Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

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Tungsten-mediated activation of a Pb(II)-N bond: A new route to tungsten-lead triple bonds

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Supporting Information

1. Experimental Section

General Part

All experiments were carried out under an atmosphere of argon using Schlenk or glove box techniques. The glassware was dried in the oven at approximately 110 °C and baked in vacuo prior to use. The solvents were dried by standard methods (pentane over CaH_2, diethyl ether and tetrahydrofurane over sodium wire/benzophenone, and toluene over sodium) and distilled under argon. The solvents were stored over $LiAlH_4$, trap-to-trap condensed, and deoxygenated by two freeze-pump-thaw cycles immediately prior to use. $[W(\eta^2\text{-}CH_2PMe_2)(H)(PMe_3)_4]$ (**2**)[1] and the aryllead(II) bromide $\{Pb(C_6H_3\text{-}2,6\text{-}Trip_2)Br\}_2$ (**1a**)[2] were prepared following literature procedures. The dinitrogen complex *cis*-$[W(N_2)_2(PMe_3)_4]$ (**3**)[3] was obtained in high yield (80-90%) upon reduction of *trans*-$[WCl_2(PMe_3)_4]$[4] with sodium powder in tetrahydrofuran (THF) under dinitrogen atmosphere, and shown by IR, ^1H NMR and $^{31}P\{^1H\}$NMR spectroscopy to be pure.[5] $LiNMe_2$ was prepared from NMe_2H and *n*BuLi. The C, H, N analyses of all compounds were carried out twice on a Leco CHNS-932 elemental analyzer. The individual C, H, N values did not differ by more than ±0.3. The mean C, H, N values are given below for each compound. Bromine was determined using Schöniger´s method followed by titration with $Hg(ClO_4)_2$.[6] The thermal behavior of the compounds was studied twice with a Büchi SMP 530 melting point apparatus (Dr Tottoli, patent 320338). The samples were sealed in capillary tubes under vacuum, and heated slowly until the compounds melted or decomposed. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300, AV-300 or AV-400 NMR spectrometer in dry deoxygenated benzene-d_6. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent (benzene-d_6, δ_H 7.15 ppm and δ_C 128.0 ppm). The $^{31}P\{^1H\}$ NMR spectra were calibrated against an external 85% aqueous H_3PO_4 solution, which was filled in a capillary and measured in a 5 mm NMR tube containing the deuterated solvent. The following abbreviations were used for the signal multiplicities: s = singlet, d =

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[1] A. C. Filippou, N. Weidemann, A. I. Philippopoulos, G. Schnakenburg, *Angew. Chem.* **2006**, *118*, 6133; *Angew. Chem. Int. Ed.* **2006**, *45*, 5987.

[2] L. Pu, B. Twamley, P. P. Power, *Organometallics* **2000**, *19*, 2874.

[3] E. Carmona, A. Galindo, M. L. Poveda, R. D. Rogers, *Inorg. Chem.* **1985**, *24*, 4033.

[4] a) P. R. Sharp, *Organometallics* **1984**, *3*, 1217; b) P. R. Sharp, J. C. Bryan, *Inorg. Synth.* **1990**, *28*, 326.

[5] For IR and NMR spectroscopic data of **3** see: A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem.* **2004**, *116*, 6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6512.

[6] F. Ehrenberger, *Quantitative organische Elementaranalyse*, VCH, Weiheim, **1991**.

doublet, t = triplet, quint = quintet, sept = septet, m = multiplet. The ^{1}H and ^{13}C NMR signals of **1b** and **4a** were assigned by a combination of H,H-COSY, H,C-COSY, HMBC, and DEPT experiments. This allowed an unequivocal assignment of all proton and carbon resonances of the *m*-terphenyl groups. The diastereotopic methyl groups of the NMe_2 substituents in **1b** and of the *ortho*-positionend isopropyl substituents of the Trip groups in **1b** and **4a** were labeled with the subscript letters A and B, respectively. IR spectra of solutions were recorded on a Bruker Vertex 70 / RAM II spectrometer in the spectral range of 2300 – 1500 cm^{-1} using a cell of KBr windows. IR spectra of the solids were recorded as nujol mulls between KBr plates in the spectral range of 4000 – 400 cm^{-1}. Nujol was dried over sodium and stored in the glovebox. The following abbreviations were used for the intensity and shape of the IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad. The solid state RAMAN spectrum of **1b** was recorded in the frequency range of 3700 – 3 cm^{-1} at ambient temperature applying a laser power of 25 mW on the sample.

