axial [RuCl₄(PR₃)₂]⁻ ions. It is known that for R = Et such an anion has g_1 = 2.51 and g_2 = 1.64,[5] while for R = Bu the corresponding g values are g_1 = 2.42 and g_2 = 1.58.[4] Thus, the assignments given in Figure 1 (where g'_1 and g'_2 are for the

quasi-axial Ru^{III} and g_1, g_2, and g_3 are for the rhombic Ru^{III}) follow straightforwardly.

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Reaction of *trans,trans*-WH(CO)₂(NO)(PR₃)₂ with Lewis Acidic Boron Compounds. X-ray Structure of *trans*-W(η²-BH₄)(CO)(NO)(PMe₃)₂

Adolphus A. H. van der Zeijden, Valery Shklover, and Heinz Berke*

Reaction of the basic hydrides *trans,trans*-WH(CO)₂(NO)(PR₃)₂ (R = Et, Me, Ph, OiPr) with BH₃·L (L = THF or SMe₂) yields air-sensitive *trans*-W(η²-BH₄)(CO)(NO)(PR₃)₂ as the main product, whereas the more acidic hydrides (R = OMe, OPh) do not yield such a borohydride. The compounds W(η²-BH₄)(CO)(NO)(PR₃)₂ are unstable with respect to elimination of BH₃·PR₃ and could therefore only be characterized by spectroscopic methods. However, we succeeded in growing crystals of W(η²-BH₄)-(CO)(NO)(PMe₃)₂, which were studied by X-ray diffractive methods: space group *Pna2₁*, a = 10.313 (1) Å, b = 14.182 (2) Å, c = 10.771 (2) Å, Z = 4, R = 0.0287, and R_w = 0.0289 for 1167 reflections with F > 6σ(F).

Introduction

We have shown that the nitrosyl ligand in complexes of the type *trans,trans*-WH(CO)₂(NO)(PR₃)₂ causes a profound hydridic, i.e. basic, polarization of the trans-NO-positioned tungsten–hydride bond.[1] This is expressed in reactions of these complexes with mild acids like acetic acid and phenol, which result in facile elimination of dihydrogen. We have also shown that the hydridic character of these complexes can be further tuned by variation of the two cis-positioned phosphorus ligands.[2] Strongly σ-donating phosphines (PEt₃, PMe₃) were found to given more basic hydrides, whereas a strongly π-accepting phosphite, like P(OPh)₃, gave a more acidic complex. Moreover, we were able to quantify the reactivity of the W–H bond, by correlating it to the ν(W–H) stretching frequency, which in turn could be correlated to Tolman's electronic parameter of the phosphorus ligands.[3] We were interested whether the hydridic character of WH(CO)₂(NO)(PR₃)₂ was also expressed in its behavior toward Lewis acids and therefore decided to investigate its reactivity toward homoleptic boron compounds.

Experimental Section

IR spectra were obtained on a Biorad FTS-45 spectrometer. ¹H and ¹³C NMR spectra were measured on a Varian Gemini 200 spectrometer, ³¹P NMR on a Varian XL-200 spectrometer, and ¹¹B on a Bruker AM-400-WB spectrometer. All reactions and manipulations were carried out under an atmosphere of dry nitrogen with freshly distilled solvents. WH(CO)₂(NO)(PR₃)₂ complexes with R = Et,[2] Me,[2] Ph,[4] OMe,[5] OiPr,[5] and OPh[5] were synthesized according to published methods.

