Reactivity of Lewis Acid/Base Stabilized Phosphanyl- and Arsanylboranes towards a Platinum(0) Complex

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Dedicated to Prof. M. Meisel on the occasion of his 65th birthday

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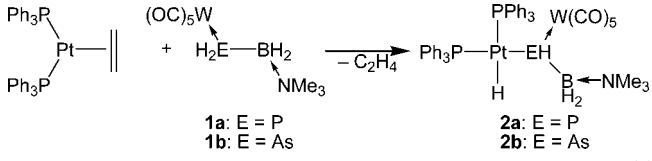
The Lewis acid/base stabilized phosphanylboranes and -arsanes [$(CO)_5W(H_2EBH_2{\cdot}NMe_3)$] (**1a**: E = P; **1b**: E = As) have been shown to react with the platinum(0) complex [$(Ph_3P)_2Pt(C_2H_4)$] under oxidative addition of the E–H bond to the platinum center. The complexes *cis*-[$(Ph_3P)_2Pt(H)(\mu\text{-}EHBH_2{\cdot}NMe_3)W(CO)_5$] (**2a**: E = P; **2b**: E = As) are formed. Complex **2a** is unstable in solution at room temperature and slowly reacts with loss of carbon monoxide to form [$(Ph_3P)_2Pt(\mu\text{-}H)(\mu\text{-}EHBH_2{\cdot}NMe_3)W(CO)_4$] (**3a**: E = P). An analogous complex **3b** (E = As) is formed from **2b** only by refluxing in CH_2Cl_2. The reaction of **2a** to **3a** can be reversed by addition of CO, whereas the arsenic compound **3b** does not show this reactivity pattern. All new compounds have been comprehensively characterized by spectroscopy and X-ray crystallography.

Introduction

A large number of phosphanylboranes $(R_2BPR'_2)_n$ have been synthesized over the years,[1] whereas only some arsanylboranes $(R_2BAsR'_2)_n$ are known so far.[2] Monomeric compounds of both types have up to now been stabilized exclusively by bulky substituents at the group 13 and group 15 elements. Otherwise an intermolecular oligomerisation occurs by the lone pair of the group 15 element and the acceptor orbital of the boron atom. For the experimentally unobserved parent compounds H_2BPH_2 and H_2BAsH_2 we have recently found a novel method of stabilization by the coordination of a Lewis acid and a Lewis base. Thus, the phosphanyl- and arsanylborane complexes [$(CO)_5W(EH_2BH_2{\cdot}NMe_3)$] (**1a**: E = P; **1b**: E = As) were synthesized by a salt elimination route starting from $Li[(CO)_5WEH_2]$ and $ClBH_2{\cdot}NMe_3$.[3] Herein we report on the reactivity of **1** towards the platinum(0) complex [$(Ph_3P)_2Pt(C_2H_4)$] and the CO elimination/addition reactions of the products.

Results and Discussion

The reaction of [$(CO)_5W(H_2EBH_2{\cdot}NMe_3)$] (**1a**: E = P; **1b**: E = As) with the platinum(0) complex [$(Ph_3P)_2Pt(C_2H_4)$] at ambient temperature results in an initial oxidative addition of the platinum center to the E–H bond of **1**, and the complexes *cis*-[$(Ph_3P)_2Pt(H)(\mu\text{-}EHBH_2{\cdot}NMe_3)W(CO)_5$] (**2a**: E = P; **2b**: E = As) are formed [Equation (1)].

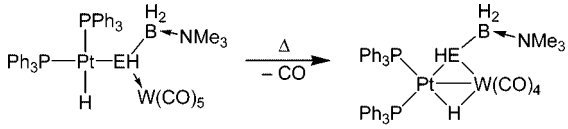


1a: E = P
1b: E = As

2a: E = P
2b: E = As

(1)

For the arsenic substituted compound **2b** the reaction is complete at this stage and **2b** can be isolated as a pure compound. In contrast, even under these conditions **2a** tends to lose 1 equiv. of CO and forms the complex [$(Ph_3P)_2Pt(\mu\text{-}H)(\mu\text{-}PHBH_2{\cdot}NMe_3)W(CO)_4$] (**3a**) bearing a bridging hydrogen ligand. For a full conversion the reaction mixture has to be heated to yield pure **3a** [Equation (2)]. Although pure crystalline **2a** can be isolated from the reaction (1) by fractional crystallization, if it is redissolved it tends to lose CO with formation of complex **3a**.



2a: E = P
2b: E = As

3a: E = P
3b: E = As

(2)

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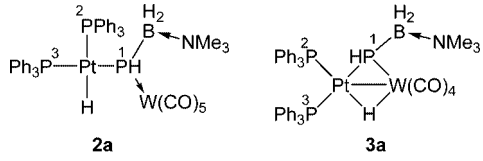
Only by heating a CH_2Cl_2 solution of the arsenic complex **2b** the formation of **3b** was detected, and the product could be isolated in pure form. Furthermore, the formation of **3a** from **2a** by loss of carbon monoxide is reversible. On saturation of a solution of **3a** with carbon monoxide, **2a** together with minor amounts of **3a** could be identified by NMR spectroscopy. In contrast, this feature has never been observed for **2b**.