Preparation of $\{Pb(C_6H_3\text{-}2,6\text{-}Trip_2)NMe_2\}_2$ (1b). A yellow solution of **1a**[7] (1.000 g, 0.6500 mmol) in 80 mL of diethyl ether was added dropwise to a suspension of $LiNMe_2$ (83 mg, 1.63 mmol, 1.25 equiv.) in 10 mL of diethyl ether at –78 °C. Upon warming to room temperature, the reaction mixture initially clarified and then became increasingly cloudy above *ca.* –30 °C. After stirring for 12 h at room temperature a bright yellow solution with a white, fine precipitate (LiBr) resulted. All volatiles were removed under reduced pressure, and the residue was treated with 10 mL of pentane. The pentane was evaporated *in vacuo* to remove traces of diethyl ether. The resultant pale yellow solid was extracted with pentane (50 mL in total) at –30 °C, and the extracts were filtered from a light grey insoluble material. The yellow filtrate was concentrated *in vacuo* to *ca.* 5 mL and stored for 3 d in a –30 °C freezer to afford the product as yellow microcrystals. The microcrystals were separated from the mother liquor by filtration at –78 °C and dried for 1 h under fine vacuum at ambient temperature to afford a pale yellow, microcrystalline solid, which was shown by NMR spectroscopy to be the pentane monosolvate of **1b**. Yield: 775 mg (0.504 mmol, 77%). The solid decolorizes to grey upon heating at 135 ºC. Elemental analysis calcd (%) for $C_{81}H_{122}N_2Pb_2$ (1538.27): C 63.25, H 7.99, N 1.82, Br 0.00; found: C 63.31, H 7.86, N 1.62, Br 0.00%. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 3039 (m), 1761 (vw), 1604 (m), 1560 (m), 1539 (vw), 1427 (m), 1420 (m), 1360 (s), 1314 (m), 1245 (w), 1236 (w), 1213 (w), 1185 (vw), 1167 (m), 1147 (m), 1142 (m), 1129 (vw), 1104

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[7] For NMR spectroscopic data of **1a**, 1,3-$Trip_2C_6H_4$ and **4b** see: A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293; *Angew. Chem. Int. Ed.* **2004**, *43*, 2243.

