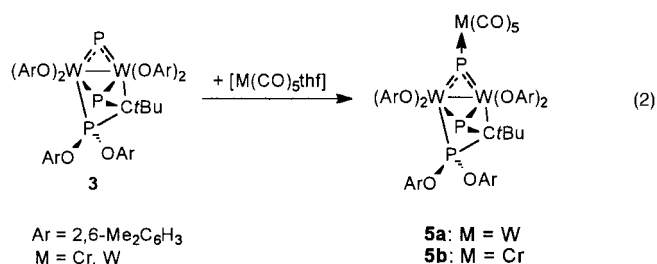


Figure 1. Molecular structure of **3** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W1–P2 2.301(2), W2–P2 2.284(2), W1–P1 2.483(2), W2–P1 2.483(2), W1–P3 2.475(2), W1–W2 2.8162(8), W2–C1 2.200(7), P1–C1 1.860(7), P3–C1 1.743(6); W1–P2–W2 75.78(6), W1–P1–W2 70.22(5), W1–P3–C1 95.1(2), P1–W1–P2 100.98(7), P1–W2–P2 103.68(7), C1–P1–W2 60.4(2), C1–P1–W1 91.9(2), P3–C1–W2 99.0(3).

through single bonds. The lone pair of electrons on the phosphorus atom P3 coordinates to the W1 atom, as indicated by the P–W distance of 2.475(2) Å. The predominant structural feature of **3** is the substituent-free phosphorus atom P2 that bridges the atoms W1 and W2. The bond lengths of the phosphorus atom P2 to the atoms W1 and W2 are 2.301(2) and 2.284(2) Å, respectively, with an angle W1–P2–W2 of 75.78(6)°. Comparison with the structural data for the complex **4**, in which the symmetrical phosphido ligand has the coordination number 3 ($d(\text{W–P})$ 2.2805(17) and 2.2806(17) Å; $\angle(\text{W–P–W})$ 76.69(7)°), demonstrates the insignificant structural influence of the additional coordination of the phosphido phosphorus atom to the W(CO)₅ moiety in **4**. Presumably the planar geometry in **4** is responsible for a shortening of the W–P bonds. The differently substituted and therefore electronically different W atoms could be the reason for the asymmetrical phosphido bridge of the P2 atom in **3**.

The ¹H-coupled as well as the ¹H-decoupled ³¹P NMR spectra of **3** show three singlets. The signal at $\delta = 831.8$ can be assigned to the naked phosphorus atom P2. In comparison with the P atom coordinating to a W(CO)₅ moiety in **4**, the signal appears shifted down field by almost 300 ppm (**4**: $\delta = 558.2$). A similar difference in the chemical shifts, combined with a high-field shift in the case of additional coordination of the P atom is observed for the phosphido complexes [(*t*BuO)₃W≡P] ($\delta = 845.0$) and [(*t*BuO)₃W≡P → W(CO)₅] ($\delta = 546.0$).^[8] Furthermore, as a result of the two ArO substituents, the signal of the phosphorus atom P3 in **3** is detected at high field ($\delta = 97.5$). However, this effect is less distinct than with the P atoms bearing single ArO substituents in the WC₂P and WCP₂ four-membered ring complexes **1b** ($\delta = -151.5$) and **2b** ($\delta = -87.1$), respectively. Only the signal of the phosphorus atom P3 shows coupling to tungsten (¹J(W,P) = 216 Hz). No coupling to the tungsten atoms was observed for either of the other singlets, including that of atom P1 at 140.4 ppm.

The bent bridged phosphorus atom P2 in **3** should be able to coordinate through its lone pair of electrons to Lewis acid complex fragments such as [M(CO)₅thf]. Thus, **3** reacts with [M(CO)₅thf] (M = W, Cr) to give the complexes **5a, b** [Eq. (2)]. The signals of **3** could no longer be observed in the ³¹P NMR spectrum of the crude mixture of reaction (2).



