

Metalated 1,3-Azaphospholes: 1*H*-1,3-Benzazaphosphole and 1,3-Benzazaphospholide Tungsten(0) and Tungsten(II) Complexes

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2-*tert*-Butyl-1*H*-1,3-benzazaphosphole (**1a**) reacts with *t*BuLi without addition to the P=C bond to form a lithium benzazaphospholide that affords the η^1 -(benzazaphospholide-*P*)tungsten(II) complex **2** upon reaction with [CpW(CO)₃Cl]. It is sensitive to alcoholysis and to air oxidation yielding **1a** and the *P*-oxo-benzazaphospholide complex **3**, respectively. The (1,3-benzazaphosphole)pentacarbonyltungsten complex **4**, obtained from **1b** and [W(CO)₅(THF)], reacts preferentially

with *t*BuLi by lithiation of the NH function and is attacked by [CpW(CO)₃Cl] at phosphorus to give the mixed valence bimetallic tungsten(II)-tungsten(0) benzazaphospholide complex **5**. A side product, (3-*tert*-butyl-2-methyl-1,3-benzazaphosphole)pentacarbonyltungsten (**6**), is attributed to side-reaction where *t*BuLi adds to the P=C bond in **4**. The composition of the products was determined from X-ray structure analysis of **3** and spectroscopic data.

Introduction

Phospholide^[1–4] and pyrrolide^[3–6] complexes have attracted considerable interest in the past years, and some di- and triazaphosphol(id)e complexes have also been reported.^[7] Azaphospholide complexes, analogues of pyrrolide or of diphospholide complexes, as well as 1,3-benzazaphospholide complexes are, however, still unknown. The recent discovery of a convenient synthetic access to 2-substituted 1*H*-1,3-benzazaphospholes^[8] prompted us to fill this gap partly and to explore the reactivity and use of these very stable but under-investigated phosphaaromatic heterocycles as ligands.^[8–11] The only 1,3-benzazaphosphole complex reported to date is pentacarbonyl- η^1 -(2-phenyl-1,3-benzazaphosphole-*P*)chromium.^[10] Lithiation of 2-phenylbenzazaphosphole by Et₂NLi has also been described,^[10] although the lithium benzazaphospholide was not isolated and separated from the secondary amine, which is preferentially attacked by electrophiles other than alkyl halides. We report here on an alternative metalation procedure avoiding this problem and the synthesis of the first 1,3-benzazaphosphole and 1,3-benzazaphospholide tungsten complexes.

Results and Discussion

Synthesis

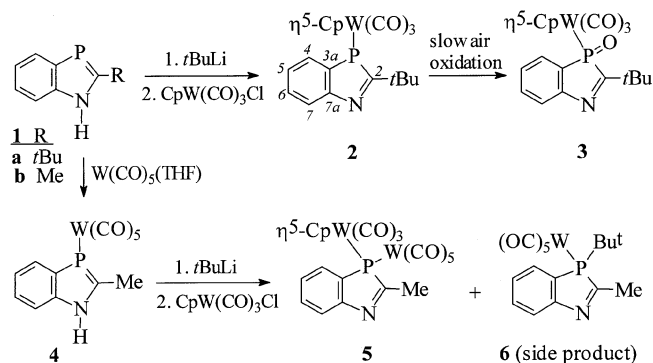
Whilst 1*H*-1,3-benzazaphospholes and *n*BuLi produce mixtures of addition and metalation products, a selective monolithiation of the NH function is achieved by treatment of **1a** with one equivalent of *t*BuLi in ether or THF at low temperature. Like ambident anions formed by the metalation of pyridylphosphanes,^[12] the resulting lithium 1,3-benzazaphospholide **Li-1a** can be used directly for the synthesis of complexes as exemplified by the reaction with [CpW(CO)₃Cl] (Scheme 1). **Li-1a** reacts selectively at phosphorus to give the dark red-brown benzazaphospholide tungsten complex **2**. It is slightly soluble in hexane and readily soluble in more polar solvents like toluene or ethers. Like related Cp(CO)₃W-phospholide^[13–15] or Cp(CO)₃W-phosphide^[16] complexes, **2** is a very reactive compound. Although less sensitive towards hydrolysis than the extremely reactive *N*-silyl- or *P*-stannyl-benzazaphospholes,^[17] the P–W bond of **2** is cleaved readily by OH/OD reagents, as shown by the addition of CD₃OD to yield **1b**. The latter is also formed on heating **2** to 80 °C in toluene for one day, whereas related but more stable Cp(CO)₃W complexes with non-anellated phospholide ligands form tungsten-bridged complexes.^[15] Compound **2** is also sensitive to air oxidation. Crystallization of a sample oxidized in THF gave single crystals of the toluene monosolvate of the *P*-oxo-benzazaphospholide tungsten complex **3**, from toluene/hexane, which allowed an X-ray crystal structure analysis (Figure 1).