(m), 1098 (m), 1072 (m), 1049 (w), 1044 (w), 955 (vw), 939 (m), 921 (vw), 903 (s), 876 (s), 847 (vw), 820 (vw), 803 (s), 778 (m), 756 (vw), 744 (w), 739 (m), 722 (vw), 692 (vw), 649 (m), 590 (vw). RAMAN (solid state, 25 mW, cm^{-1}): ν = 3111 (vw), 3041 (m), 3029 (m), 2960 (s), 2908 (vs), 2868 (s), 2828 (vw), 2780 (w), 2755 (w), 2710 (w), 1606 (s), 1560 (m), 1464 (s), 1445 (m), 1428 (w), 1405 (vw), 1384 (w), 1362 (vw), 1346 (w), 1306 (m), 1286 (s), 1238 (w), 1214 (w), 1186 (vw), 1168 (w), 1144 (w), 1128 (vw), 1105 (m), 1070 (w), 1057 (w), 1002 (m), 955 (w), 938 (vw), 912 (w), 884 (s), 838 (w), 820 (w), 804 (vw), 791 (vw), 779 (vw), 758 (vw), 742 (vw), 683 (vw), 651 (vw), 633 (w), 597 (m), 537 (w), 499 (m), 472 (m), 446 (vw), 377 (w), 351 (vw), 282 (m), 255 (m), 167 (s), 137 (vs). ^{1}H NMR (400.1 MHz, $\mathrm{C_6D_6}$, 298 K, ppm): δ = 0.87 (t, ^{3}J(H,H) = 7.1 Hz, 6H, 2 × $\mathrm{C}\mathit{H}_3$, $\mathrm{C_5H_{12}}$), 1.06 (d, ^{3}J(H,H) = 6.8 Hz, 24H, 8 × *o*-$\mathrm{CH(C}\mathit{H}_3)_\mathrm{A}(\mathrm{CH_3})_\mathrm{B}$, Trip), 1.30 (d, ^{3}J(H,H) = 6.8 Hz, 24H, 4 × *p*-$\mathrm{CH(C}\mathit{H}_3)_2$, Trip), 1.23 – 1.25 (m, 6H, 3 × $\mathrm{C}\mathit{H}_2$, $\mathrm{C_5H_{12}}$), 1.35 (d, ^{3}J(H,H) = 6.8 Hz, 24H, 8 × *o*-$\mathrm{CH(CH_3)_A(C}\mathit{H}_3)_\mathrm{B}$, Trip), 1.70 (s, 6H, 2 × $\mathrm{N(C}\mathit{H}_3)_\mathrm{A}(\mathrm{CH_3})_\mathrm{B}$), 2.85 (sept, ^{3}J(H,H) = 6.8 Hz, 4H, 4 × *p*-$\mathrm{C}\mathit{H}(\mathrm{CH_3})_2$, Trip), 3.12 (sept, ^{3}J(H,H) = 6.8 Hz, 8H, 8 × *o*-$\mathrm{C}\mathit{H}(\mathrm{CH_3})_\mathrm{A}(\mathrm{CH_3})_\mathrm{B}$, Trip), 4.17 (s, 6H, 2 × $\mathrm{N(CH_3)_A(C}\mathit{H}_3)_\mathrm{B}$), 7.15 (s, 8H, 8 × *m-H*, Trip; this signal overlaps with the residual proton resonance of the deuterated solvent), 7.22 (t, ^{3}J(H,H) = 7.5 Hz, 2H, 2 × *p-H*, $\mathrm{C_6H_3}$), 7.45 (d, ^{3}J(H,H) = 7.5 Hz, 4H, 4 × *m-H*, $\mathrm{C_6H_3}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{C_6D_6}$, 298 K, ppm): δ = 14.2 (s, 2 × $\mathit{C}\mathrm{H_3}$, $\mathrm{C_5H_{12}}$), 22.7 (s, 2 × $\mathit{C}\mathrm{H_2}$, $\mathrm{C_5H_{12}}$), 23.0 (s, 8 × *o*-$\mathrm{CH(CH_3)_A(}\mathit{C}\mathrm{H_3)_B}$, Trip), 24.5 (s, 4 × *p*-$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$, Trip), 26.7 (s, 8 × *o*-$\mathrm{CH(}\mathit{C}\mathrm{H_3)_A(CH_3)_B}$, Trip), 31.3 (s, 8 × *o*-$\mathit{C}\mathrm{H(CH_3)_A(CH_3)_B}$, Trip), 34.4 (s, 1 × $\mathit{C}\mathrm{H_2}$, $\mathrm{C_5H_{12}}$) 34.8 (s, 4 × *p*-$\mathit{C}\mathrm{H(CH_3)_2}$, Trip), 43.0 (s, 2 × $\mathrm{N(}\mathit{C}\mathrm{H_3)_A(CH_3)_B}$), 49.3 (s, 2 × $\mathrm{N(CH_3)_A(}\mathit{C}\mathrm{H_3)_B}$), 121.7 (s, 8 × *m-C*, Trip), 124.3 (s, 2 × *p-C*, $\mathrm{C_6H_3}$), 135.4 (s, 4 × *m-C*, $\mathrm{C_6H_3}$), 140.6 (s, 4 × *ipso-C*, Trip), 146.7 (s, 8 × *o-C*, Trip), 147.3 (s, 4 × *o-C*, $\mathrm{C_6H_3}$), 148.1 (s, 4 × *p-C*, Trip), 244.8 (s, 2 × *ipso-C*, $\mathrm{C_6H_3}$).