Reaction of WH(CO)₂(NO)(PR₃)₂ with BH₃·L (L = THF, SMe₂). In a typical procedure, an orange solution of 0.2 mmol of the tungsten hydride in hexane (THF or toluene was used for R = Ph and OPh) was cooled to −80 °C and 1.5–2 equiv of either BH₃·THF (1 M in THF) or BH₃·SMe₂ (1 M in CH₂Cl₂) were added. When the temperature was slowly raised to +20 °C, the clear reaction mixture turns red for R = Ph and OiPr and violet for R = Me and Et between −20 and −10 °C,

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Table I. Crystal Data for W(η²-BH₄)(CO)(NO)(PMe₃)₂

formula	C₇H₂₂BNO₂P₂W
mol wt	408.9
cryst dimens, mm	0.3 × 0.3 × 0.4
cryst syst	orthorhombic
space group	*Pna2₁*
a, Å	10.313 (1)
b, Å	14.182 (2)
c, Å	10.771 (2)
V, Å³	1575.2 (4)
Z	4
ρ(calcd), g cm⁻³	1.724
μ, cm⁻¹	76.75
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite
data collcn T, K	233
index ranges	−3 ≤ h ≤ 12, −4 ≤ k ≤ 17, −13 ≤ l ≤ 12
θ range, deg	1.0 ≤ θ ≤ 26.0
scan type	2θ-θ
no. of collcd reflcns	1585
no. of indep reflcns	1452
no. of obsd reflcns	1167 (F > 6σ(F))
R, R_w	0.0287, 0.0289

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) of W(η²-BH₄)(CO)(NO)(PMe₃)₂ (Except Those for the C-Bound H's)

atom	x	y	z	U(eq)
W	0.20336 (4)	0.97477 (3)	0	0.0470 (1)
P1	0.0094 (3)	0.8737 (3)	0.002 (2)	0.062 (1)
P2	0.3831 (4)	1.0907 (2)	−0.000 (1)	0.063 (1)
O1	0.328 (4)	0.877 (3)	−0.213 (3)	0.14 (1)
O2	0.317 (3)	0.850 (2)	0.210 (3)	0.085 (8)
N	0.278 (2)	0.912 (2)	−0.119 (2)	0.073 (8)
C1	0.276 (3)	0.898 (3)	0.130 (4)	0.08 (1)
C2	−0.104 (4)	0.902 (2)	0.125 (3)	0.10 (1)
C3	−0.085 (3)	0.868 (2)	−0.142 (3)	0.09 (1)
C4	0.048 (2)	0.751 (1)	−0.018 (4)	0.073 (9)
C5	0.395 (5)	1.163 (4)	−0.132 (5)	0.08 (1)
C6	0.380 (5)	1.176 (4)	0.135 (5)	0.08 (1)
C7	0.540 (1)	1.039 (1)	−0.010 (6)	0.090 (9)
B	0.068 (2)	1.108 (1)	0.024 (4)	0.10 (1)
H1B	0.112 (8)	1.191 (5)	0.01 (1)	0.08
H2B	0.141 (8)	1.064 (8)	0.099 (9)	0.08
H3B	0.067 (9)	1.066 (9)	−0.079 (9)	0.08
H4B	−0.045 (7)	1.112 (6)	0.068 (9)	0.08

Scheme I

Table III. IR Data (cm⁻¹) for W(η^2-BH₄)(CO)(NO)(PR₃)₂[a]

R	ν(CO)	ν(NO)	ν(BH₁)
Et	1901	1630	2450, 2416
Me	1905	1635	2450, 2415
Ph	1910	1645	2465, 2425
OiPr	1926	1645	2470, 2430

[a] s, s, m, w intensities; hexane solution for R = Et, Me, and OiPr; C₆D₆ solution for R = Ph.

Table IV. NMR Data (ppm) for W(η^2-BH₄)(CO)(NO)(PR₃)₂[a]

R	W–¹³CO	W–³¹PR₃	¹¹B	W(μ-H)₂BH₂	W(μ-H)₂BH_2
Et	246.5 (4.8)	26.4 (286)	−1.4	no	no
Me	244.4 (4.8)	−28.3 (285)	nm	no	no
Ph	241.9 (4.6)	39.9 (296)	3.1	−2.7 (vbr), −1.6 (vbr)	4.0 (vbr)
OiPr	237.8 (8.3)	149.1 (441)	0.6	−3.71 (br), −2.58 (br)	4.61 (br)