The (1,3-benzazaphosphole)pentacarbonyltungsten complex **4**, obtained from **1b** and [W(CO)₅(THF)], can be lithiated in an analogous manner with *tert*-butyllithium and trapped with [CpW(CO)₃Cl]. The formation of the mixed valence bimetallic complex **5**, with zero- and two-valent

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Scheme 1

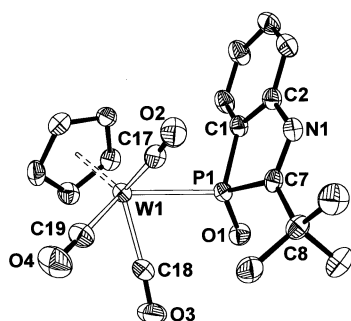


Figure 1. Solid state structure of **3** (anisotropic displacement parameters drawn at 50% probability level, hydrogen atoms and toluene omitted for clarity); selected bond lengths [Å] and angles[°]: W1–P1 2.5591(7), W–C(O) 1.989(3) – 2.005(3), W–C(Cp) 2.314(3) – 2.361(3), P1–O1 1.507(2); W1–P1–O1 116.91(8), O1–P1–C1 114.18(12), O1–P1–C7 113.32(12), W1–P1–C1 107.79(9), W1–P1–C7 113.12(8), P1–W1–C17 78.03(8), P1–W1–C18 73.43(8), C17–W1–C19 76.77(12), C19–W1–C18 77.28(12); for ring parameters see Table 1

tungsten bound at the phosphorus atom, shows that the blockage of the phosphorus lone electron pair does not favor an attack at nitrogen, but that the lithiated pentacarbonyl tungsten complex **Li·4** also prefers substitution at the softer nucleophilic site. The lithiation itself proceeds less selectively, as seen from the occurrence of **6**. It is assumed that **6** is formed by the addition of *t*BuLi to the P=C double bond of **4** followed by reaction with [CpW(CO)₃Cl] and elimination of [CpW(CO)₃H]. In the crude product the ratio **5**:**6** was found to be ca. 2:1.

Structure

The ¹H, ¹³C and ³¹P NMR chemical shifts and coupling patterns, the observance of molecular ions in the mass spectrum and satisfactory elemental analysis give evidence for the structures of **2**, **4** and **5**. Like related Cp(CO)₃W-phospholide complexes,^[15] compound **2** (δ = –102.4, ¹J_{P–W} = 50.1 Hz) reveals a strong up-field coordination shift Δδ(**2**–**Li·1a**) = –159 and a very small one-bond P–W coupling constant. The acyclic [Cp(CO)₃W–PPh₂] (δ = –63.3, ¹J_{P–W} = 52 Hz)^[16] exhibits a similar low P–W coupling constant, but a much smaller upfield coordination shift relative to the corresponding alkali metal phosphides (Ph₂PLi: δ = –21.4^[18]). The larger upfield coordination