Preparation of *trans*-[$\mathbf{H(PMe_3)_4W{\equiv}Pb{-}C_6H_3\text{-}2,6\text{-}Trip_2}$] (4a) from [$\mathbf{W(\eta^2\text{-}CH_2PMe_2)(H)(PMe_3)_4}$] (2) and 1b. A Schlenk tube was charged with [$\mathrm{W(\eta^2\text{-}CH_2PMe_2)(H)(PMe_3)_4}$] (**2**) (77 mg, 0.14 mmol) and **1b**·(*n*-$\mathrm{C_5H_{12}}$) (100 mg, 0.0650 mmol). The mixture was dissolved in 15 mL of toluene at –78 °C with rapid stirring, and the resultant yellow solution was allowed to warm to room temperature. Upon heating to 80 °C the reaction solution became quickly a red-brown color, which intensified upon further stirring for 16 h at 80 °C. Then an aliquot was taken from the reaction solution and after evaporation of the solvent was studied by ^{1}H and $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy in $\mathrm{C_6D_6}$. The NMR spectra revealed the presence of the product **4a**, 1,3-$\mathrm{Trip_2C_6H_4}$[7] and the starting material **2** in the molar ratio of *ca.* 1.0 : 0.71 : 0.45, and showed furthermore that the lead(II) amide **1b** had been consumed. The cloudy, red-brown solution was then evaporated to dryness to give an oily residue, which was dried by a freeze-pump-thaw cycle. The residue was extracted with pentane (2 × 10 + 5 mL), and the extracts were filtered from a grey, insoluble material (14 mg). The combined red-brown filtrates were concentrated *in vacuo* to incipient crystallization (ca. 1 mL) and stored over dry ice to afford brown microcrystals of the product **4a**, which were separated from the mother liquor by filtration at −78 °C and dried under fine vacuum for 1 h at ambient temperature. Yield: 30 mg (0.030 mmol, 20% from **1b**·(n-C_5H_{12})). The product was shown by ^{1}H and ^{31}P{^{1}H}spectroscopy to be pure (vide infra).

Preparation of *trans*-[H(PMe_3)$_4$W≡Pb–C_6H_3-2,6-Trip$_2$] (4a) from *cis*-[W(N_2)$_2$(PMe_3)$_4$] (3) and 1b. A Schlenk tube was charged with *cis*-[W(N_2)$_2$(PMe_3)$_4$] (**3**) (250 mg, 0.459 mmol) and **1b**·(n-C_5H_{12}) (337 mg, 0.219 mmol). The mixture was dissolved in 20 mL of toluene, and the stirred orange solution was immersed in an oil bath, that was preheated to 120 °C. The progress of the reaction was followed by IR spectroscopy. After heating for 30 min, the IR spectrum of the reaction solution showed still the presence of the ν(N_2) absorption bands of **3** at 1984 and 1923 cm^{-1}. Heating was continued for additional 15 min, after which time the starting material **3** had been almost consumed. The cloudy, red-brown solution was evaporated to dryness and the residue was dried by a freeze-pump-thaw cycle. The solid was extracted with pentane (70 mL in total), and the extracts were filtered from a green-grey insoluble material. The combined brown filtrates were concentrated in *vacuo* to approximately 1 mL and stored for two weeks in a freezer at −30 °C. The brown precipitate was separated from the mother liquor by filtration at –78 °C and dried under fine vacuum for 1 h at ambient temperature to give **4a** as a brown, microcrystalline solid. Yield: 248 mg (0.210 mmol, 48% from **1b**·(n-C_5H_{12})). The product was shown by ^{1}H and ^{31}P{^{1}H}spectroscopy to be pure (vide infra).

Preparation of *trans*-[Br(PMe_3)$_4$W≡Pb–C_6H_3-2,6-Trip$_2$] (4b) from [W(η^2-CH_2PMe_2)(H)(PMe_3)$_4$] (2) and {Pb(C_6H_3-2,6-Trip$_2$)Br}$_2$ (1a). A solution of PMe_3 (0.026 mL, 0.019 g, 0.25 mmol) in 20 mL of toluene was added via a double ended needle to a mixture of **2** (142 mg, 0.252 mmol) and **1a** (194 mg, 0.126 mmol) at −78 °C with rapid stirring.The resulting yellow solution was allowed to warm to ambient temperature in steps of 20 K. At ca. 0 °C, the colour of the reaction solution turned light brown, but did not intensify, when stirring was continued for 30 min at 0 °C and ambient temperature, respectively. Then the reaction mixture was heated for 3 h at 50 °C in an oil bath. The resultant cloudy, red-brown solution was evaporated to dryness, and the brown residue dried by several freeze-pump-thaw cycles. A ^{1}H and ^{31}P{^{1}H} NMR spectrum of the obtained solid in C_6D_6 confirmed the complete conversion of **1a** and the quite selective formation of **4b**. The residue was treated with pentane (10 + 5 mL), and the extracts were filtered from a tiny amount of an insoluble material. The combined red-brown filtrates were concentrated in vacuo to incipient crystallization (ca. 2 mL) and stored for 24 h in a freezer at –30 °C. The resultant red-brown, microcrystalline precipitate was separated from the mother liquor by filtration at –78 °C and dried under fine vacuum for 2 h at ambient temperature to give a brown microcrystalline solid, which was found by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy to contain complex **4b** and 1,3-Trip$_2C_6H_4$[7] in the molar ratio of 100 : 17. Crude yield: 208 mg. Recrystallisation of the solid from a minimum volume of pentane afforded the red-brown, microcrystalline complex **4b** in pure form.[7]

