Phosphenium Complexes, 42[◇]

Reaction of the Phosphenium Complexes $Cp(OC)_2W{=}P(tBu)(R)$ with Ethyl Isothiocyanate: Unprecedented Formation of the Phosphametalla Spiro Compound $\{Cp(OC)_2W–P(tBu)(R)–N(Et)–C^a[N(Et)–(CH)–N(Et)C^bH_2]–S(W–S)(C^a–C^b)\}Cl$ (R = *t*Bu, Ph)

Wolfgang Malisch*, Christa Abd El Baky, Klaus Grün, and Joachim Reising

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
E-mail: Wolfgang.Malisch@mail-uni-wuerzburg.de

Received May 12, 1998

Keywords: Phosphenium complexes / Cycloadditions / Heteroallenes / Phosphametallacycles / Diastereoselectivity / Spiro compounds

Reaction of the phosphenium complexes $Cp(OC)_2W{=}P(tBu)(R)$ [R = *t*Bu (**2a**), Ph (**2b**)] with ethyl isothiocyanate (**3**) leads to the formation of the phosphametallacycles $Cp(OC)_2W–P(tBu)(R)–C(=NEt)–S(W–S)$ (**4a**, **b**) by [2 + 2] cycloaddition. In contrast, the "in situ" reaction of **2a**, **b**, generated from $Cp(OC)_2[H(tBu)(R)P]W–Cl$ (**1a**, **b**) with DBU in the presence of **3** leads to the spirocyclic phosphorus metal compounds $\{Cp(OC)_2W–P(tBu)(R)–N(Et)–C^a[N(Et)–(CH)–N(Et)C^bH_2]–S(W–S)(C^a–C^b)\}Cl$ (**6a**, **b**). The structure of **6a** has been proved by X-ray analysis.

Introduction

Transition metal mediated synthesis of organic compounds is one of the outstanding areas of organometallic chemistry. Extension of this approach to organophosphorus chemistry has drawn increasing attention in recent times, involving phosphenium ($M{=}PR_2$)[1] or phosphinidene ($M{=}PR$)[2] complexes. In this context it has been demonstrated that the $M{=}P$ unit of the phosphenium complexes $Cp(OC)_2M{=}PR_2$ (M = Mo, W) exhibits a pronounced propensity for the addition of Brønstedt acids, carbenoids, and their analogues as well as diverse organic multiply bonded systems, offering efficient routes to new types of organophosphorus units. Within the scope of this topic we recently described the chemo- and regioselective cycloaddition of the phosphenium complexes $Cp(OC)_2M{=}P(R)(o\text{-Tol})$ (M = Mo, W; R = Ph, *o*-Tol) to organic isocyanates yielding the [2 + 2] cycloaddition products $Cp(OC)_2M-P(R)(o\text{-Tol})-C(=O)-NEt(M-N)$[3].

We now report about the cycloaddition reaction between the diorganophosphenium complexes $Cp(OC)_2W{=}P(tBu)(R)$ [R = *t*Bu (**2a**), Ph (**2b**)] bearing one or two *tert*-butyl ligands at the phosphorus atom and EtNCS affording, in addition to the expected cycloadduct, an unusual coupling product as a consequence of "in situ" generation.

Results

Reaction of the phosphenium complexes **2a**, **b**, obtained from the bifunctional complexes **1a**, **b** by DBU-assisted dehydrohalogenation, with EtNCS in toluene at room temperature after 12 (**2b**) and 24 h (**2a**), leads to the formation of the four-membered phosphametallacycles **4a**, **b**, representing the product of a [2 + 2] cycloaddition. The coupling reaction exclusively involves the C=S bond of the isothiocyanate, whereby, in contrast to the isocyanate reaction, not the nitrogen but the sulfur atom is coordinated to the metal atom while the electrophilic carbon atom is in both cases bonded to the phosphorus atom. This finding characterizes the isothiocyanate reaction as chemo- and regiospecific (Scheme 1).

Pure **4a**, **b** is isolated by column chromatography in good yield as a deep red and orange crystalline powder, respectively. The structure is proved by the ^{31}P-NMR spectra, with signals at $\delta = 39.7$ (**4a**) and 11.9 (**4b**) and $^1J(WP)$ couplings of 213.8 (**4a**) and 230.2 Hz (**4b**) appearing in the characteristic range of four-membered phosphametallacycles[3]. The signal of the *P*-bonded sp^2-carbon atom of **4b** is observed in the ^{13}C-NMR spectrum as a doublet in the typical low-field region at $\delta = 183.0$ with a $^1J(PC)$ coupling of 49.6 Hz. **4b**, which contains two stereogenic centers as i.e. the metal and the phosphorus atoms, is generated highly diastereoselectively, according to the NMR spectra.