Interestingly, only the diorgano-substituted phosphane complexes of the type $[(CO)_5M(PPh_2H)]$ show a similar reaction behavior of **1** when treated with $[(C_2H_4)Pt(PPh_3)_2]$. Here, initially the complexes *cis*-$[(CO)_5M(\mu\text{-}PPh_2)\text{-}Pt(H)(PPh_3)_2]$ (M = Cr, Mo, W) are formed, which have a strong tendency to lose CO, resulting in the compounds $[(CO)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PPh_3)_2]$. For these complexes the initial oxidative addition products could only be identified by NMR spectroscopy.[4] In contrast, the complexes $[(Ph_3P)_2Pt(H)(\mu\text{-}EH_2)W(CO)_5]$ (E = P, As)[5] and $[(Ph_3P)_2\text{-}Pt(H)(\mu\text{-}PRH)M(CO)_5]$ (R = Ph, cyclohexyl; M = Cr, Mo, W),[6] which are structurally more closely related to **2** and are formed in a manner similar to that for **2**, both show no loss of carbon monoxide even at elevated temperatures. Thus, the occurrence of this CO loss does not seem to be caused by steric factors. Furthermore, the complexes $[(Ph_3P)_2Pt(H)(\mu\text{-}EH_2)W(CO)_5]$ (E = P, As)[5] show a *cis*/*trans* isomerization, whereas for **2a** and **2b** only the *cis*-addition products are detected in solution. It is interesting to note that in a related reaction of the phosphane–borane adducts $PhRPH{\cdot}BH_3$ (R = H, Ph) with $Pt(PEt_3)_3$ an oxidative addition of the P–H bond to the platinum center occurs, but in this case the *trans*-substituted complexes $[(Et_3P)_2\text{-}Pt(H)(PPhR{\cdot}BH_3)]$ (R = H, Ph) are formed exclusively.[7]

Complexes **2** are colorless compounds and moderately soluble in CH_2Cl_2 and toluene, whereas complexes **3** are orange crystalline complexes readily soluble in CH_2Cl_2 and toluene. In the vibrational spectra all products show bands for the CO, PH and BH functional groups. The EI mass spectra do not show the molecular ion peaks, but decomposition products including $[(CO)_5W(PPh_3)]$ and $[(CO)_5\text{-}W(H_2EBH_2{\cdot}NMe_3)]$ (E = P, As) can be identified.

In its $^{31}P\{^1H\}$ NMR spectrum **2a** shows a signal at δ = –174.8 ppm ($^1J_{P1,Pt}$ = 1286, $^2J_{P1,P3}$ = 223 Hz) for the P^1 atom of the phosphido group which is only slightly shifted to lower field when compared with free **1a** (δ = –184.2 ppm). The signal is very broad because of the quadrupolar moment of the neighboring boron atom, which is directly bound to the phosphorus atom. Upon recording a $^{31}P\{^{11}B,^1H\}$ NMR spectrum, the coupling to the tungsten atom and to the P^2 atom *cis* to P^1 (see Scheme 1) is also revealed ($^2J_{P1,P2}$ = 11, $^1J_{P1,W}$ = 153 Hz). The P^2 atom shows a pseudo-triplet at δ = 29.4 ppm ($^1J_{P2,Pt}$ = 2099, $^2J_{P2,P1}$ = 11, $^2J_{P2,P3}$ = 14 Hz) and P^3 is detected as a doublet of doublets at δ = 25.9 ppm ($^1J_{P3,Pt}$ = 2199, $^2J_{P3,P2}$ = 14, $^2J_{P3,P1}$ = 223 Hz). This coupling pattern clearly shows the *cis* arrangement of the phosphanidoboranyl ligand relative to the hydrido ligand. The latter ligand is detected in the ^1H NMR spectrum of **2a** as a doublet of doublets of doublets at δ = –4.48 ppm showing platinum satellites. The PH proton appears as a doublet at δ = 2.38 ppm. A signal for the BH_2 protons could not be assigned, as this resonance is too broad to be clearly identified from the background in the spectrum.



Scheme 1.

Complex **3a** shows a similar $^{31}P\{^1H\}$ NMR spectrum, which is depicted in Figure 1. Here, the P^1 atom shows a broad doublet at δ = –8.7 ppm. Upon additional boron decoupling the signal shows a doublet of doublets bearing platinum satellites. The large downfield shift of the signal compared to **2a** can be explained by the bridging position of the phosphidoboranyl ligand.[8] Also the phosphorus–platinum coupling constant (951 Hz) is much smaller than in **2a** (1286 Hz). A coupling to the tungsten atom is not obvious, but it is presumably hidden under the main signals. Signals for the P^2 and P^3 atoms appear at δ = 15.7 and 19.5 ppm, respectively, and show the same coupling pattern as in **2a**. In its ^1H NMR spectrum **3a** shows a doublet of doublet of doublets with platinum satellites at δ = –7.43 ppm (Figure 1). Due to the small intensity of the hydride signals, the expected tungsten satellites cannot be clearly differentiated from the background noise. The resonance for the PH protons appears as a doublet at δ = 2.60 ppm. As in the case for **2a** the BH_2 signal for **3a** could not be detected.