Preparation of *trans*-[H(PMe$_3$)$_4$W≡Pb–C$_6$H$_3$-2,6-Trip$_2$] (4a) from *trans*-[Br(PMe$_3$)$_4$W≡Pb–C$_6$H$_3$-2,6-Trip$_2$] (4b) and LiNMe$_2$. A mixture of **4b** (750 mg, 0.597 mmol) and LiNMe$_2$ (61 mg, 1.2 mmol, 2.0 equiv.) was dissolved in 20 mL of THF and stirred in the glove box at ambient temperature. The colour of the solution turned gradually from red-brown to black-brown. After 20 h of stirring a ^{1}H NMR and ^{31}P{^{1}H} NMR spectrum of an aliquot of the reaction solution in C_6D_6 showed that conversion of **4b** into **4a** was not complete (molar ratio **4a** : **4b** = 7 : 3). LiNMe$_2$ (30 mg, 0.59 mmol) was then added to the reaction mixture and stirring was continued for additional 24 h at ambient temperature, after which time completion of the reaction was confirmed by ^{31}P{^{1}H} NMR spectroscopy. Removal of the solvent *in vacuo* afforded a brown oily residue, which was solidified by a freeze-pump-thaw cycle. The resultant black-brown powder was extracted with 25 mL of pentane at –78 °C, the extract was filtered from an insoluble material, and the filtrate was evaporated to dryness. The same procedure was repeated twice, and the brown filtrate resulting from the last extraction was concentrated *in vacuo* to approximately 2.5 mL and stored for 72 h in a freezer at –30 °C. Dark brown microcrystals of **4a** were formed, which were separated from the mother liquor at –78 °C and dried under fine vacuum for 1 h at ambient conditions. Yield: 298 mg (0.253 mmol, 42%), m.p. 186 ºC (dec.). Elemental analysis calcd (%) for $C_{48}H_{86}P_4PbW$ (1178.16): C 48.93, H 7.36, N 0.00, Br 0.00.[8] IR (nujol,

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[8] Despite several attempts, correct C, H elemental analysis values could not be obtained from samples of **4a**, which were checked before by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy to be pure. The C, H values varied strongly for one and the same sample suggesting an oxidative degradation of the extremely air sensitive samples of complex **4a** during manipulation. The elemental analyses confirmed, however, the absence of bromine and nitrogen in the samples.

