Heavily π-Bond-Loaded Tungsten Phosphonio−Alkylidyne Complexes via a Domino Transylidation Cascade at (Organoimido)tungsten Tetrachlorides

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Summary: Transylidation reactions of (arylimido)tungsten(II) complex sten tetrachlorides [W(NR)Cl₄] with 7 equiv of Ph₃P− CH₂ lead to the tetrahedral complexes [W(NR)(C− PPh₃)(CH−PPh₃)₂] (R = Dip (**1**), Mes (**2**)), exhibiting one metal−nitrogen and three metal−carbon multiple bonds. The crystal structure analysis of **1** presents the first example of a terminal phosphonio−methylidyne functionality, [M≡C−PR₃] ↔ [M=C=PR₃], formed via a transylidation reaction. Due to the high level of π-bond competition of four π-donor ligands, the M=C=P axis is considerably bent: 154.0(4)°.*

The organometallic chemistry of phosphorus ylides with high-valent d^0 metal oxo and imido complexes is still a largely unexplored field of research.[1−5] We focused our attention on the question whether α-H abstractions at metalated phosphorus ylides, the so-called phosphonio−methylidene complexes [M=CH−PR₃], may open access to triply bonded terminal phosphonio−methylidyne functionalities, [M≡C−PR₃]. This pattern would resemble α-H abstractions at *Schrock*-type non-heteroatom-stabilized alkylidene complexes to yield alkylidyne complexes or α-H abstractions at high-valent primary amino complexes to yield the amido complexes [M= NHR] and finally the imido complexes [M≡NR].

Only few complexes with a terminal [M≡C−PR₃] function have been discovered so far.[6−9] Their syntheses were realized by reaction of a phosphine with a tungsten chlorocarbyne functionality[6] or by insertion of a tung-

sten(II) complex fragment into the C=C bond of Ph₃P= C=C=O.[8] The only complexes of d^0 electronic configuration [X₂Ti(μ-C−PR₃)₂TiX₂] contain the ligand [R₃P− C]²⁻ in a bridging coordination mode.[10] They have interesting applications in C−C coupling reactions as a synthon for [C]⁴⁻.[11]

We have found that transylidation reactions of [W(NR)Cl₄] (R = Dip, Mes)[12] with 7 equiv of triphenylmethylenephosphorane afford **1** and **2**, the first complexes having phosphonio−methylidene and phosphonio− methylidyne functionalities in one and the same ligand regime (Scheme 1).[13]

The reaction mechanism is proposed as follows: on the basis of our previous mechanistic investigations of stepwise transylidation reactions at [W(NR)₂Cl₂] leading

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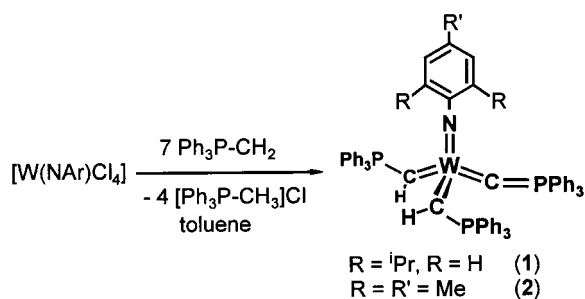
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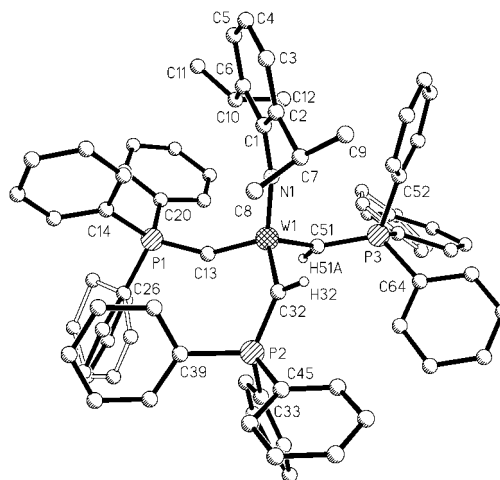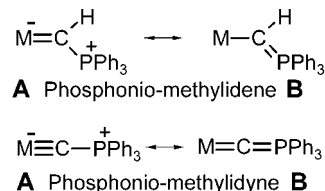(8) List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2010.