The ³¹P NMR data of **5a, b** support the coordination of the bridging atom P2 to the corresponding M(CO)₅ group (M = Cr, W) with a significant high field shift of 180 ppm (M = W: 650.5 ppm) and 115 ppm (M = Cr: 715.0 ppm), respectively, for the resonance signal of this phosphorus atom. A pair of satellites with a coupling constant of 210 Hz (**5a**) and 197 Hz

(**5b**), respectively, appears on this signal, which has to be assigned to the coupling with the tungsten atoms of the W(OAr)₂ moieties. No couplings to the W(OR)₂ groups were found, either in complex **4**^[9] with the coordination number 3 on the phosphido phosphorus atom or in its *t*Bu-substituted analogues.^[8] This highlights the different geometry at the tungsten alkoxide groups of **5** in comparison with those of **3** and **4**, respectively. All other chemical shifts of the phosphorus atoms in **5a, b** are slightly different from those in **3** (a down field shift of 10–12 ppm in each case).

The cause of the so far unique formation of the bent bridged P₁ ligand of **3** is the predominant tendency of the phosphorus atom to incorporate its lone pair of electrons into the bonding mode to form either the coordination number 3 or the linear coordination modes **B** or **C**. Thus, in the complex **3** optimum conditions for the realization of this coordination mode **D** are present: 1) the high tendency of (RO)₃W fragments to eliminate RO groups under formation of a W–W bond^[9] and 2) optimal steric parameters of the substituents at the tungsten alkoxide and on the phosphalkyne, which prevent a subsequent reaction with the alkoxide dimer to form [(RO)₃W]₂(μ₃-P) (R = 2,6-Me₂C₆H₃), as we had observed for R = neopentyl.^[8] Furthermore, the reaction procedure is also very important; long reaction times at very low temperatures give the metathesis product [(ArO)₃W≡P] the possibility to react with a second molecule and *t*BuC≡P simultaneously to give the complex **3**. The exclusive reaction of the phosphido complex with *t*BuC≡P leads to complex **2b**. Therefore, the accessibility of complexes of type **D** for the heavier homologues of phosphorus seems to be only possible after the first synthesis of the corresponding arsa- and stibaalkynes.

Experimental Section

1a and **2a**: [W₂(OAr)₆]^[20] (Ar = 2,6-Me₂C₆H₃) (550 mg, 0.5 mmol) was dissolved in toluene (25 mL) and frozen with liquid nitrogen. A solution of MeC≡P^[21] (Mes = 2,4,6-Me₃C₆H₂) (162 mg, 1 mmol) in *n*-hexane (20 mL) was added at –78 °C. The reaction mixture was allowed to warm to room temperature over a period of 15 h. All volatile materials were then removed under high vacuum. The reddish brown residue was characterized by ³¹P{¹H} NMR spectroscopy, which revealed the presence of **1a** and **2a**. No separation of **1a** and **2a** was achieved either by fractional crystallization or by column chromatographic work-up on silica gel and Al₂O₃, respectively. ³¹P{¹H} NMR (101.256 MHz, [D₆]benzene, 298 K, 85% H₃PO₄ ext.): **1a**: $\delta = -154.8$ (s); **2a**: $\delta = 434.2$ (d, ¹J(P,P) = 442 Hz), –89.5 (d, ¹J(P,P) = 442 Hz).

3: [W₂(OAr)₆] (Ar = 2,6-Me₂C₆H₃) (550 mg, 0.5 mmol) was dissolved in THF (15 mL) and cooled to –60 °C. To this solution was added a solution of *t*BuC≡P^[22] (100 mg, 1 mmol) in *n*-pentane (15 mL) over 3 h. The reaction mixture was allowed to warm to room temperature over a period of 15 h. After removal of the solvent, the residue was extracted with *n*-pentane (30 mL) and filtered through celite. After the volume of solvent had been reduced to about 10 mL, dark red crystals of **3** (75 mg, 12%) were obtained. The solid reaction residue was dissolved in toluene (30 mL) and filtered through celite. Fractional crystallization failed to separate the four-membered ring derivatives **1b** and **2b**. ³¹P{¹H} NMR (101.256 MHz, [D₆]benzene, 298 K, 85% H₃PO₄ ext.): **1b**: $\delta = -151.5$ (s); **2b**: $\delta = 446.0$ (d, ¹J(P,P) = 449 Hz), –87.1 (d, ¹J(P,P) = 449 Hz). **3**: ³¹P{¹H} NMR (101.256 MHz, [D₆]benzene, 298 K, 85% H₃PO₄ ext., P_A = P2, P_B = P1, P_C = P3): $\delta = 831.8$ (P_A: s), 140.4 (P_B: s), 97.5 (P_C: s; ¹J(W,P) = 216 Hz); ¹H NMR [250.113 MHz, [D₆]benzene, 298 K, TMS): $\delta = 6.58$ –7.16 (18H, aromatic protons) 2.50 (12H, Me), 2.05 (12H, Me), 1.36 (9H, *t*Bu); EI-MS