cm^{-1}): $\tilde{\nu}$ = 3047 (w), 1764 (vw), 1678 (m, br) [ν(W-H)], 1608 (m), 1567 (w), 1559 (w, sh), 1429 (s), 1417 (m,sh), 1402 (w, sh), 1361 (s), 1336 (vw), 1315 (m), 1294 (m), 1273 (s), 1249 (vw), 1239 (w), 1182 (vw), 1168 (w), 1153 (vw), 1125 (vw), 1099 (w br), 1083 (vw), 1070 (w), 1056 (w), 1009 (vw), 954 (m, sh), 935 (vs), 890 (vw), 878 (s), 848 (m), 825 (vw), 809 (w), 798 (w), 776 (w), 759 (vw), 734 (vw), 722 (m), 693 (m), 688 (m), 668 (m), 654 (s), 584 (vw), 454 (vw). ^{1}H NMR (300.1 MHz, C_6D_6, 298 K, ppm): δ = –6.52 (quint, ^2J(P,H) = 30.7 Hz, ^1J(W,H) = 63 Hz, 1H, W-*H*), 1.18 (d, ^3J(H,H) = 6.9 Hz, 12H, 4 × *o*-CH(C*H*$_3$)$_A$(CH$_3$)$_B$, Trip), 1.28 (d, ^3J(H,H) = 6.9 Hz, 12H, 2 × *p*-CH(C*H*$_3$)$_2$, Trip), 1.36 (d, ^3J(H,H) = 6.9 Hz, 12H, 4 × *o*-CH(CH$_3$)$_A$(C*H*$_3$)$_B$, Trip), 1.55 (m, 36H, 4 × P(C*H*$_3$)$_3$), 2.91 (sept, ^3J(H,H) = 6.9 Hz, 2H, 2 × *p*-C*H*(CH$_3$)$_2$, Trip), 3.34 (sept, ^3J(H,H) = 6.9 Hz, 4H, 4 × *o*-C*H*(CH$_3$)$_A$(CH$_3$)$_B$, Trip), 7.17 (s, 4H, 4 × *m-H*, Trip), 7.26 (t, ^3J(H,H) = 7.3 Hz, 1H, *p-H*, C_6H_3), 7.48 (d, ^3J(H,H) = 7.3 Hz, 2H, 2 × *m-H*, C_6H_3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K, ppm): δ = –34.5 (s, ^1J(W,P) = 258 Hz, 4 × *P*(CH$_3$)$_3$). No ^{207}Pb satellites were observed in the ^{31}P{^{1}H} NMR spectrum. ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K, ppm): δ = 24.7 (s, 4 × *o*-CH(CH$_3$)$_A$(*C*H$_3$)$_B$, Trip), 24.8 (s, 2 × *p*-CH(*C*H$_3$)$_2$, Trip), 25.3 (s, 4 × *o*-CH(*C*H$_3$)$_A$(CH$_3$)$_B$, Trip), 30.8 (s, 4 × *o*-*C*H(CH$_3$)$_A$(CH$_3$)$_B$, Trip), 34.7 (s, 2 × *p*-*C*H(CH$_3$)$_2$, Trip), 36.7 (m, 4 × P(*C*H$_3$)$_3$), 122.2 (s, 4 × *m-C*, Trip), 123.0 (s, *p-C*, C_6H_3), 136.6 (s, 2 × *m-C*, C_6H_3), 142.3 (s, 2 × *ipso-C*, Trip), 144.0 (s, 2 × *o-C*, C_6H_3), 146.3 (s, 4 × *o-C*, Trip), 147.4 (s, 2 × *p-C*, Trip), 267.2 (s, 1 × *ipso-C*, C_6H_3).

Crystal structure determination of 1b and 4a·2(*n*-C_5H_{12}). Suitable yellow prismatic single crystals of **1b** were grown upon slow evaporation of the solvent from a concentrated pentane solution at ambient temperature in the glove-box. Dark brown irregularely shaped crystals of **4a**·2(*n*-C_5H_{12}) were grown upon slow cooling of a concentrated pentane solution from ambient temperature to –30 °C. The data collection of **1b** was performed on a STOE IPDS diffractometer and the data collection of **4a**·2(*n*-C_5H_{12}) on a STOE IPDS-IIT diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and a low–temperature device (Cryostream, Oxford Cryosystems). Unit cell parameters were determined from least-squares analyses using 5000 reflections (10.0° < 2θ < 40.0°, **1b**) and 40846 reflections (6.32° < 2θ < 59.26°, **4a**·2(*n*-C_5H_{12})). Intensities were measured by φ-oscillation scans and corrected for background, polarization and Lorentz effects. ABSCOR was applied for the absorption correction of **1b.**[9] A semiempirical absorption correction from equivalent

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[9] STOE, *ABSCOR*, **1997**, a modific ation of DIFABS (N. Walker, D. Stuart, *Acta Cryst. A* **1983**, *39*, 158).

reflections was applied for **4a**·2(n-C_5H_{12}) according to Blessing's method.[10] The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[11] The hydrogen atoms were included isotropically using the riding model on the bound carbon atoms. The tungsten-bonded hydrogen atom in **4a**·2(n-C_5H_{12}) was localized in the Fourier difference electron density and refined isotropically. The illustrations of the molecular structures were prepared with Diamond 2.1c.[12]

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[10] R. H. Blessing, *Acta Cryst. A* **1995**, *51*, 33.

[11] G. M. Sheldrick, *SHELXS97* and *SHELXL97,* University of Göttingen, Germany, **1997**.

[12] K. Brandenburg, DIAMOND 2.1c, Crystal Impact GbR, Bonn, Germany, **1999**.