[a] ¹H NMR in CD₂Cl₂ at −80 °C; other nuclei in C₆D₆ solution at +24 °C; nm = not measured, no = not observed, br = broad, vbr = very broad. δ_C relative to C₆D₆ (128.0 ppm), with ^2J(¹³C–³¹P) (Hz) in parentheses; δ_P relative to external H₃PO₄, with ^1J(³¹P–¹⁸³W) (hz) in parentheses; δ_B relative to external BF₃·Et₂O, 15% in CHCl₃.

while no color change was observed for R = OMe and OPh. The resulting very air-sensitive reaction mixtures were analyzed by IR and NMR spectroscopy. For R = Et, Me, Ph, and OiPr the compounds W(η^2-BH₄)(CO)(NO)(PR₃)₂ and BH₃·PR₃ were found to be the main constituents, poisoned by trace amounts of WH(CO)₂(NO)(PR₃)₂ and other unknown tungsten compounds, while for R = OMe and OPh no tungsten borohydride compounds could be detected. Attempts to purify the tungsten borohydride compounds were frustrated by the fact that they slowly eliminate BH₃·PR₃, with concomitant formation of various tungsten-containing compounds, among which WH(CO)₂(NO)(PR₃)₂ was identified.

Slow cooling of the crude reaction mixture of WH(CO)₂(NO)(PMe₃)₂ and BH₃·THF in hexane to −80 °C resulted in the coprecipitation of dark purple crystals of W(η^2-BH₄)(CO)(NO)(PMe₃)₂, colorless crystals of BH₃·PMe₃, and a few orange crystals of WH(CO)₂(NO)(PMe₃)₂. The former ones turned out to be stable enough for an X-ray diffraction study at low temperature.

Reaction of WH(CO)₂(NO)(P(OiPr)₃)₂ with B(C₆F₅)₃. Syntheses of [*trans,trans*-W(CO)₂(NO)(P(OiPr)₃)₂(S)]⁺[BH(C₆F₅)₃]⁻ (S = Acetone, THF, Methanol). To a solution of 0.39 g (0.76 mmol) of B(C₆F₅)₃ in 15 mL of acetone was added at room temperature 0.44 g (0.64 mmol) of WH(CO)₂(NO)(P(OiPr)₃)₂. Instant formation of [*trans,trans*-W-(CO)₂(NO)(P(OiPr)₃)₂(acetone)]⁺[BH(C₆F₅)₃]⁻ was observed spectroscopically. Evaporation of solvent and washing of the residue with petrol ether afforded 0.75 g (94%) of this salt as an orange oil, which was characterized by IR and NMR spectroscopy and MS. FAB-POS MS: *m/e* 686 (cation − acetone). EI-NEG MS: *m/e* 513 (anion).

Similarly, when the same reaction was conducted in solvents (S) like THF or methanol [*trans,trans*-W(CO)₂(NO)(P(OiPr)₃)₂(S)]⁺[BH-(C₆F₅)₃]⁻ could be isolated in almost quantitative yield. However, if this reaction was conducted in dichloromethane, benzene, toluene, or hexane, decomposition was observed.

The same solvated cations can be synthesized by the reaction of WH-(CO)₂(NO)(P(OiPr)₃)₂ with Ph₃CPF₆, HPF₆, HBF₄, or BF₃·Et₂O in the aforementioned coordinating solvents.

Reaction of WH(CO)₂(NO)(PR₃)₂ with Other Homoleptic Boron Compounds. No reaction of WH(CO)₂(NO)(PR₃)₂ with either BEt₃, B(OMe)₃, or BPh₃ was observed in any solvent.