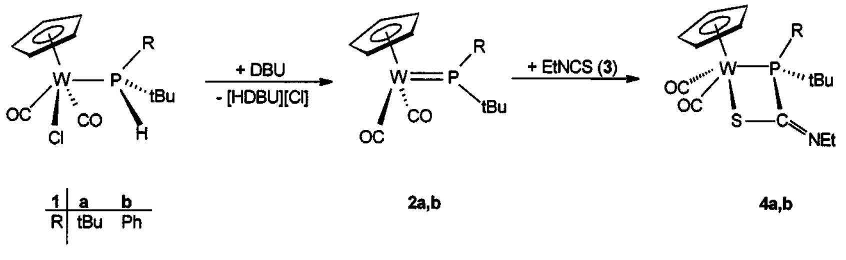
In order to promote metal-assisted organophosphorus synthesis it is reasonable to avoid isolation of the thermally

---

[◇] Part 41: O. Fey, J. Reising, W. Malisch, *Organometallics*, submitted.

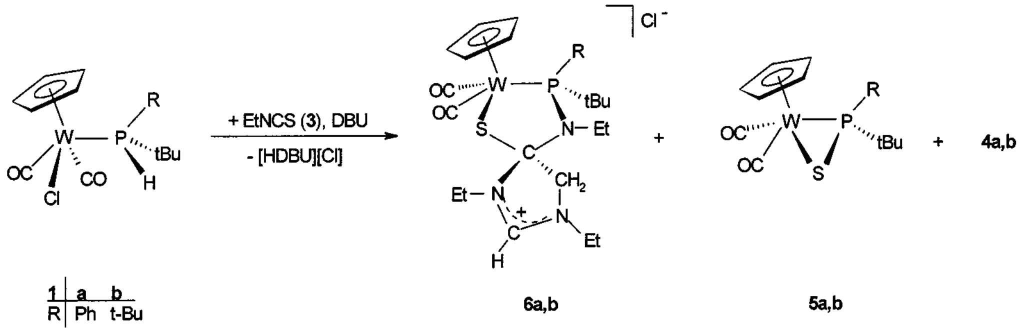
1434−1948/98/1212−1945 $ 17.50+.50/0

Scheme 1



unstable phosphenium complexes. According to this approach **2a**, **b** were generated "in situ" by combining the precursor complex **1** with **3** followed by addition of DBU. After removal of insoluble material, mainly [HDBU]Cl, the solution was reduced to a volume of 2 ml and the residue separated by column chromatography. This procedure yields, besides **4a**, **b**, the spirocyclic compounds **6a**, **b** as well as the three-membered heterocycles **5a**, **b**.

Scheme 2



The spirocycles **6a**, **b** are isolated in yields of 25% as orange powders, which show good solubilities in all organic solvents except for alkanes. Heterocycles **5a**, **b** could not be separated from **4a**, **b** but were alternatively prepared by the well-established addition of elemental sulfur to the W=P double bond of **2a**, **b**.

The spirocyclic compounds **6a**, **b** contain a five-membered phosphametalla heterocycle showing the ^{31}P-NMR low-field signals at δ = 143.4 (**6a**), 127.5 (**6a′**) and 120.0 (**6b**), 139.8 (**6b′**) with ^{1}J(WP) coupling constants of 277.0 (**6a**), 265.7 (**6a′**) Hz and 280.8 (**6b**), 280.5 (**6b′**) Hz. Presumably it is formed by a 1,3-dipolar cycloaddition of ethyl isothiocyanate to the W=P double bond. The carbon atom of the added isothiocyanate is responsible for the spirocyclic structure, formed by the coupling with two ethyl isocyanate molecules followed by protonation of the carbon atoms. The generation of the ethyl isocyanate incorporated in the spirocycle is verified under the reaction conditions by ring contraction of the [2 + 2] cycloadducts **4a**, **b** to give W−P−S cycles, as proved in a separate experiment. This is a further example of easy cleavage of the carbon−sulfur bond in isothiocyanates in the presence of a transition metal resulting in the generation of complexes having both the sulfur atom and the isocyanide incorporated[4].