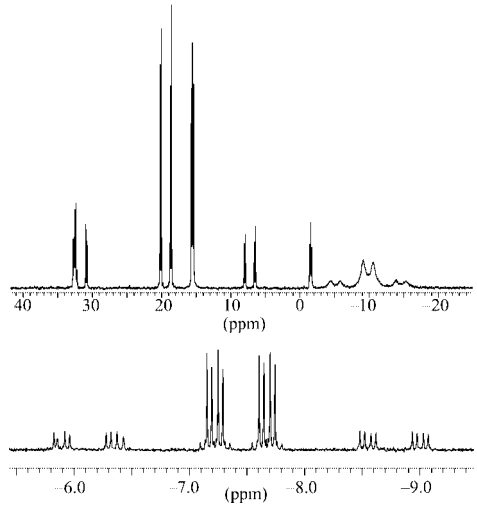
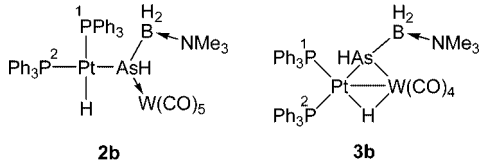


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **3a** (top). Hydride region of the ^1H NMR spectrum of **3a** (bottom).

The $^{31}P\{^1H\}$ NMR spectrum of compound **2b** (Scheme 2) shows two doublets at δ = 30.7 ppm and 23.6 ppm, both bearing platinum satellites ($^2J_{P1,P2}$ = 13, $^1J_{P1,Pt}$ = 2145Hz, $^1J_{P2,Pt}$ = 2531Hz). In its ^1H NMR spectrum **2b** displays a doublet of doublets at δ = –4.76 ppm with platinum satellites for the hydrido ligand bound to the platinum atom ($^2J_{H,P1}$ = 177, $^2J_{H,P2}$ = 19 Hz). In accord-

ance with the $^{31}P\{^1H\}$ NMR spectrum this coupling pattern shows the *cis* arrangement of the phosphane ligands around the platinum center. In the ^1H NMR spectrum the protons bound to the arsenic atom give rise to a complex signal centered at δ = –1.27 ppm.



Scheme 2.

In the $^{31}P\{^1H\}$ NMR spectrum complex **3b** (Scheme 2) shows two doublets with platinum satellites at δ = 15.2 ppm and 16.9 ppm ($^2J_{P1,P2}$ = 16, $^1J_{P1,Pt}$ = 2657, $^1J_{P2,Pt}$ = 3433 Hz) for both non-equivalent phosphorus atoms. The ^1H NMR spectrum of **3b** shows the same characteristic signals as that of complex **3a**. The hydrido ligand bound to the platinum atom gives rise to a doublet of doublets with platinum satellites at δ = –6.74 ppm ($^2J_{H,P1}$ = 116, $^2J_{H,P2}$ = 24, $^1J_{H,Pt}$ = 669 Hz). Signals for the nine protons of the trimethylamine group and the 30 protons of the phenyl groups are detected at δ = 1.95 ppm and 6.8–7.6 ppm, respectively.

In order to confirm the proposed structures of **2** and **3** X-ray crystal structure determinations have been performed on all compounds. Single crystals of complex **2** could be obtained from CH_2Cl_2 solutions. Whereas **2b** crystallizes as a dichloromethane solvate, for **2a** no solvent molecule was found in the unit cell. As an example the molecular structure of **2a** is depicted in Figure 2; in Table 1 the bond lengths and angles are compared.

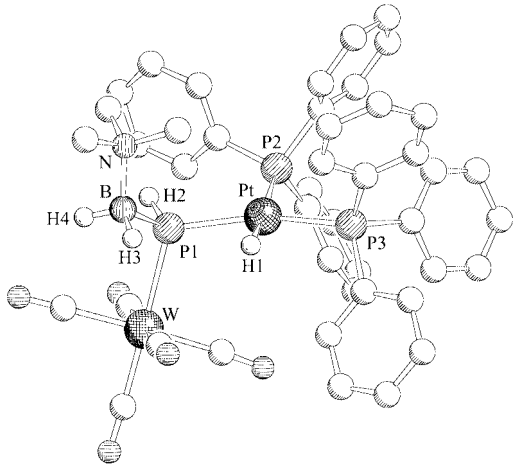


Figure 2. Molecular structure of **2a** in the crystal. Hydrogen atoms at the carbon atoms are omitted for clarity.

The key structural feature of **2** is a central platinum atom which shows an almost perfect planar coordination sphere. Two phenylphosphane ligands are in *cis* arrangement to each other. A hydrido and the phosphanidoboranyl or arsanidoboranyl ligand (**2a** or **2b**) complete the coordination sphere of the 16-electron complexes. The sum of the bond angles around the platinum atom are close to 360° [**2a**: 359.87(5)°; **2b**: 359.01(7)°]. Despite the planar coordination around the platinum atom the bond angles are far from 90° required for a square-planar coordination. All ligands are shifted towards the hydrido ligand to alleviate steric crowding. The Pt–P bond lengths in both compounds are comparable and in a range usually found for such bonds. In comparison to the starting material the B–E [**1a**: 195.5(4); **2a**: 198.1(6): **1b**: 206.7(9): **2b**: 209.4(9) pm] and the E–W bonds [**1a**: 254.2(2); **2a**: 260.5(1); **1b**: 263.5(1); **2b**: 270.15(8) pm] are elongated.[3] The elongation of the E–W bond can be explained by the back-bonding of the E atom to two metal atoms instead of one metal atom as in compound **1**. The same effect can be observed for $[(CO)_5W(\mu\text{-}PH_2)PtH(PPh_3)_2]$ [W–P 260.3(3) pm] in comparison to $[(CO)_5WPH_3]$ [W–P 249.1(2) pm].[5] The change of the electron density at the E atom in **2** and **3** can also explain the elongation of the E–B bond.