shift in the formal 6π- or 10π-heterocyclic phosphido complexes with the same ML_n fragment reflects a larger increase in the electron density at phosphorus and may be attributed to a reduced ability of the π-electrons at phosphorus to take part in cyclodelocalization; it may also be supported by a more effective back donation compared to that in Ph₂P–W(CO)₃Cp or in the W⁰(CO)₅-benzazaphosphole complex **4**. The ¹³C nuclei of the five-membered ring and of C-5 to C-7 are markedly deshielded by the complexation, Δδ(**2**–**1a**) ≈ 20 (C-2), 12 (C-3a, C-7, C-7a) and 7 (C-5, C-6), whilst the one-bond P–C couplings show different trends, ¹J_{P–C2} increases from 57 Hz in **1a** to 61.8 Hz in **2**, and ¹J_{P–C3a} decreases from 41 to 14 Hz. The chemical shift values are significantly closer to those of 3*H*-1,3-benzazaphospholes^[17,19,20] than to those of **1** although the one-bond coupling constants of **2** are significantly larger than in the 3*H*-isomers. These findings imply that the nature of **2** is in-between that of the aromatic 1*H*- and the non-aromatic 3*H*-3-alkyl-1,3-benzazaphospholes,^[21–23] although probably closer to the latter. For the related phospholide CpW(CO)₃ complexes a similar situation was deduced from the X-ray crystal structure analysis.^[15] The compounds were classified from the structural standpoint as halfway between phospholes with pyramidal P and localized π-bonds and phospholes with planar P and delocalized π-bonds.

In the oxidation product **3** the framework of **2** is preserved (Figure 1) but the transition to four-coordinate phosphorus consolidates a non-aromatic, 3*H*-indole-like π-system. The lack of cyclodelocalization becomes evident by comparison of selected bond lengths and angles of the five-membered ring in **3** and the corresponding parameters of its phosphaaromatic precursor **1a**^[17] (Table 1). Within the P–C–N fragment the P–C bond is considerably widened and becomes longer than the P–C(aryl) bond, whilst the C–N bond is shortened. The smaller N1–C7 bond and the approximation of the C1–C2–N angle in **3** to an ideal sp² geometry at the expense of the C2–C1–P angle reflects the strengthening of a coplanar *N*-phenyl-azomethine π-system. In the acyclic metallaphosphane oxide [oTol₂P(O)–W(CO)₃Cp],^[16b] the P1–W1 distances of the two independent molecules in the unit cell are slightly longer [2.571(8), 2.589(9) Å] than in **3**, although shorter than the sum of the covalent radii (2.65 Å),^[24] and the P–O bonds (double bond character) are slightly shorter [1.46(2), 1.49(2) Å]. The W–P–O angle is larger in **3** due to the small C–P–C angle within the five-membered ring.

The known compound η¹-(2-phenyl-1,3-benzazaphosphole-*P*)pentacarbonylchromium exhibits a very low positive complexation shift (Δδ = 4.4) and classifies 1*H*-1,3-benzazaphospholes as weak donors.^[10] The tungsten pentacarbonyl complex **4** even displays a negative coordination shift (Δδ = –35.0). The upfield shift of the tungsten relative to the related chromium complex reflects the typical core-effect in transition metal phosphane complexes^[25] and is also observed for related (phosphaindolizine)metallapentacarbonyls (M = Cr, Mo, W).^[26] The one bond ³¹P–¹⁸³W coupling constant is much larger than in **2**, **5** and **6** and

Table 1. Comparison of selected structure data of **3** and corresponding data of **1a**^[17]

Bond length [Å], angle [°]	3	1a
P1–C1	1.817(3)	1.793(3)
P1–C7	1.882(3)	1.712(4)
N1–C7	1.290(3)	1.374(4)
N1–C2	1.430(3)	1.380(4)
C1–C2	1.404(4)	1.389(4)
C7–C8	1.522(4)	1.514(4)
P1–C7–N1	113.43(19)	112.3(2)
C1–P1–C7	87.88(12)	90.1(2)
C2–N1–C7	112.6(2)	115.1(3)
C1–C2–N1	117.1(2)	111.9(3)
C2–C1–P1	108.27(19)	110.7(2)

similar to that in pentacarbonyltungsten complexes of less-basic triorganophosphanes.^[25] The effect of the complexation on the 1*H*-1,3-benzazaphosphole π -system is rather small and limited mainly to the carbon atoms adjacent to phosphorus. C-2 and C-3a of **4** are shifted by $\Delta\delta \approx 7$ in the ¹³C NMR spectrum and display much lower P–C coupling constants. For C-4 and the methyl carbon in the β -position to the phosphorus this trend is much smaller, and the other nuclei show no marked influence. In the tungsten complexes **5** and **6**, however, the cyclodelocalization seems to be lost. Both, the tungsten(II)- and the 3-*tert*-butyl-substituted 1,3-benzazaphosphole tungsten pentacarbonyl species, exhibit the signals of the ¹³C nuclei C-5 to C-7a at significantly lower field than in **1** or **4**, in regions typical for 3-alkyl-1,3-benzazaphospholes.^[17,19,20] The phosphido-character of the benzazaphospholide ligand is markedly reduced by complexation with W(CO)₅ as indicated by the less-negative phosphorus resonance of **5** relative to **2** ($\Delta\delta = 26.4$) and the increased ¹J_{P–W}^{II} coupling constant, whereas ¹J_{P–W}⁰ is smaller than in **4** and **6** due to the higher donor strength of the benzazaphospholide relative to the 1*H*- and 3*H*-1,3-benzazaphospholes.