X-ray Analysis of W(η^2-BH₄)(CO)(NO)(PMe₃)₂. A suitable crystal was placed under argon in a glass capillary. Relevant data on the X-ray
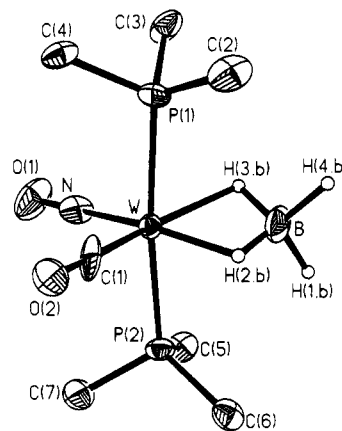
Figure 1. ORTEP diagram of *trans*-W(η^2-BH₄)(CO)(NO)(PMe₃)₂. The ellipsoids are drawn to the 50% probability level except for the H atoms. The C-bound H atoms were omitted for clarity.

investigations are given in Table I. Lattice parameters were based on 24 centered reflections with 2Θ values between 25 and 28°. The intensities of 1585 reflections with 2 < 2Θ < 52° were measured by using the Θ/2Θ scan technique on a Siemens P3 diffractometer using graphite-monochromated Mo Kα radiation. Three check reflections, which were measured every 100 reflections, showed no decay during data collection. The structure was solved by automated heavy-atom methods and refined by full-matrix least-squares methods in anisotropic approximation for non-hydrogen atoms. The hydrogens of the Me groups were refined with constrained tetrahedral geometry (C–H = 0.96 Å, U_{iso} = 0.08 Å²). The hydrogen atoms of the BH₄ unit could all be located but not refined successfully. They were therefore constrained to tetrahedral geometry with a refinable common value for the B–H distance and U_{iso} = 0.08 Å². An empirical absorption correction was applied (μ = 76.7 cm⁻¹) based on the azimuthal scan of equivalent reflections. The positional and thermal parameters of the non-hydrogen atoms are listed in Table II. All calculations were performed on a Microvax 2000 computer using the SHELXTL PLUS program package.[6]

Results

The tungsten hydrides *trans,trans*-WH(CO)₂(NO)(PR₃)₂ (R = Et, Me, Ph, OMe, OiPr, OPh) reacted with 1.5–2 equiv of borane (as its THF or SMe₂ adduct) to produce purple (R = Et, Me), red (R = Ph, OiPr), or orange solutions (R = OMe, OPh). Spectroscopic analysis of these solutions (see Tables III and IV) show them to be mixtures of mainly *trans*-W(η^2-BH₄)(CO)-(NO)(PR₃)₂ and the known BH₃·PR₃ for R = Et, Me, Ph, and OiPr (Scheme 1), while for R = OMe and OPh only the borane–phosphite adduct could be observed in solution. The use of less of the aforementioned amount of BH₃·L leads to an incomplete conversion, whereas more BH₃·L increases the production of BH₃·PR₃.

The efficiency of the conversion of the tungsten hydride to the tungsten borohydride under optimal conditions, i.e. with 1.5–2 equiv of borane, was estimated (by ¹H NMR) to be 40–60 % at best. The fact that more than 1 equiv of borane is needed to drive the reaction to completion, suggests that the attack of borane proceeds not exclusively on the hydride atom but also on the

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Table V. Selected Bond Lengths (Å)

W–P1	2.461 (4)	W–H2B	1.8 (1)
W–P2	2.478 (4)	W–H3B	2.1 (1)
W–N	1.74 (2)	(P–C)$_{av}$	1.81 (4)
W–C1	1.93 (3)	N–O1	1.24 (5)
W–B	2.36 (2)	C1–O2	1.17 (5)

adjacent carbonyl and/or phosphine ligands, resulting in partial decomposition of the tungsten hydride. Attempts to isolate the tungsten borohydrides were frustrated by the fact that these compounds slowly eliminate BH$_3$·PR$_3$ in solution. Their identification is therefore mainly based on spectroscopic evidence in solvent media. However, by slowly cooling down the crude reaction mixture of WH(CO)$_2$(NO)(PMe$_3$)$_2$ and BH$_3$·THF in hexane, we succeeded in growing single crystals of W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$ corroborating our spectroscopic findings (vide infra).