Table 1. Comparison of selected bond lengths [pm] and angles [°] in **2a** and **2b**.

Bond lengths[a]	**2a**	**2b**
Pt–E	233.0(2)	243.6(1)
Pt–P_{cis}	233.1(1)	232.1(2)
Pt–P_{trans}	231.0(2)	229.9(2)
E–W	260.5(1)	270.2(1)
E–B	198.1(6)	209.4(9)
B–N	161.8(7)	162(1)
Angles	**2a**	**2b**
E–Pt–P_{cis}	98.29(5)	100.06(5)
E–Pt–P_{trans}	159.71(5)	157.60(5)
P_{cis}–Pt–P_{trans}	101.87(5)	101.35(7)
Pt–E–W	111.20(5)	112.07(3)
Pt–E–B	118.1(3)	116.0(3)
W–E–B	106.1(2)	106.3(3)
E–B–N	116.4(4)	115.2(6)

[a] **2a**: E = P1, P_{cis} = P2, P_{trans} = P3; **2b**: E = As, P_{cis} = P1, P_{trans} = P2.

The compounds **3a** and **3b** are isostructural and crystallize in the triclinic space group $P\bar{1}$ as the dichloromethane solvates. As an example the molecular structure of **3a** is depicted in Figure 3; in Table 2 the bond lengths and angles are compared.

The essential feature of the structures is a $(CO)_4WPt(PPh_3)_2$ moiety which is bridged by a hydrido ligand and a phosphanidoboranyl and an arsanidoboranyl ligand (**3a** or **3b**), respectively. Like in the compounds **2** the platinum atoms show a nearly planar coordination geometry [sum of bond angles **3a**: 357.74(7)°; **3b**: 357.49(7)°]. The long distance between the platinum and the tungsten atom [**3a**: 302.8(1); **3b**: 307.72(9) pm] implies indirect multi-centered bonding through the bridging ligands, rather than a direct metal–metal bond, as was discussed for the structurally related compound $[(CO)_4Cr(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PEt_3)_2]$.[4b] The E–B distances [**3a**: 197.5(8); **3b** 207.3(8) pm] are comparable to **2a** and **2b**, respectively. In comparison to **2a** and **2b**, respectively, the E–W bond lengths in **3a** and **3b** are significantly reduced [**3a**: 246.0(1); **3b**: 255.57(9) pm] but in a range normally found for similar complexes {$[(CO)_4$-

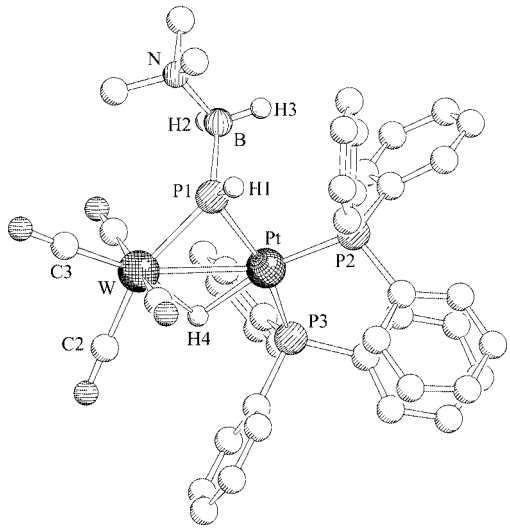


Figure 3. Molecular structure of **3a** in the crystal. Hydrogen atoms at the carbon atoms are omitted for clarity.

Table 2. Comparison of selected bond lengths [pm] and angles [°] of **3a** and **3b**.

Bond lengths[a]	**3a**	**3b**
Pt–E	233.7(2)	245.1(1)
Pt–P_{cis}	228.5(2)	229.0(2)
Pt–P_{trans}	232.3(2)	231.0(2)
Pt–W	302.8(1)	307.7(1)
E–W	246.0(2)	255.6(1)
E–B	197.5(8)	207.3(8)
B–N	162(1)	161(1)
W–C2	199.6(8)	200.6(8)
W–C3	194.9(8)	195.1(8)
Angles	**3a**	**3b**
E–Pt–P_{cis}	95.18(7)	94.89(6)
E–Pt–P_{trans}	159.79(6)	159.50(5)
P_{cis}–Pt–W	144.09(5)	144.90(5)
P_{cis}–Pt–P_{trans}	102.77(7)	103.10(7)
P_{trans}–Pt–W	111.97(5)	110.96(5)
E–Pt–W	52.68(5)	53.63(3)
W–E–B	125.48(5)	125.44(5)
E–B–N	111.04(7)	111.58(6)

[a] **3a**: E = P1, P_{cis} = P2, P_{trans} = P3; **3b**: E = As, P_{cis} = P1, P_{trans} = P2.