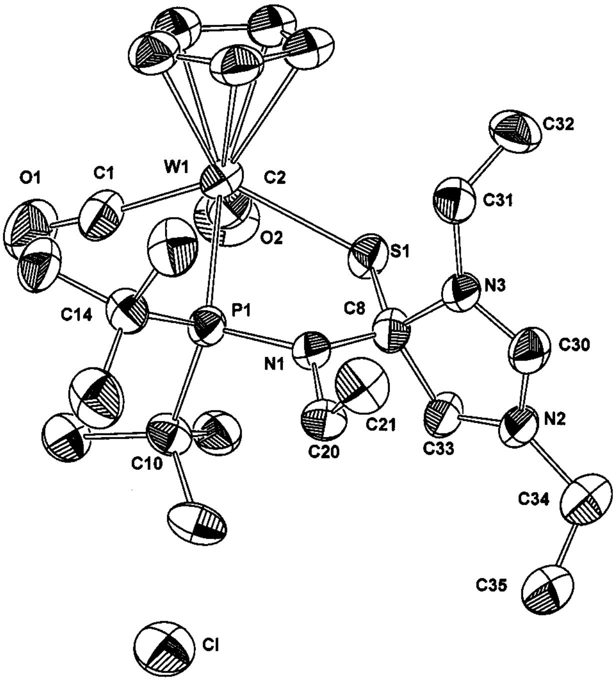
Despite the large number of postulated reaction steps, **6a**, **b**, which have two or three stereogenic centers, are formed highly diastereoselectively [*d. r.* = 96:4 (**6a**), 85:15 (**6b**)], indicating efficient stereocontrol by the metal fragment.

Final proof for the structure of **6a**, composed of two five-membered cycles connected by a spiro-carbon atom, is obtained by X-ray analysis. The spiro junction adopts a *syn* arrangement of the nitrogen atom N3 and the Cp ligand at the metal. The metal-phosphorus-containing ring shows an envelope conformation with a nearly planar P1−N1−C8−S1 unit [torsion angle: 12.9(10)°] with the folding along the W1−N1 axis resulting in an inclination of the phosphorus towards the Cp ligand. This arrangement is obvious from the different torsion angles W1−S1−C8−N1 [17.0(8)°] and W1−P1−N1−C8 [−35.4(8)°] and has its origin in the sterical interaction of the *tert*-butyl moiety (C14−C17) with the Cp unit. In the diaza ring the atoms N3, C30, N2, C33 are found in a plane [torsion angle: 6.9(13)°] from which the spiro atom C8 is only slightly deflected [C8−C33−N2−C30 15.4(12)°]. As shown by the angle Cp(Z)−W1−C8−N3 (1.16°), the plane of the ring is oriented nearly perpendicularly to the Cp(Z)−W axis.

Delocalization within the bonding system N2−C30−N3, involving an sp^2-hybridized carbon atom, is proved by the nearly identical values of the bond lengths N2−C30 [1.341(13) Å] and N3−C30 [1.345(13) Å], while the sp^3-hybridized carbon atom C33 is saturated by two hydrogen atoms.

The W1−P1 distance of 2.540(3) Å lies within the range of a single bond and is comparable with the values of other phosphane-substituted tungsten complexes[3][5]. The W1−S1 distance is slightly shorter than expected for a single bond [2.459(3) Å], while for the P1−N1 bond [1.720(8) Å] a single bond character is found[6].

Figure 1: ORTEP plot of $\{Cp(OC)_2W-P(tBu)_2-N(Et)-C^a[N(Et)-C(H)-N(Et)-C^bH_2]-S\mathit{(W-S)(C^a-C^b)}\}Cl$ (**6a**)[a]



[a] Selected bond lengths [Å], bond and torsion angles [°]: W1−C2 1.927(12), W1−C1 1.948(12), W1−P1 2.540(3), W1−S1 2.459(3), S1−C8 1.823(11), P1−N1 1.720(8), N1−C8 1.437(12), N2−C30 1.341(13), N2−C33 1.449(12), N3−C30 1.345(13), N3−C8 1.472(12), C8−C33 1.558(13); W1−S1−C8 112.8(2), P1−W1−S1 74.2(8), W1−P1−N1 107.4(5); C8−S1−W1−P1 28.7(6), S1−W1−P1−N1 31.4(5), W1−P1−N1−C8 35.4(1), P1−W1−S1−C8 12.9(5); N1−C8−S1−W1 16.9(9), C30−N3−C8−C33 13.9(4), N3−C8−C33−N2 16.7(2), C8−C33−N2−C30 15.5(1), C33−N2−C30−N3 6.9(4), Cp(Z)−W1−C8−N3 1.16.