Conclusion

The aim of this work was to investigate the metalation of 1*H*-1,3-benzazaphospholes and to present novel 1,3-benzazaphospholide complexes as P–C homologues of indolides. It was shown that 1*H*-1,3-benzazaphospholes and tungsten pentacarbonyl complexes, represented by **1a** and **4**, may be lithiated by *t*BuLi selectively or preferentially at the NH function. The resulting ambident 1,3-benzazaphospholide anions react with the [CpW(CO)₃Cl] exclusively at the softer nucleophilic site and furnish the η^1 -*P*-coordinated tungsten(II) complex **2** and the mixed valence bimetallic tungsten(II)-tungsten(0) species **5**. The benzazaphospholide complexes are sensitive to hydrolysis and oxidation. A crystal structure analysis of the benzazaphospholide oxide complex **3** (toluene monosolvate) gave evidence of the molecular composition and, by comparing the bond lengths with those of **1a**, of a non-aromatic, 3*H*-indole-like π -system.

The P-tetracoordinated di-tungsten complex **5** and the side product **6**, a 3-alkyl-benzazaphosphole W(CO)₅ complex, reveal ¹³C NMR spectroscopic data which likewise are in accordance with a non-aromatic nature. Compound **2** is a borderline case: its carbon chemical shifts resemble those of 3*H*-1,3-benzazaphospholes whilst the magnitude of the ¹J_{P–C2} coupling constant is significantly larger. Only the electronic structure of the neutral benzazaphosphole W(CO)₅ complex **4** is similar to that in the phosphaaromatic heterocycles **1**.

Experimental Section

General: All manipulations were carried out under an atmosphere of dry argon using standard Schlenk and cannula techniques. Ether, THF and hydrocarbons were refluxed over sodium/benzophenone and distilled prior to use. C₆D₆ and [D₈]THF were dried with sodium or LiAlH₄ and recondensed. NMR spectra were recorded on a multinuclear FT NMR spectrometer Bruker Model ARX300 at 300.1 (¹H), 75.5 (¹³C), and 121.5 (³¹P) MHz. The ¹H, ¹³C and ³¹P chemical shifts are δ values relative to Me₄Si or H₃PO₄ (85%); coupling constants are quoted in Hz. IR spectra were measured on a Perkin–Elmer Model system 2000 and mass spectra on a single-focussing mass spectrometer AMD40 (Intectra). Melting points were determined in sealed capillaries under argon and are uncorrected. Elemental analyses were carried out using an elemental analyzer LECO Model CHNS-932 with standard combustion conditions (carbon combustion sometimes incomplete) and handling of the samples in air.

Materials: Compounds **1a** and **1b** were synthesized as reported recently;^[8] [W(CO)₅(THF)] and [CpW(CO)₃Cl] were obtained by known procedures.^[27] Other materials were used as purchased unless stated otherwise.