$W(\mu\text{-}PPh_2)_2Pt(MeO_2CC{\equiv}CCO_2Me)]$: W–P: 244.3(3) and 243.5(3) pm}.[9]

Conclusions

The results have shown that the Lewis acid/base stabilized phosphanylborane and arsanylborane undergo oxidative addition reactions at a Pt^0 center only at the P–H bond. Initially we had expected that the B–H bond also shows some addition behavior, as it is known for Rh and Ir complexes.[10] However, the boranyl substituent in **1** only functions as an electron-withdrawing substituent at the group 15 atom. Furthermore, in comparison to organo-substituted PH-containing phosphanes, the boranyl-substituted complexes **1** show a similar reaction behaviour toward Pt^0 centers. Oxidative addition of the E–H bond leads to exclusive formation of *cis*-substituted Pt^{II} complexes, which can lose CO to form a complex with a bridging hydrido and pnicogenido substituent, respectively.

Experimental Section

General Remarks: All manipulations were carried out under dinitrogen using standard Schlenk techniques. All solvents were dried using standard procedures and distilled freshly before use. $[(CO)_5W(H_2EBH_2{\cdot}NMe_3)]$ (**1a**: E = P; **1b**: E = As)[3] and $[(Ph_3P)_2Pt(C_2H_4)]$[11] were prepared according to the literature. All NMR spectra were recorded with a Bruker AC 250 with δ referenced to external $SiMe_4$ (^{1}H), $F_3B{\cdot}OEt_2$ (^{11}B) or H_3PO_4 (^{31}P), respectively. IR spectra were measured with a Bruker IFS-28, Raman spectra with a Bruker FRA 106 spectrometer. All mass spectra were recorded with a Varian MATR 711.

***cis*-$[(Ph_3P)_2Pt(H)(\mu\text{-}PHBH_2{\cdot}NMe_3)W(CO)_5]$ (2a):** A mixture of $[W(CO)_5(H_2PBH_2{\cdot}NMe_3)]$ (**1a**) (467 mg, 1.09 mmol) and $[(C_2H_4)Pt(PPh_3)_2]$ (814 mg, 1.09 mmol) was stirred in toluene (20 mL) at room temperature for 14 h. The solution turned to an orange color during this time and a yellow precipitate was formed. The precipitate was separated by filtration and dissolved in a minimum amount of CH_2Cl_2 (ca. 4–5 mL). After 2 d, **2a** was obtained at 4 °C as colorless crystals (if the solution is too concentrated, orange crystals of **3a** crystallize additionally). Yield: 638 mg (51%). $C_{44}H_{43}BNO_5P_3PtW$ (1148.45): calcd. C 46.02, H 3.77, N 1.22; found C 46.23, H 3.87, N 1.14. Raman (solid state) $\tilde{\nu}$ = 3061 (vs), 3006 (w), 2949 (w), 2370 (w), 2295 (w), 2048 (s), 1951 (vs), 1895 (m), 1873 (s), 1518 (s), 1573 (m), 1097 (m), 1029 (m), 1002 (vs), 789 (w), 461 (m), 439 (m), 260 (w), 174 (w), 114 (s) cm^{-1}. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = –4.48 (ddd, $^1J_{Pt,H}$ = 971, $^2J_{P,H}$ = 176, $^2J_{P,H}$ = 33, $^2J_{P,H}$ = 22 Hz, 1 H, HPt), 2.38 (m, $^1J_{P,H} \approx$ 300 Hz, 1 H, PH), 2.49 (s, 9 H, NMe_3), 7.0–7.5 (m, 30 H, PPh_3) ppm. ^{31}P{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = –174.8 (br. d, $^2J_{P,P}$ = 223, $^1J_{Pt,P}$ = 1286 Hz, $PHBH_2$), 25.9 (dd, $^2J_{P,P}$ = 223, $^2J_{P,P}$ = 14, $^1J_{Pt,P}$ = 2199 Hz, PPh_3), 29.4 (t, $^2J_{P,P}$ = 14, $^1J_{Pt,P}$ = 2099 Hz, PPh_3) ppm. ^{31}P{^{11}B,^{1}H} NMR (101 MHz, CD_2Cl_2): δ = –174.8 (dd, $^2J_{P,P}$ = 11 Hz $^2J_{P,P}$ = 223, $^1J_{W,P}$ = 153, $^1J_{Pt,P}$ = 1286 Hz, $PHBH_2$), 25.9 (dd, $^2J_{P,P}$ = 223, $^2J_{P,P}$ = 14, $^1J_{Pt,P}$ = 2199 Hz, PPh_3), 29.4 (t, $^2J_{P,P}$ = 14, $^1J_{Pt,P}$ = 2099 Hz, PPh_3) ppm. EI-MS (170 °C): *m*/*z* (%) = 586 (16) $[W(CO)_5PPh_3]^+$, 558 (4) $[W(CO)_4PPh_3]^+$, 530 (2) $[W(CO)_3PPh_3]^+$, 502 (93) $[W(CO)_2PPh_3]^+$, 474 (1) $[W(CO)PPh_3]^+$, 446 (100) $[WPPh_3]^+$, 429 (22) $[(CO)_5WPH_2BH_2NMe_3]^+$, 401 (11) $[(CO)_4WPH_2BH_2NMe_3]^+$, 373 (14) $[(CO)_3WPH_2BH_2NMe_3]^+$, 370 (50) $[(CO)_5WPH_2BH_2]^+$, 345 (6) $[(CO)_2WPH_2BH_2NMe_3]^+$, 342 (31) $[(CO)_4WPH_2BH_2]^+$, 317 (4) $[(CO)WPH_2BH_2NMe_3]^+$, 314 (15) $[(CO)_3WPH_2BH_2]^+$, 286 (10) $[(CO)_2WPH_2BH_2]^+$, 262 (89) $[PPh_3]^+$.