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(13) (a) Preparation of **1**: 1.98 g (3.95 mmol) of [W(NDip)Cl₄] was dissolved in 50 mL of toluene. To this solution was added dropwise 7.66 g (27.66 mmol) of Ph₃P−CH₂ in 100 mL of toluene at −20 °C. The reaction mixture was stirred for 3 h at room temperature. During this period the reaction solution turned red and a precipitate of [Ph₃- PMe]Cl formed. The solution was filtered through 1 cm of Celite. Evaporation of the filtrate under vacuum followed by extraction of the residue with Et₂O gave a red solution, which upon cooling to −30 °C gave orange-red crystals: yield of raw material of **1** ca. 70%, yield after two crystallizations to remove impurities of PPh₃ and ylide 0.52 g (11%). Anal. Calcd for C₆₉H₅₄NP₃W (mol wt 1173.95): C, 70.60; H, 4.64; N, 1.19. Found: C, 70.89; H, 5.08; N, 1.22. ¹H NMR (C₆D₆): δ 1.12 (d, 12 H, CH*Me*₂, ³*J*$_{HH}$ = 7.0 Hz), 4.22 (d, 2 H, ²*J*$_{PH}$ = 1.7 Hz, WC*H*P), 6.93−7.09, 7.54−7.73, 7.81−8.02 (m, 45 H, P*Ph*₃). ¹³C NMR (C₆D₆): δ 23.9 (s, CH*Me*₂), 27.5 (s, *C*HMe₂), 85.7 (d, WC*H*P, ¹*J*$_{PC}$ = 60.1 Hz), 121.7 (s), 127.5 (s), 128.3 (d, ³*J*$_{PC}$ = 12.6 Hz), 128.5 (d, ³*J*$_{PC}$ = 13.5 Hz), 130.1 (s), 131.2 (d, ⁴*J*$_{PC}$ = 2.7 Hz), 132.3 (d, ²*J*$_{PC}$ = 9.9 Hz), 133.4 (d, ²*J*$_{PC}$ = 8.4 Hz), 141.0 (s), 157.8 (s), 213.7 (s br, W*C*P). ³¹P NMR (C₆D₆): δ −13.0 (t, WC*P*, ⁴*J*$_{PP}$ = 5.1 Hz, ²*J*$_{WP}$ = 166.6 Hz), 22.6 (d, WCH*P*, ⁴*J*$_{PP}$ = 5.1 Hz, ²*J*$_{WP}$ = 39.4 Hz). (b) **2** is obtained under the same conditions as **1**: orange-red crystalline substance; yield of raw material **2** ca. 80%, yield after two crystallizations to remove impurities of PPh₃ and ylide 11%. Anal. Calcd for C₆₆H₅₈NP₃W (mol wt 1141.95): C, 69.42; H, 5.12; N, 1.23. Found: C, 69.60; H, 5.11; N, 1.77. ¹H NMR (C₆D₆): δ 2.20 (s, 6 H , *Me*), 2.29 (s, 3 H, *Me*), 4.30 (d, 2 H, ²*J*$_{PH}$ = 1.8 Hz, WC*H*P), 6.84 (s, 2 H, *Mes*), 6.94−7.05, 7.59−7.71, 7.91−8.00 (m, 45 H, P*Ph*₃). ¹³C NMR (C₆D₆): δ 19.9 (s), 21.3 (s), 85.1 (d, WC*H*P, ¹*J*$_{PC}$ = 58.6 Hz), 128.7 (s), 130.1 (s), 132.3 (d, ¹*J*$_{PC}$ = 84.2 Hz), 133.2 (s), 133.7 (s), 133.8 (s), 133.9 (s), 134.4 (s), 134.9, 136.0, 138.1, 157.5 (s), 212.4 (s br, W*C*P). ³¹P NMR (C₆D₆): δ −11.1 (t, WC*P*, ⁴*J*$_{PP}$ = 5.1 Hz, ²*J*$_{WP}$ = 163.4 Hz), 23.1 (d, WCH*P*, ⁴*J*$_{PP}$ = 5.1 Hz, ²*J*$_{WP}$ = 38.1 Hz).