η^5 -(2-*tert*-Butyl-1,3-benzazaphosphol-3-yl-*P*)(η^5 -cyclopentadienyl)-tricarbonyltungsten (2**):** A solution of **1a** (290.6 mg, 1.52 mmol) in ether was cooled to –78 °C and lithiated with an equimolar amount of *t*BuLi dissolved in pentane (³¹P NMR in [D₈]THF: $\delta = 56.6$). After 30 min. a solution of [CpW(CO)₃Cl] (560 mg, 1.52 mmol) in ether was added (–78 °C) affording a red brown mixture. This was allowed to warm to room temperature and stirred for one day. The precipitate was then removed, and the solvent was evaporated in vacuo. The residue was crystallized from hot toluene affording 614 mg (77%) of red solid **2**, slightly contaminated by **1a**. It is insoluble in hexane, m.p. 80–83 °C. – ¹H NMR ([D₈]THF): $\delta = 1.41$ (d, ⁴J_{P–H} = 0.6, 9 H, CMe₃), 5.34 (s, 5 H, Cp), 7.08 (“t”dd, ³J = 7.5, ⁴J_{P–H} = 3.3, ⁴J = 1.2, 1 H, H-5), 7.22 (m, ³J = 7.4, 7.7, ⁴J $\approx$ ⁵J_{P–H} $\approx$ 1, 1 H, H-6), 7.75 (br. d, ³J = 7.7 Hz, 1 H) and 7.78 (d, ³J = 8.1, 1 H) (H-4 and H-7). – ¹³C{¹H} NMR ([D₈]THF): $\delta = 32.2$ (d, ³J = 5.6, CMe₃), 40.7 (d, ²J = 20.3, CMe₃), 94.3 (Cp), 123.8 (d, ³J = 6, C-5), 124.7 (C-7), 126.3 (C-6), 127.1 (d, ²J = 20, C-4), 150.3 (d, ¹J = 14, C-3a), 155.5 (d, ²J = 9, C-7a), 209.3 (d, ¹J = 62, C-2), 214.9, 218.3, 233.4 (3 CO). – ³¹P{¹H} NMR ([D₈]THF): $\delta = -102.4$ (¹J_{P–W} = 50.1). – EI-MS (70 eV): *m/z* (%) = 523 (23) [M⁺ (¹⁸⁴W)], 480 (27), 455 (44), 196 (72), 184 (93), 28 (100). – C₁₉H₁₈NO₃PW (523.17): calcd. C 43.62, H 3.47, N 2.68; found C 40.52, H 3.50, N 2.47.

η^5 -(2-*tert*-Butyl-3-oxo-1,3-benzazaphosphol-3-yl-*P*)(η^5 -cyclopentadienyl)tricarbonyltungsten Toluene Monosolvate (3**):** A small amount of **2** dissolved in THF was oxidized by allowing slow diffusion of air into the Schlenk tube. Since addition of hexane failed

to give a precipitate the solvent was removed in vacuum and replaced by toluene. On addition of hexane small, pale-yellow single crystals of the toluene monosolvate **3** deposited at +4 °C within 3 days (yield not determined). The crystal and molecular structure was determined by X-ray diffraction (Table 1, Figure 1). – ^1H NMR (C_6D_6): δ = 1.71 (s, 9 H, CMe_3), 2.11 (s, 3 H, toluene), 4.60 (s, 5 H, Cp), 6.93 (ddd, 3J = 7.1, $J_{\text{P-H}}$ = 3.6, 4J = 1.3, 1 H, 4- or 7-H), 6.97–7.13 (m, toluene), 7.05 and 7.40 (both “t”m, 3J $\approx$ 6, 7, 5- and 6-H, partially superimposed by C_6D_6 side band), 7.65 (ddd, ca. 3J = 7.2, J = 2, 1, 1 H, 7- or 4-H). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): δ = 61.3 ($J_{\text{P-W}}$ = 135).