***cis*-$[(Ph_3P)_2Pt(H)(\mu\text{-}AsHBH_2{\cdot}NMe_3)W(CO)_5]$ (2b):** A mixture of $[W(CO)_5(H_2AsBH_2{\cdot}NMe_3)]$ (**1b**) (75 mg, 0.16 mmol) and $[(C_2H_4)Pt(PPh_3)_2]$ (119 mg, 0.16 mmol) was stirred in toluene (10 mL) at room temperature for 16 h. During this time the orange solution turned to a yellow suspension. The precipitate was separated by filtration and dissolved in a minimum amount of CH_2Cl_2 (3–4 mL). The resulting solution was stored at –25 °C. After 2 d, **2b** was obtained as colorless crystals. Yield: 134 mg (70%). $C_{44}H_{43}AsBNO_5P_2PtW{\cdot}0.5CH_2Cl_2$ (1234.87): calcd. C 43.28, H 3.59, N 1.13; found C 43.43, H 3.32, N 1.28. Raman (solid state) $\tilde{\nu}$ = 3060 (vs), 3006 (w), 2948 (w), 2093 (w), 2046 (s), 1951 (vs), 1874 (s), 1858 (w), 1587 (vs), 1574 (m), 1158 (w), 1096 (m), 1029 (s), 1002 (vs), 465 (m), 439 (m), 259 (w), 205 (w), 175 (w), 110 (s) cm^{-1}. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = –4.95 (dd, $^2J_{P,H}$ = 177,

$^2J_{P,H}$ = 19, $^1J_{Pt,H}$ = 904 Hz, 1 H, HPt), –1.27 (m, 2 H, AsH_2), 2.48 (s, 9 H, NMe_3), 7.11–7.29 (m, 30 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 23.6 (d, $^2J_{P,P}$ = 13, $^1J_{Pt,P}$ = 2531 Hz, PPh_3), 30.7 (d, $^2J_{P,P}$ = 13, $^1J_{Pt,P}$ = 2145 Hz, PPh_3) ppm. ^{31}P NMR (101 MHz, CD_2Cl_2): δ = 23.6 (s, 1 P, PPh_3), 30.7 (d, $^2J_{H,P}$ = 177 Hz, PPh_3). EI-MS (200 °C): *m*/*z* (%) = 586 (15) $[(CO)_5WPPh_3]^+$, 558 (16) $[(CO)_4WPPh_3]^+$, 530 (3) $[(CO)_3WPPh_3]^+$, 502 (70) $[(CO)_2WPPh_3]^+$, 446 (67) $[WPPh_3]^+$, 445 (35) $[(CO)_4WAsH_2BH_2{\cdot}NMe_3]^+$, 262 (100) $[PPh_3]^+$.