In conclusion, these studies demonstrate a metal-mediated multistep synthesis, starting from easily accessible secondary phosphane complexes with the corresponding phosphenium complexes as the crucial intermediates. Furthermore, this process proceeds with a high degree of diastereoselectivity, a feature which promises future application of these phosphametallaspirocycles in enantioselective synthesis.

Support of this research by the *Deutsche Forschungsgemeinschaft* (Sonderforschungsbereich 347, *"Selektive Reaktionen Metall-aktivierter Moleküle"*) is gratefully acknowledged.

Experimental Section

General: All manipulations were performed under dried and purified nitrogen. Solvents were rigorously dried with an appropriate drying agent, distilled before use and saturated with nitrogen. $Cp(OC)_2[H(tBu)(R)P]W-Cl$ and $Cp(OC)_2W=P(tBu)(R)$ (R = *t*Bu[7], Ph[1j]) were prepared according to the literature. All other reagents were obtained commercially and used without further purification. − ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained on a Bruker AMX 400 spectrometer. $\delta(^1H)/(^{13}C)$ chemical shifts are reported downfield from Me_4Si referenced to the residual proton signal (^{1}H) or natural abundance carbon signal (^{13}C) of the deuterated solvent. $\delta(^{31}P)$ chemical shifts are measured relative to external H_3PO_4 (85%). Shifts downfield from the standard were assigned positive δ values. − Infrared spectra were measured in solution on a Perkin-Elmer 283 grating spectrometer in NaCl cells with 0.1-mm path length. − Melting points: Differential thermoanalysis (Du Pont 9000). − Elemental analyses were performed in the laboratory of the Institut für Anorganische Chemie der Universität Würzburg.

1. *$Cp(OC)_2W-P(tBu)_2-C(=NEt)-S(W-S)$* (**4a**): A solution of 170 mg (0.38 mmol) of $Cp(OC)_2W=P(tBu)_2$ (**2a**) in 10 ml of toluene was combined with 33 mg (0.38 mmol) of ethyl isothiocyanate (**3**) and the mixture stirred for 24 h at room temperature. The reaction mixture was reduced in vacuo to a volume of 1 ml and worked up by column chromatography (column 10 × 1.5 cm, alumina III, neutral, toluene). The eluate of the dark red zone was concentrated in vacuo and remaining **4a** was recrystallized from 7 ml of pentane. − Yield: 153 mg (75%). − Dark red microcrystalline powder. − M.p. 183°C. − ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 4.91 (s, 5 H, H_5C_5), 3.73 [qd, ^3J(HCCH) = 7.4 Hz, ^4J(PCNCH) = 2.5 Hz, 2 H, H_2CN], 1.32 [d, ^3J(PCCH) = 16.5 Hz, 9 H, $(H_3C)_3C$], 1.26 [t, ^3J(HCCH) = 7.4 Hz, 3 H, H_3CCH_2N], 1.04 [d, ^3J(PCCH) = 16.5 Hz, 9 H, $(H_3C)_3C$]. − ^{31}P NMR (162.0 MHz, [D$_6$]benzene): δ = 39.7 [s, ^1J(WP) = 213.8 Hz]. − IR (toluene): ṽ = 1936, 1853 (CO) cm^{-1}. − $C_{18}H_{28}NO_2PSW$ (537.31): calcd. C 40.24, H 5.25, N 2.61, S 5.97; found C 40.44, H 5.37, N 2.57, S 5.88.