η^1 -(2-Methyl-1H-1,3-benzazaphosphole-*P*)pentacarbonyltungsten (4): A solution of $[\text{W}(\text{CO})_5(\text{THF})]$, prepared by irradiation of $[\text{W}(\text{CO})_6]$ (2.324 g, 6.60 mmol) in THF (300 mL; 145 mL of CO evolved), was added to a solution of **1b** (0.984 g, 6.60 mmol) in THF (5 mL). After one day at room temperature the solvent and volatile tungsten complexes were removed in vacuo and the residue fractionally extracted with hexane yielding in the later fractions 1.272 g (41%) of orange **4**, m.p. 122–124 °C. – ^1H NMR (CDCl_3): δ = 2.73 (d, $^3J_{\text{P-H}}$ = 17.8, 3 H, Me), 7.23 (“t”dd, 3J $\approx$ 7.6, 8, $^4J_{\text{P-H}}$ = 3.8, 4J = 0.9, 1 H, H-5), 7.36 (“t”t”, 3J $\approx$ 7.6, $^5J_{\text{P-H}}$ $\approx$ 4J $\approx$ 1.2, 1 H, H-6), 7.52 (d, 3J = 8.6, 1 H, H-7), 7.87 (“t”t”, 3J $\approx$ $^3J_{\text{P-H}}$ $\approx$ 7.8, 1 H, H-4), 9.60 (br, 1 H, NH). – ^1H NMR (C_6D_6): δ = 2.04 (d, $^3J_{\text{P-H}}$ = 18, 3 H, Me), 6.98 (br. d, 3J = 8.3, 1 H, H-7), 7.06 (dddd, 3J = 7.0, 8.0, $^4J_{\text{P-H}}$ = 2.8, 4J = 1.0, 1 H, H-5), 7.20 (“t”t”, 3J = 8.3, 7.0, $^5J_{\text{P-H}}$ $\approx$ 4J $\approx$ 1.3, 1 H, H-6), 7.98 (“t”t” br., 3J $\approx$ $^3J_{\text{P-H}}$ $\approx$ 7, 8, 1 H, H-4). – $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 15.8 (d, 2J = 15.0, Me), 114.3 (d, 3J = 3.2, C-7), 121.4 (d, 3J = 14.0, C-5), 125.8 (d, 4J = 3.5, C-6), 126.5 (d, 2J = 13.5, C-4), 136.3 (d, 1J = 21.9, C-3a), 141.9 (s, C-7a), 167.6 (d, 1J = 30.8, C-2), 194.6 (d sat, 2J = 8.5, $^1J_{\text{C-W}}$ = 124, 4 CO), 199.8 (d, 2J = 29.1, 1 CO). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 36.7 (sat, $J_{\text{P-W}}$ = 242.6). – IR (Nujol): $\tilde{\nu}$ = 3405 m (NH), 2071 m, 1981 vs, 1946 vs, 1880 s (CO) cm^{-1} . – EI-MS (70 eV): m/z (%): data for ^{184}W = 473 (80) [M^+], 445 (4), 417 (64) [$\text{M}^+ - 2\text{CO}$], 389 (68) [$\text{M}^+ - 3\text{CO}$], 361 (41) [$\text{M}^+ - 4\text{CO}$], 333 (62) [$\text{M}^+ - 5\text{CO}$], 149 (100) [1b^+], 148 (98). – $\text{C}_{13}\text{H}_8\text{NO}_5\text{PW}$ (473.02): calcd. C 33.01, H 1.70, N 2.96; found C 33.20, H 2.11, N 2.60.

η^1 -(2-Methyl-3-[(η^5 -cyclopentadienyl)tricarbonyltungsten]-1,3-benzazaphosphole-*P*)pentacarbonyltungsten (5) and η^1 -(3-*tert*-Butyl-2-methyl-1,3-benzazaphosphole-*P*)pentacarbonyltungsten (6): $[\text{CpW}(\text{CO})_3\text{Cl}]$ (277 mg, 0.754 mmol) was added at –70 °C to a solution prepared from **4** (358 mg, 0.757 mmol) in ether (10 mL) and *t*BuLi in pentane (0.45 mL, 0.754 mmol) as described above. The mixture was allowed to stir at room temperature for 3 days. Then it was filtered and washed with ether. Removal of the solvent in vacuo afforded a mixture of **5** and **6** in a molar ratio of ca. 2:1 (based on ^1H integral ratio of the CH_3 signals) along with a small amount of unchanged **4**. Fractional crystallization with hexane and then with toluene gave 300 mg (49%) of **5** (from toluene) and 80 mg (20%) of **6** (from hexane) as red solids. Compound **6** was impure and identified by its characteristic NMR spectroscopic data. **5**: ^1H NMR ($[\text{D}_8]\text{THF}$): δ = 2.72 (d, 3J = 7.4, 3 H, Me), 5.20 (d, J = 2.0, 5 H, Cp), 7.27–7.35 (m, 1 H H-5), 7.37 (“t”, 3J $\approx$ 7.3, 1 H, H-6), 7.78 (d, 3J = 7.6, 1 H, H-7), 7.85 (dd, 3J = 6.7, $^3J_{\text{P-H}}$ = 5, 1 H, H-4). – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): δ = 20.1 (d, 2J = 28.8, Me), 94.9 (s, Cp), 124.7 (d, 2J = 2.0, C-7), 126.7 (d, 3J = 8.2, C-5), 127.3 (d, 2J = 14.1, C-4), 129.9 (d, 4J = 1.2, C-6), 148.4 (d, 1J = 28.7, C-3a), 152.5 (d, 2J = 16.6, C-7a), 193.1 (d, 1J = 15.3, C-2), 198.6 (d, sat, 2J = 5.4, $^1J_{\text{C-W}}$ = 126, 4 CO), 200.6 (d, 2J = 18.3, 1 CO), 216.9 (d, 2J = 17.7, 1 CO), 217.6 (d, 2J = 18.2, 1 CO), 219.9 (d, 2J = 5.5, 1 CO). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): δ = –