$[(Ph_3P)_2Pt(\mu\text{-}H)(\mu\text{-}PHBH_2{\cdot}NMe_3)W(CO)_4]$ (3a): A mixture of $[W(CO)_5(H_2PBH_2{\cdot}NMe_3)]$ (**1a**) (467 mg, 1.09 mmol) and $[(C_2H_4)Pt(PPh_3)_2]$ (814 mg, 1.09 mmol) was stirred in toluene (20 mL) at room temperature for 14 h. The solution turned to an orange color during this time and a yellow precipitate was formed. The precipitate was separated by filtration and dissolved in CH_2Cl_2 (10 mL). The resulting solution was heated under reflux for 6 h while a slow stream of nitrogen was passed through the apparatus. Reduction of the solvent to a volume of ca. 2 mL and storage at 4 °C yielded **3a** as orange crystals. Yield: 733 mg (60%). $C_{43}H_{43}BNO_4P_3PtW{\cdot}0.5CH_2Cl_2$ (1162.91): calcd. C 44.93, H 3.81, N 1.20; found C 44.84, H 3.72, N 1.08. Raman (solid state) $\tilde{\nu}$ = 3058 (vs), 3004 (w), 2943 (w), 2392 (w), 2291 (m), 2050 (m), 1987 (m), 1956 (s), 1861 (s), 1821 (w), 1586 (s), 1482 (m, br), 1096 (m), 1028 (m), 1001 (vs), 704 (w), 496 (m), 436 (m), 116 (s) cm^{-1}. ^1H NMR (250 MHz, CD_2Cl_2): δ = –7.43 (ddd, $^1J_{Pt,H}$ = 664, $^2J_{P,H}$ = 113, $^2J_{P,H}$ = 24, $^2J_{P,H}$ = 10 Hz, 1 H, HPt), 2.60 (m, $^1J_{P,H}$ = 287 Hz, 1 H, PH), 2.45 (s, 9 H, NMe_3), 7.0–7.5 (m, 30 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = –8.7 (br. d, $^2J_{P,P}$ = 147, $^1J_{Pt,P}$ = 951 Hz, $PHBH_2$), 15.7 (t, $^2J_{P,P}$ = 17, $^1J_{Pt,P}$ = 3462 Hz, PPh_3), 19.5 (dd, $^2J_{P,P}$ = 147, $^2J_{P,P}$ = 17, $^1J_{Pt,P}$ = 2463 Hz, PPh_3) ppm. $^{31}P\{^{11}B,^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = –8.7 (dd, $^2J_{P,P}$ = 15, $^2J_{P,P}$ = 147, $^1J_{Pt,P}$ = 951 Hz, $PHBH_2$), 15.7 (t, $^2J_{P,P}$ = 17, $^1J_{Pt,P}$ = 3462 Hz, PPh_3), 19.5 (dd, $^2J_{P,P}$ = 147, $^2J_{P,P}$ = 17, $^1J_{Pt,P}$ = 2463 Hz, PPh_3) ppm. EI-MS (90 °C) *m*/*z* = 586 (6) $[W(CO)_5PPh_3]^+$, 558 (8) $[W(CO)_4PPh_3]^+$, 530 (1) $[W(CO)_3PPh_3]^+$, 502 (22) $[W(CO)_2PPh_3]^+$, 474 (1) $[W(CO)PPh_3]^+$, 446 (19) $[WPPh_3]^+$, 429 (19) $[(CO)_5WPH_2BH_2NMe_3]^+$, 401 (6) $[(CO)_4WPH_2BH_2NMe_3]^+$, 373 (6) $[(CO)_3WPH_2BH_2NMe_3]^+$, 370 (16) $[(CO)_5WPH_2BH_2]^+$, 345 (2) $[(CO)_2WPH_2BH_2NMe_3]^+$, 342 (13) $[(CO)_4WPH_2BH_2]^+$, 317 (3) $[(CO)WPH_2BH_2NMe_3]^+$, 314 (6) $[(CO)_3WPH_2BH_2]^+$, 286 (3) $[(CO)_2WPH_2BH_2]^+$, 262 (100) $[PPh_3]^+$.

$[(Ph_3P)_2Pt(\mu\text{-}H)(\mu\text{-}AsHBH_2{\cdot}NMe_3)W(CO)_4]$ (3b): Complex **2b** (70 mg, 0,059 mmol) was dissolved in CH_2Cl_2 (15 mL) and refluxed for 12 h which led to a color change from yellow to orange. Reduction of the volume of the solution to ca. 2 mL and storage at –25 °C yielded **3b** as orange crystals. Yield: 41 mg (60%). $C_{43}H_{43}AsBNO_4P_2PtW{\cdot}0.5CH_2Cl_2$ (1206.86): calcd. C 43.29, H 3.67, N 1.16; found C 43.46, H 3.50, N 1.29. Raman (solid state): $\tilde{\nu}$ = 3054 (vs), 2380 (w), 2294 (w), 2092 (m), 2051 (m), 2031 (s), 1962 (w), 1860(b), 1586 (s), 1185 (w), 1160 (w), 1095 (m), 1028 (m), 1001 (vs), 773 (w), 703 (w), 475 (m), 437 (m), 172 (w), 113 (s) cm^{-1}. ^1H NMR (250 MHz, C_6D_6): δ = –6.74 (dd, $^2J_{P,H}$ = 116, $^2J_{P,H}$ = 24, $^1J_{Pt,H}$ = 669 Hz, 1 H, HPt), 0.32 (s, 1 H, AsH), 1.95 (s, 9 H, NMe_3), 6.8–7.6 (m, 30 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6): δ = 15.2 (d, $^2J_{P,P}$ = 16, $^1J_{Pt,P}$ = 3433 Hz, PPh_3), 16.9 (d, $^2J_{P,P}$ = 16, $^1J_{Pt,P}$ = 2657 Hz, PPh_3) ppm. ^{31}P NMR (101 MHz, C_6D_6): δ = 15.2 (d, $^2J_{H,P}$ = 123 Hz, PPh_3), 16.9 (s, PPh_3) ppm. EI-MS (200 °C): *m*/*z* = 586 (20) $[(CO)_5WPPh_3]^+$, 558 (16) $[(CO)_4WPPh_3]^+$, 530 (3) $[(CO)_3WPPh_3]^+$, 502 (70) $[(CO)_2WPPh_3]^+$, 446 (67) $[WPPh_3]^+$, 445 (35) $[(CO)_4WAsH_2BH_2{\cdot}NMe_3]^+$, 262 (100) $[PPh_3]^+$.

X-ray Crystallographic Study: Data were collected with a STOE IPDS area-detector diffractometer using Ag-K_α (λ = 0.56087 Å) radiation. Machine parameters, crystal data and data collection parameters are summarized in Table 3. The structures were solved by direct methods using SHELXS-97,[12a] full-matrix-least-squares

Table 3. Crystallographic data for **2a**,**b** and **3a**,**b**.