2. *$Cp(OC)_2W-P(tBu)(Ph)-C(=NEt)-S(W-S)$* (**4b**): Prepared as described for **4a** from 242 mg (0.51 mmol) of $Cp(OC)_2W=P(tBu)(Ph)$ (**2b**) and 44 mg (0.51 mmol) of ethyl isothiocyanate (**3**) in 10 ml of toluene after stirring for 12 h. − Yield: 216 mg (76%). − Orange microcrystalline powder. − M.p. 193°C. − ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 8.04 (m, 2 H, H_5C_6), 7.13 (m, 3 H, H_5C_6), 4.77 (s, 5 H, H_5C_5), 3.88 (m, 2 H, H_2CN), 1.43 [t, ^3J(HCCH) = 7.6 Hz, 3 H, H_3CCH_2N], 1.38 [d, ^3J(PCCH) = 15.2 Hz, 9 H, $(H_3C)_3C$]. − ^{13}C NMR (100.6 MHz, [D$_6$]benzene): δ = 245.5 [d, ^2J(PWC) = 22.9 Hz, *cis*-CO], 230.8 [d, ^2J(PWC) = 3.8 Hz, *trans*-CO], 183.0 [d, ^1J(PC) = 49.6 Hz, C=N], 133.9 [d, ^1J(PC) = 51.5 Hz, C-1], 133.0 [d, ^3J(PCCC) = 8.6 Hz, C-3/5], 130.0 [d, ^2J(PCC) = 1.9 Hz, C-2/6], 127.5 (s, C-4), 44.8 [d, ^1J(PC) = 19.1 Hz, $C(CH_3)_3$], 36.1 [d, ^3J(PCNC) = 20.0 Hz, CH_2N], 26.0 [d, ^2J(PCC) = 2.9 Hz, $(CH_3)_3C$], 15.0 (s, CH_3CH_2N). − ^{31}P NMR (162.0 MHz, [D$_6$]benzene): δ = 11.9 [s, ^1J(WP) = 230.2 Hz]. − IR (toluene): ṽ = 1924, 1839 (CO) cm^{-1}. − $C_{20}H_{24}NO_2PSW$ (557.30): calcd. C 43.10, H 4.34, N 2.51, S 5.75; found C 43.36, H 4.65, N 2.14, S 5.50.

3. *$\{Cp(OC)_2W-P(tBu)_2-N(Et)-C^a[N(Et)-(CH)-N(Et)-C^bH_2]-S(W-S)(C^a-C^b)\}Cl$* (**6a**): A solution of 312 mg (0.64 mmol) of $Cp(OC)_2[H(tBu)_2P]W-Cl$ (**1**) and 167 mg (1.92 mmol) of ethyl isothiocyanate (**3**) was combined with 97 mg (0.64 mmol) of DBU and stirred for 24 h at room temperature. The reaction mixture was reduced in vacuo to a volume of 2 ml and worked up by column chromatography (column 25 × 2.5 cm, alumina III, neutral, toluene). The eluate of the second orange zone was evaporated in vacuo and remaining **6a** recrystallized from 7 ml of pentane. − Yield: 56 mg (25%). − Orange microcrystalline powder. − M.p. 78°C. − Diastereomeric ratio: 96:4 (determined by integration of the Cp signals in the ^{1}H-NMR). − *Main diastereomer*: ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 5.06 (s, 5 H, H_5C_5), 4.14 [d, ^2J(HCH) = 11.2 Hz, 1 H, H_2CCNP], 3.83 (m, 2 H, H_2CCH_3), 3.74 [d, ^2J(HCH) = 11.2 Hz, 1 H, H_2CCNP], 3.35 (m, 2 H, H_2CCH_3), 2.87 (m, 2 H, H_2CCH_3), 1.81 [t, ^3J(HCCH) = 7.0 Hz, 3 H, H_3CCH_2], 1.32 [d, ^3J(PCCH) = 13.1 Hz, 18 H, $(H_3C)_3C$], 1.10 [t, ^3J(HCCH) = 7.0 Hz, 3 H, H_3CCH_2], 0.95 [t, ^3J(HCCH) = 7.0 Hz, 3 H, H_3CCH_2]. − ^{13}C NMR (100.6 MHz, [D$_6$]benzene):