Scheme 1. Synthesis of Complexes 1 and 2

$$[\text{W(NAr)Cl}_4] \xrightarrow[\substack{-\ 4\ [\text{Ph}_3\text{P-CH}_3]\text{Cl} \\ \text{toluene}}]{7\ \text{Ph}_3\text{P-CH}_2}$$

R = ^{i}Pr, R = H (**1**)
R = R' = Me (**2**)

to phosphonio−methylidene complexes [W(NR)$_2$(CH−PPh$_3$)$_2$][3,14] the reaction should proceed via the hexacoordinate classical ylide adduct [W(NR)Cl$_4$(CH$_2$−PPh$_3$)]. In THF or pyridine as solvent for [W(NR)Cl$_4$], the transylidation does not proceed, as the coordination site for the ylide activation is efficiently blocked by the solvent. We were not able to isolate this classical ylide complex or any other intermediates of this reaction cascade. When the reaction was monitored by ^{31}P NMR in toluene-d_8, only free ylide, some PPh$_3$ resulting from redox side reactions, soluble parts of the byproduct [Ph$_3$PMe]Cl, and the two signals for the final product were observed. The first transylidation step triggers the whole cascade of four consecutive transylidations. This could be explained by a rate-limiting first step of nucleophilic ligand displacement by ylide. After the transylidation steps, the deprotonation at the acidic α-CH bonds of coordinated ylide by free ylide seems to proceed at a much faster rate. With respect to the formation of traces of Ph$_3$P as byproduct, we do not want to exclude the possibility of a SET chain-propagating mechanism. **1** and **2** have been fully characterized by NMR, elemental, and X-ray structure analysis.[13]

The ^{31}P NMR spectra of **1** and **2** reveal a triplet for [W≡C−PPh$_3$] and a doublet for the two [W=CH−PPh$_3$] functionalities ($^4J_{PP} \approx 5$ Hz). Both ^{31}P NMR signals show satellites due to coupling with ^{183}W ($I = \frac{1}{2}$). The coupling constant $^2J_{WP}$ is not observed for phosphonio−methyl complexes [W−CH$_2$−PR$_3$]; it is ∼40 Hz for the phosphonio−methylidene complex [W=CH−PR$_3$] and ∼160 Hz for the phosphonio−methylidyne complex [W≡C−PPh$_3$]. The differences in metal−carbon bond orders are also reflected in the ^{13}C NMR spectra of **1** and **2**, showing resonances at ∼85 ppm for [W=CH−PPh$_3$] and ∼213 ppm for [M≡C−PPh$_3$]. In the non-heteroatom-stabilized alkylidene and alkylidyne complexes [M=CH−CR$_3$] and [M≡C−CR$_3$], the negative charge of the carbanion is exclusively stabilized by the π-acidic metal center; therefore, M−C bond orders tend to be higher than in corresponding isoelectronic heteroatom-substituted functionalities (−CR$_3$ being replaced by −SiR$_3$ and −PR$_3$$^+$). Due to the prominent electron-withdrawing effect of the phosphonio substituents, the notation [W=CH−PR$_3$] resembles a σ bond with additional π bond character comparable to an isoelectronic silylamido ligand, and [W≡C−PR$_3$] represents a double bond with partial triple-bond character (σ, 2π; Scheme 2) comparable with an silylimido [W≡N−SiR$_3$] ligand.

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Scheme 2. Polarizable π-Bonds in 1 and 2

A Phosphonio-methylidene **B**

A Phosphonio-methylidyne **B**

Figure 1. Molecular structure of **1**. Selected bond distances (Å) and angles (deg): W1−N1, 1.779(5); W1−C13, 1.813(6); W1−C32, 1.994(3); W1−C51, 2.022(7); P1−C13, 1.714(7); P1−C14, 1.800(7); P1−C26, 1.813(3); P1−C20, 1.813(6); P2−C32, 1.680(3); P2−C33, 1.811(7); P2−C39, 1.816(7); P2−C45, 1.828(6); P3−C51, 1.691(7); P3−C58, 1.771(6); P3−C52, 1.815(7); P3−C64, 1.826(8); N1−C1, 1.406(8); N1−W1−C13, 116.5(3); N1−W1−C32, 106.06(18); N1−W1−C51, 111.7(3); C13−W1−C32, 106.5(2); C13−W1−C51, 104.5(3); C32−W1−C51, 111.4(2); P1−C13−W1, 154.0(4); P2−C32−W1, 133.48(19); P3−C51−W1, 133.2(4); W1−C32−H32, 113.3; P2−C32−H32, 113.3; P3−C51−H51a, 113.4; W1−C51−H51a, 113.4. W1−N1−C1, 167.8(5).

Suitable crystals for an X-ray analysis[15] of **1** were obtained from pentane. The molecular structure is presented in Figure 1.