76.1 (sat, $J_{\text{P-W}}$ = 180.8, 90.8). – EI-MS (70 eV, 240 °C): m/z = 804 (34), [$\text{M}^+ - 1$ (^{184}W)], 776 (20), 749 (12) [$\text{M}^+ - 2\text{CO}$], 721 (32) [$\text{M}^+ - 3\text{CO}$], 683 (54) [$\text{M}^+ - 2\text{CO-Cp}$], 665 (100) [$\text{M}^+ - 5\text{CO}$], 645 (41), 625 (62), 604 (48), 396 (61), 341 (62), 309 (50), 149 (65). – $\text{C}_{21}\text{H}_{12}\text{NO}_8\text{PW}_2$ (804.77): calcd. C 31.34, H 1.50, N 1.74; found C 29.00, H 1.76, N 1.64.

6 (hexane): ^1H NMR ($[\text{D}_8]\text{THF}$): δ = 1.19 (d, 3J = 16.1, 9 H, CMe_3), 2.63 (d, 3J = 6.8 Hz, 3 H, Me), 7.41–7.45 (m, 1 H, H5), 7.54 (“t”t”, 3J $\approx$ 7.4, 7.8, 4J $\approx$ $^5J_{\text{P-H}}$ $\approx$ 1.2, 1 H, H-6), 7.70–7.75 (m, 2 H, H-4, H-7). – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): δ = 21.7 (d, 2J = 15, Me), 124.7 (d, 2J = 4, C-7), 127.8 (d, 3J = 8.4, C-5), 130.2 (d, 2J = 13.3, C-4), 132.5 (br., C-6), 133.5 (d, 1J = 48.2, C-3a), 156.8 (d, 2J = 16, C-7a), 181.3 (br., uncertain due to low intensity, C-2). – $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): δ = 50.8 (sat, $J_{\text{P-W}}$ = 216.4).

Crystal Data and Structure Determination for 3: The data set was collected at low temperature using an oil-coated shock-cooled crystal^[28] on a Bruker APEX-CCD diffractometer equipped with Mo- K_α (λ = 71.073 pm) radiation and a low temperature device at 173(2) K. The structure was solved by Patterson methods (SHELXS-NT 97)^[29] and refined by full-matrix least-squares methods against F^2 (SHELXL-NT 97).^[30] R values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$. SADABS 2.0 was employed as the program for empirical absorption correction.^[31]

3: $\text{C}_{26}\text{H}_{26}\text{NO}_4\text{PW}$, M = 631.30, monoclinic, space group $P2_1/n$, a = 11.3819(3), b = 10.4653(3), c = 21.1456(6) Å, β = 104.5600(10)°, V = 2.43787(12) nm³, Z = 4, $\rho_{\text{cal.}}$ = 1.720 Mg/m³, μ = 4.836 mm^{–1}, $F(000)$ = 1240, 41621 reflections measured, 6055 unique, $R(\text{int})$ = 0.0383, $wR2(\text{all data})$ = 0.0545, $R1[I > 2\sigma(I)]$ = 0.0230, g_1 = 0.0301, g_2 = 0.8837 for 5742 data, 228 restraints and 363 parameters. In addition to the tungsten complex the unit cell contains a non-coordinating disordered toluene molecule. The occupancy factors of the solvent molecule refined to 0.788 and 0.272. The toluene molecule was assigned ideal positions and refined using ADP restraints. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the cyclopentadienyl ligand were taken from the difference Fourier map and refined freely, all other hydrogen atoms were geometrically idealized and refined using a riding model. Selected bond lengths and angles of **3** can be found in Table 1.

Crystallographic data for the structure of **3** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161162. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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