δ = 244.1 [d, ^{2}J(PWC) = 16.2 Hz, *cis*-CO], 228.9 [d, ^{2}J(PWC) = 1.9 Hz, *trans*-CO], 179.3 (s, CNP), 93.7 (s, C_5H_5), 62.1 (s, CH_2CNP), 49.0 [d, ^{1}J(PC) = 7.5 Hz, $C(CH_3)_3$], 43.8 [d, ^{4}J(PNCNC) = 3.8 Hz, CH_2NCNP], 41.3 [d, ^{2}J(PNC) = 17.2 Hz, CH_2NP], 38.1 (s, CH_2NC), 31.7 [d, ^{2}J(PCC) = 2.9 Hz, $(CH_3)_3C$], 15.8 (s, CH_3CH_2), 15.2 [d, ^{3}J(PNCC) = 2.9 Hz, CH_3CH_2NP], 11.9 (s, CH_3CH_2); δ(CHN) = 128.9 ($CDCl_3$, 150.9 MHz). – ^{31}P NMR (162.0 MHz, [D_6]benzene): δ = 143.4 [s, ^{1}J(WP) = 277.0 Hz]. – *Minor diastereomer*: ^{1}H NMR (400.1 MHz, [D_6]benzene): δ = 5.02 (s, 5 H, H_5C_5), 3.57 [d, ^{2}J(HCH) = 10.3 Hz, 1 H, H_2CCNP], 3.48 (m, 2 H, H_2CCH_3), 3.39 [d, ^{2}J(HCH) = 10.3 Hz, 1 H, H_2CCNP], 3.06 (m, 2 H, H_2CCH_3), 2.62 (m, 2 H, H_2CCH_3), 1.86 [t, ^{3}J(HCCH) = 7.6 Hz, 3 H, H_3CCH_2], 1.27 [d, ^{3}J(PCCH) = 13.5 Hz, 18 H, $(H_3C)_3C$], 0.89 [t, ^{3}J(HCCH) = 7.1 Hz, 3 H, H_3CCH_2], 0.56 [t, ^{3}J(HCCH) = 7.6 Hz, 3 H, H_3CCH_2]. – ^{13}C NMR (100.6 MHz, [D_6]benzene): δ = 244.2 [d, ^{2}J(PWC) = 15.2 Hz, *cis*-CO), 229.1 [d, ^{2}J(PWC) = 1.9 Hz, *trans*-CO], 180.8 (s, CNP), 93.0 (s, C_5H_5), 63.8 (s, CH_2CNP), 48.0 [s, $C(CH_3)_3$], 44.0 [d, ^{2}J(PNC) = 3.8 Hz, CH_2NP], 40.8 [d, ^{4}J(PNCNC) = 2.9 Hz, CH_2NCNP], 39.6 (s, CH_2NC), 31.0 [d, ^{2}J(PCC) = 2.9 Hz, $(CH_3)_3C$], 15.3 (s, CH_3CH_2), 13.9 [d, ^{3}J(PNCC) = 2.9 Hz, CH_3CH_2NP], 11.8 (s, CH_3CH_2); δ(CHN) = 128.8 ($CDCl_3$, 130.9 MHz). – ^{31}P NMR (162.0 MHz, [D_6]benzene): δ = 127.5 [s, ^{1}J(WP) = 265.7 Hz]. – IR (toluene): ṽ = 1936, 1837 (CO) cm^{-1}. – $C_{24}H_{41}ClN_3O_2PSW$ (685.95): calcd. C 42.02, H 6.02, N 6.13, S 4.67; found C 40.34, H 6.04, N 5.58, S 8.60.

4. *{Cp(OC)$_2$W–P(tBu)(Ph)–N(Et)–C^a[N(Et)–(CH)–N-(Et)C^{b}H$_2$]–S(W–S)(C^a–C^b)}Cl* (**6b**): Prepared as described for **6a** from 275 mg (0.54 mmol) of $Cp(OC)_2$[H(*t*Bu)(Ph)P]W–Cl (**1b**), 141 mg (1.62 mmol) of ethyl isothiocyanate (**3**) and 83 mg (0.54 mmol) of DBU. **6b** is obtained from the eluate of the second red zone. – Yield: 50 mg (13%). – Dark orange microcrystalline powder. – M.p. 83°C. – Diastereomeric ratio: 85:15 (determined by integration of the Cp signals in the ^{1}H NMR). – *Main diastereomer*: ^{1}H NMR (400.1 MHz, [D_6]benzene): δ = 7.76–6.98 (m, 5 H, H_5C_6), 4.75 (s, 5 H, H_5C_5), 4.08 [d, ^{2}J(HCH) = 11.8 Hz, 1 H, H_2CCNP], 3.86 (m, 2 H, H_2CCH_3), 3.80 [d, ^{2}J(HCH) = 11.8 Hz, 1 H, H_2CCNP], 3.43 (m, 2 H, H_2CCH_3), 3.17 (m, 2 H, H_2CCH_3), 1.80 [t, ^{3}J(HCCH) = 7.4 Hz, 3 H, H_3CCH_2], 1.29 [d, ^{3}J(PCCH) = 14.8 Hz, 9 H, $(H_3C)_3C$], 0.99 [t, ^{3}J(HCCH) = 6.5 Hz, 3 H, H_3CCH_2], 0.85 [t, ^{3}J(HCCH) = 6.5 Hz, 3 H, H_3CCH_2]. – ^{31}P NMR (162.0 MHz, [D_6]benzene): δ = 120.0 [s, ^{1}J(WP) = 280.8 Hz]. – *Minor diastereomer*: ^{1}H NMR (400.1 MHz, [D_6]benzene): δ = 4.78 (s, 5 H, H_5C_5), 3.81 [d, ^{2}J(HCH) = 10.3 Hz, 1 H, H_2CCNP], 3.53 [d, ^{2}J(HCH) = 10.3 Hz, 1 H, H_2CCNP], additional signals not assigned. – ^{31}P NMR (162.0 MHz, [D_6]benzene): δ = 139.8 [s, ^{1}J(WP) = 280.5 Hz]. – $C_{26}H_{37}ClN_3O_2PSW$ (705.94): calcd. C 44.24, H 5.28, N 5.95, S 4.54; found C 44.43, H 5.41, N 5.88, S 4.67.