The tungsten atom is tetrahedrally coordinated by one [N-Dip]$^{2-}$, one [C−PPh$_3$]$^{2-}$, and two [CH−PPh$_3$]$^-$ ligands. The structure is related to the structure of [W(N^{t}Bu)$_2$-(CH−PPh$_3$)$_2$][3] by formal replacement of the two isoelectronic ligands [N−CR$_3$]$^{2-}$ and [C−PR$_3$]$^{2-}$. The α-CH hydrogen atoms at the [W=CHPPh$_3$] functions have been found in the difference Fourier analysis and were anisotropically refined. The corresponding W−CHP distances, 1.994(3) and 2.022(7) Å, respectively, fall at the upper end of the range typical for W−C double bonds, while the distance W1−C13 = 1.813(6) Å is more

(15) Crystallographic data for **1** (C$_{69}$H$_{64}$NP$_3$W, M_r = 1183.97): crystal size 0.17 × 0.07 × 0.04 mm^3, triclinic, space group P$\bar{1}$, a = 13.893(2) Å, b = 13.951(2) Å, c = 15.744(2) Å, α = 87.262(9)°, β = 75.196(9)°, γ = 76.208(8)°, V = 2864.9(5) Å^3, D_c = 1.372 g cm^{-3} for Z = 2, $F(000)$ = 1208, μ = 2.142 mm^{-1}, Stoe IPDS image plate diffractometer, λ = 0.710 69 Å, T = 193 K, 32 570 reflections, θ$_{max}$ = 25.3°, 10 419 independent and 7000 observed reflections ($F \geq 4\sigma(F)$), empirical absorption correction (multiscanned reflections), hydrogens calculated, disorder of one phenyl group, 718 refined parameters, R1 = 0.0481 (observed data), wR2 = 0.0921 (independent data). Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 171751. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

typical for an elongated triple bond than for a double bond.[16] In $[W(C-CMe_3)(CH-CMe_3)(CH_2-CMe_3)(dmpe)]$[17] reference values for $W-C$ = 2.258(9) Å, $W=C$ = 1.942-(9) Å, and $W\equiv C$ = 1.785(8) Å were observed, while an elongated $W-C$ triple bond has also been observed in $[WCl_2(CO)(PMePh_2)_2(C-PPh_3)]$[8] (1.823(7) Å). The corresponding $W-C$ distances in related $[W(N^tBu)_2(CH-PPh_3)_2]$ are 2.043(3) and 2.051(3) Å.[3] Both carbanionic centers C(32) and C(51) are planar within the accuracy limits of the measurement (sum of angles 360.1 and 360.0°) with $W-CH-P$ angles of ~133°. The phosphacumulene bond axis $W-C13-P1$ is slightly bent, revealing an angle of 154.0(4)°. This deviation from linearity is higher than in known phosphonio–carbyne complexes of lower valency, and it is reminiscent of the flexibility of the $P-C-P$ angle found in the carbodiphosphorane $Ph_3P-C-PPh_3$.[18]

The three ylidic $C_{yl}-P$ distances P1–C13 = 1.714(7) Å, P2–C32 = 1.680(3) Å, and P3–C51 = 1.691(7) Å are substantially shorter than the other $C_{ar}-P$ distances of the PPh_3 group (1.771–1.828 Å). This shortening reflects a considerable contribution of the phosphonio substituents in stabilizing the carbanion by negative hyperconjugation.[19] It is interesting to note that the longest $C_{yl}-P$ distance correlates with the shortest $W-C_{yl}$ distance of these highly polarizable multiple bonds. From the structural point of view the resonance forms A (Scheme 2) should contribute more than B to the ground state of these ligand functionalities. However, in d-metal compounds with a heavily π-loaded[20] tetrahedral regime of four competing π-donor ligands, it has to be taken into account that symmetry restrictions are limiting the number of metal–ligand π-interactions to five.[21]

Compounds **1** and **2** are reactive toward CO, CH_3NC, $Ph_2C=C=O$, CS_2, $PhC\equiv CH$, ^tBuSH, Me_3SiCl, and certain olefins in the presence of $B(C_6F_5)_3$. Currently we are investigating these reactions. Furthermore, we will follow up on the possibility of using the $[C-PR_3]^{2-}$ functionality as a spectator ligand in olefin polymerization catalysts isoelectronically related to known $[N-PR_3]^-$-containing catalysts.[22]

Supporting Information Available: Tables containing complete crystal and data collection parameters and positional parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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