	2a	**2b**·0.5CH_2Cl_2	**3a**·0.5CH_2Cl_2	**3b**·0.5CH_2Cl_2
Empirical formula	$C_{44}H_{43}BNO_5P_3PtW$	$C_{44.5}H_{44}AsBClNO_5P_2PtW$	$C_{43.5}H_{44}BClNO_4P_3PtW$	$C_{43.5}H_{44}AsBClNO_4P_2PtW$
M_r	1148.45	1234.87	1162.91	1206.86
T [K]	203(2)	203(2)	203(2)	203(2)
Crystal size	0.20×0.20×0.06	0.18×0.12×0.03	0.20×0.10×0.04	0.25×0.15×0.10
Space group	*Pbcn*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
a [Å]	20.017(4)	14.891(3)	10.661(2)	10.774(2)
b [Å]	24.139(5)	18.897(3)	12.458(3)	12.490(3)
c [Å]	18.389(4)	18.195(3)	18.995(4)	18.976(4)
α [°]	90	90	82.06(3)	81.72(3)
β [°]	90	108.06(3)	76.89(3)	76.18(3)
γ [°]	90	90	71.84(3)	71.67(3)
V [Å^{-3}]	8885(3)	4867.7(15)	2328.5(8)	2347.2(8)
Z	8	4	2	2
d_c [g cm^{-3}]	1.717	1.685	1.659	1.708
μ_c [mm^{-1}]	3.185	3.275	3.066	3.393
2θ range [°]	2.72–41.82	3.40–42.00	3.60–45.00	3.12–44.78
hkl range	$-23 \le h \le 24$	$-19 \le h \le 18$	$-14 \le h \le 14$	$-14 \le h \le 14$
	$-16 \le k \le 29$	$-24 \le k \le 24$	$-16 \le k \le 16$,	$-16 \le k \le 16$
	$-23 \le l \le 23$	$-21 \le l \le 23$	$-25 \le l \le 25$	$-23 \le l \le 24$
Data/restraints/parameters	7960/0/524	10245/0/547	11790/0/528	11591/2/533
No. of unique data	7960 (R_{int} = 0.0501)	10245 (R_{int} = 0.0653)	11790 (R_{int} = 0.0464)	11591 (R_{int} = 0.0519)
Independent reflections [$I > 2\sigma(I)$]	6127	7547	8543	8300
Goodness-of fit on F^2	1.008	1.040	1.022	0.997
R_1[a], wR_2[b] [$I > 2\ \sigma(I)$]	0.0309, 0.0671	0.0415, 0.0953	0.0426, 0.1027	0.0447, 0.1053
R_1[a], wR_2[b] [all data]	0.0492, 0.0731	0.0690, 0.1059	0.0702, 0.1156	0.0724, 0.1176
Largest diff. peak/hole [e·Å^{-3}]	0.611, –0.554	2.015, –0.823	2.238, –1.527	3.172, –1.127

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\omega(F_o^2 - F_c^2)^2]/[\Sigma(F_o^2)^2]]^{0.5}$.

refinement on F^2 in SHELXL-97[12b] with anisotropic displacement for non-H atoms, hydrogen atoms placed in idealized positions and refined isotropically according to the riding model. The H atoms at the heavy atoms were found as residue electron densities and could be freely refined except for the H atom at the As atom in **2b**, which was placed in an idealized position. The use of restraints was necessary for the refinement of **3b** to fix the Cl atoms at the solvent molecule in appropriate distances. CCDC-249065 to -249068 (**2a**,**b** and **3a**,**b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For a review see: R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343–379.
[2] Compare: a) M. S. Lube, R. L. Wells, P. S. White, *Main Group Met. Chem.* **1996**, *13*, 733–741; b) M. A. Mardones, A. H. Cowley, L. Contreras, R. A. Jones, C. J. Carrano, *J. Organomet. Chem.* **1993**, *455*, C1–C2; c) M. A. Petrie, M. M. Olmstead, H. Hope, R. A. Bartlett, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 3221–3226; d) R. Goetze, H. Nöth, *Z. Naturforsch.* **1975**, *30B*, 875–882.
[3] U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.
[4] a) J. Powell, M. R. Gregg, J. F. Sawyer, *J. Chem. Soc., Chem. Commun.* **1984**, 1149–1150; b) J. Powell, M. R. Gregg, J. F. Sawyer, *Inorg. Chem.* **1989**, *28*, 4451–4460.
[5] U. Vogel, M. Scheer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1593–1598.
[6] J. Schwald, P. Peringer, *J. Organomet. Chem.* **1987**, *323*, C51–C53.
[7] C. A. Jaska, H. Dorn, A. J. Lough, I. Manners, *Chem. Eur. J.* **2003**, *9*, 271–281.
[8] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229–266.
[9] E. D. Morrison, A. D. Harley, M. A. Marcelli, G. L. Geoffroy, A. L. Rheingold, W. C. Fultz, *Organometallics* **1984**, *3*, 1407–1413.
[10] For recent reviews see: a) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1–51; b) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882–1898; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1786–1801; c) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R: Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685–2722.
[11] U. Nagel, *Chem. Ber.* **1982**, *115*, 1998–1999.
[12] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1997**; b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

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