(70 eV; 140 °C): m/z (%): 1256 (1) [M^+], 1014 (4) [$M^+ - 2\text{OAr}$], 772 (10) [$M^+ - 4\text{OAr}$].

5a, b: Complex **3** (50 mg, 0.04 mmol) was added to a solution of $[\text{M}(\text{CO})_5\text{thf}]$ (0.06 mmol; $M = \text{W}, \text{Cr}$) in THF (25 mL) and stirred for 24 h at room temperature. Then all of the volatiles were removed under high vacuum and the residue was recrystallized from toluene to give the dark red complexes **5a** (45 mg; 71%) and **5b** (35 mg; 60%), respectively. $^{31}\text{P}\{^1\text{H}\}$ NMR (101.256 MHz, $[\text{D}_6]\text{benzene}$, 298 K, 85% H_3PO_4 ext.): **5a** ($M = \text{W}$): $\delta = 650.5$ (s, $^1J(\text{W,P}) = 210$ Hz), 152.8 (s), 107.2, (s, $^1J(\text{W,P}) = 233$ Hz); **5b** ($M = \text{Cr}$): $\delta = 715.0$ (s, $^1J(\text{W,P}) = 197$ Hz), 153.7 (s), 108.0 (s, $^1J(\text{W,P}) = 233$ Hz).

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- [19] Crystal structure analyses of **3**·0.5 C_5H_{12} and $[(\text{ArO})_6\text{W}_2]$. STOE IPDS area-detector diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-86^[23a] and refined by full-matrix least-squares on F^2 using SHELXL-93^[23b], with anisotropic displacement for non-H atoms. Hydrogen atoms were placed in idealized positions and refined isotropically using a riding model. **3**·0.5 C_5H_{12} : $\text{C}_{33}\text{H}_{63}\text{O}_6\text{P}_3\text{W}_2$ ·0.5 C_5H_{12} , $M_r = 1292.72$, crystal size $0.11 \times 0.08 \times 0.04$ mm, triclinic, space group $P\bar{1}$ (no. 2); $a = 13.077(3)$, $b = 13.777(3)$, $c = 18.069(4)$ Å, $\alpha = 86.55(3)^\circ$, $\beta = 83.35(3)^\circ$, $\gamma = 64.56(3)^\circ$, $T = 200(2)$ K, $Z = 2$, $V = 2919.6(10)$ Å³, $\rho_{\text{calcd}} = 1.470$ Mg m^{−3}, $\mu(\text{MoK}\alpha) = 40.63$ cm^{−1}, 10490 independent reflections ($2\theta_{\text{max}} = 52^\circ$) of which 7715 observed with $F_o = 4\sigma(F_o)$; 614 parameters, $R_1 = 0.0381$, $wR_2 = 0.1050$; $[(\text{ArO})_6\text{W}_2]$: $\text{C}_{48}\text{H}_{54}\text{O}_6\text{W}_2$, $M_r = 1094.62$, crystal size $0.15 \times 0.15 \times 0.02$ mm, monoclinic, space group $P2_1/n$ (no. 14); $a = 11.830(2)$, $b = 9.935(2)$, $c = 18.193(4)$ Å, $\beta = 90.85(3)^\circ$, $T = 183(1)$ K, $Z = 2$, $V = 2138.0(7)$ Å³, $\rho_{\text{calcd}} = 1.700$ Mg m^{−3}, $\mu(\text{MoK}\alpha) = 54.24$ cm^{−1}, 3935 independent reflections ($2\theta_{\text{max}} = 53^\circ$), 3360 of which observed with $F_o = 4\sigma(F_o)$; 259 parameters, $R_1 = 0.0384$, $wR_2 = 0.1090$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135166 (**3**·0.5 C_5H_{12}) and CCDC-135167 ($[(\text{ArO})_6\text{W}_2]$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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