5. *Cp(OC)$_2$W–P(tBu)$_2$–S(W–S)* (**5a**): A solution of 165 mg (0.36 mmol) of $Cp(OC)_2W=P$(*t*Bu)$_2$ (**2a**) in 7 ml of toluene was combined with 12 mg (0.36 mmol) of elemental sulfur and stirred for 4 h at room temperature. The reaction mixture was reduced in vacuo to a volume of 1 ml and worked up by column chromatography (column 10 × 1.5 cm, alumina III, neutral, toluene). The eluate of the red zone was evaporated in vacuo and remaining **5a** recrystallised from 5 ml of pentane. Yield: 142 mg (85%). – Dark red microcrystalline powder. – M.p. 120°C. – ^{1}H NMR (400.1 MHz, [D_6]benzene): δ = 5.16 (s, 5 H, H_5C_5), 1.53 [d, ^{3}J(PCCH) = 16.4 Hz, 9 H, $(H_3C)_3C$], 1.27 [d, ^{3}J(PCCH) = 16.2 Hz, 9 H, $(H_3C)_3C$]. – ^{31}P NMR (162.0 MHz, [D_6]benzene): δ = 60.9 [s, ^{1}J(WP) = 195.1 Hz] – IR (toluene): ṽ = 1937, 1851 (CO) cm^{-1}. – $C_{15}H_{23}O_2PSW$ (482.23): calcd. C 37.36, H 4.08; found C 37.54, H 5.20.

6. *Cp(OC)$_2$W–P(tBu)(Ph)–S(W–S)* (**5b**): Prepared as described for **5a** from 182 mg (0.39 mmol) of $Cp(OC)_2W=P$(*t*Bu)(Ph) (**2b**) and 12 mg (0.39 mmol) of elemental sulfur in 7 ml of toluene after stirring for 2 h. Yield: 174 mg (89%). – Red microcrystalline powder. – M.p. 180°C. – ^{1}H NMR (400.1 MHz, [D_1]chloroform): δ = 7.76–7.39 (m, 5 H, H_5C_6), 5.19 (s, 5 H, H_5C_5), 1.18 [d, ^{3}J(PCCH) = 18.7 Hz, 9 H, $(H_3C)_3C$]. – ^{13}C NMR (100.6 MHz, [D_1]chloroform): δ = 240.0 [d, ^{2}J(PWC) = 29.3 Hz, *cis*-CO], 228.3 (s, *trans*-CO), 133.8 [d, ^{3}J(PCCC) = 11.8 Hz, C3/5], 132.4 [d, ^{1}J(PC) = 36.6 Hz, C1], 130.4 [d, ^{4}J(PCCCC) = 3.1 Hz, C4], 127.9 [d, ^{2}J(PCC) = 11.1 Hz, C2/6], 91.1 (s, C_5H_5), 27.9 [d, ^{1}J(PC) = 34.5 Hz, $C(CH_3)_3$], 26.8 [d, ^{2}J(PCC) = 4.5 Hz, $(CH_3)_3C$]. – ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 39.4 [^{1}J(WP) = 221.1 Hz). – IR (toluene): ṽ = 1940, 1854 (CO) cm^{-1}. – $C_{17}H_{19}O_2PSW$ (502.26): calcd. C 40.66, H 3.81; found C 40.80, H 3.84.

7. *Reaction of Cp(OC)$_2$W–P(tBu)$_2$–C(=NEt)–S(W–S) with [HDBU][Cl]:* A solution of 125 mg (0.23 mmol) of $Cp(OC)_2W–P$(*t*Bu)$_2$–C(=NEt)–S(*W*–*S*) (**4a**) in 7 ml of toluene is combined with an excess of [HDBU][Cl]. After stirring for 2 d insoluble [HDBU][Cl] is separated and pure **5a** is identified by ^{31}P-NMR spectroscopic comparison with an authentic sample.

8. *X-ray Structure Analysis of* **6a**: Orange crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a saturated solution of **6a** in benzene at room temperature. $C_{24}H_{41}ClN_3O_2PSW$, M = 685.95; Crystallographic data for **3a**: monoclinic, $P2_1/c$ (Nr. 14), Z = 4, a = 15.675(4), b = 12.375(2), c = 16.219(5) Å, β = 110.79(1)°, V = 2941(1) Å^3, $\rho_{calcd.}$ = 1.637 $g \cdot cm^{-3}$, Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71073 Å), 4078 independent reflections with $2.12° < \theta < 22.93°$ collected, 2781 reflections used in refinement with $I > 2\sigma(I)$; R_1 = 0.0479; wR_2 = 0.0978. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101571. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] [1a] W. Malisch, U.-A. Hirth, K. Grün, M. Schmeußer, O. Fey, U. Weis, *Angew. Chem.* **1995**, *107*, 2717–2719; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2500–2502. – [1b] A. Fried, W. Malisch, M. Schmeußer, U. Weis, *Phosphorus Sulfur* **1992**, *65*, 75–78. – [1c] W. Malisch, U.-A. Hirth, T. A. Bright, H. Käb, T. S. Ertel, S. Hückmann, H. Bertagnolli, *Angew. Chem.* **1992**, *104*, 1537–1539; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1525–1527. – [1d] W. Malisch, K. Grün, N. Gunzelmann, S. Möller, R. Lankat, J. Reising, M. Neumayer, O. Fey in *Selective Reactions of Metal-Activated Molecules*, H. Werner, W. Adam, G. Bringmann, W. Kiefer (Eds.), Vieweg-Verlag, Braunschweig **1995**, p. 183–190. – [1e] W. Malisch, U.-A. Hirth, A. Fried, H. Pfister, *Phosphorus Sulfur* **1993**, *77*, 17–20. – [1f] H. Lang, M. Leise, L. Zsolnai, *Organometallics* **1993**, *12*, 2393–2397. – [1g] H.-U. Reisacher, E. N. Duesler, R. T. Paine, *Chem. Ber.* **1996**, *129*, 279–281. – [1h] H.-U. Reisacher, W. F. McNamara, E. N. Duesler, R. T. Paine, *Organometallics* **1997**, *16*, 449–455. – [1i] H.-U. Reisacher, E. N. Duesler, R. T. Paine, *J. Organomet. Chem.* **1997**, *539*, 37–44. – [1j] W. Malisch, A. Meyer, K. Jörg, U. Hofmockel, M. Schmeußer, R. Schemm, W. S. Sheldrick, *Phosphorus Sulfur* **1987**, *30*, 205–208.

[2] [2a] C. C. Cummins, R. R. Schrock, W. M. Davis, *Angew. Chem.* **1993**, *105*, 758–761; *Angew. Chem. Int. Ed. Engl.* **1993**, *23*, 756–760. – [2b] A. Mathieu, A. Igau, J.-P. Majoral, *Phosphorus Sulfur* **1995**, *104*, 235–239. – [2c] T. L. Breen, D. W. Stephan, *Organometallics* **1996**, *15*, 4509–4514. – [2d] T. L. Breen, D. W. Stephan, *Organometallics* **1997**, *16*, 365–369.

[3] W. Malisch, C. Hahner, K. Grün, J. Reising, R. Goddard, C. Krüger, *Inorg. Chim. Acta* **1996**, *244*, 147−150.

[4] [4a] W. P. Fehlhammer, A. Mayr, *J. Organomet. Chem.* **1980**, *191*, 153−159. − [4b] H. Fischer, *J. Organomet. Chem.* **1981**, *222*, 241−250. − [4c] H. Fischer, R. Märkl, *Chem. Ber.* **1982**, *115*, 1349−1354. − [4d] G. Hogarth, E. Skordalakis, *J. Organomet. Chem.* **1993**, *458*, C8−C9.

[5] [5a] W. Malisch, H. Pfister, *Organometallics* **1995**, *14*, 4443−4445. − [5b] B. K. Schmiedeskamp, J. G. Reising, W. Malisch, K. Hindahl, R. Schemm, W. S. Sheldrick, *Organometallics* **1995**, *14*, 4446−4448.

[6] C. Bueno, M. R. Churchill, *Inorg. Chem.* **1981**, *20*, 2197−2202.

[7] K. Jörg, W. Malisch, A. Meyer, W. Reich, U. Schubert., *Angew. Chem.* **1986**, *98*, 103−104; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 92−93.

[98142]