The IR spectra (Table III) of W(η^2-BH$_4$)(CO)(NO)(PR$_3$)$_2$ show the presence of one NO and one CO ligand, as well as absorptions arising from terminal BH bonds (bands for bridging BH's could not be assigned with certainty, due to overlap with those of the phosphorus ligand).

The ^{13}C NMR spectra of W(η^2-BH$_4$)(CO)(NO)(PR$_3$)$_2$ show a triplet splitting $^2J(^{13}$C–^{31}P) of the carbonyl carbon, confirming the presence of two, mutually trans-positioned phosphorus ligands cis to the carbonyl. No carbonyl–hydride coupling, $^2J(^1$H–^{13}C), could be observed, even at –80 °C; in the parent complex, WH(CO)$_2$(NO)(PR$_3$)$_2$ this coupling amounts to ca. 10 Hz.[2]

The ^{11}B NMR spectra show a broad featureless signal (unchanged from +20 to –80 °C) at around 0 ppm, from which no information concerning the bonding mode of the tetrahydroborate group can be extracted.

The (^{11}B-decoupled) ^{1}H NMR spectra, taken at room temperature, did not reveal the resonances of the borohydride group of either of the four tungsten complexes. This is probably due to severe broadening of those signals by ^{11}B quadrupolar relaxation. Even at –80 °C in CD$_2$Cl$_2$, we were not able to detect these signals for the PEt$_3$ and PMe$_3$ derivatives. For W(η^2-BH$_4$)(CO)(NO)(PPh$_3$)$_2$, however, we observed at that temperature very broad signals at ca –2.7, –1.6, and +4.0 ppm, while for W(η^2-BH$_4$)(CO)(NO)[P(OiPr)$_3$]$_2$ well resolved, but still broad singlets could be observed at –3.71, –2.58, and +4.61 ppm in a 1:1:2 integral ratio. These data indicate the presence of an η^2-bonded BH$_4$ unit, the low-field signal being associated with the two terminal H atoms and both high-field signals with the ones bridging between tungsten and boron. One of these H atoms must therefore be trans positioned to the CO ligand, the other one trans to NO. The absence of a mirror plane running through the phosphorus atoms was demonstrated by the appearance of two signals for the diastereotopic methyl groups in the W(η^2-BH$_4$)(CO)(NO)[P(OiPr)$_3$]$_2$ complex.

The spectroscopic findings on the structure of W(η^2-BH$_4$)(CO)(NO)(PR$_3$)$_2$ were confirmed by an X-ray diffraction study on W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$, an ORTEP view of which is shown in Figure 1.

Relevant bond lengths and angles are given in Tables V and VI, respectively. It is noticed that the tetrahydroborate group was refined as a constrained regular tetrahedron, and therefore the geometry of this group and its coordination must be considered with some care. The coordination around tungsten may be described as distorted octahedral. The W and B atom, as well as the NO and CO ligands lie in one plane (maximum deviation 0.03 Å). The P–W–P vector is almost rectangular to this plane. Although the CO and NO ligands fit in the octahedral description of the molecule ($\angle$C–W–N = 94 (1)°), the coordination of the BH$_4$ unit presents the major distortion from this ideal geometry. The BH$_4$ unit occupies, through two bridging hydrogens, two coordination sites around tungsten, but is thereby forced to a very small H–W–H bite angle of 64 (4)°. The boron atom slightly deviates from the axis bisecting the N–W–C(1) bond angle ($\angle$N–W–B = 139 (1) and $\angle$C–W–B = 127 (2)°).

The bidentate coordination of BH$_4$ in our complex shows a resemblance to that of other isolobal octahedral d^6 compounds

Table VI. Selected Bond Angles (deg)

P1–W–P2	174.0 (1)	N–W–H2B	166 (4)
P1–W–N	93.9 (8)	C1–W–H2B	94 (4)
P2–W–N	90.5 (8)	P1–W–H3B	79 (3)
P1–W–C1	89 (1)	P2–W–H3B	95 (3)
P2–W–C1	94.9 (9)	N–W–H3B	108 (3)
N–W–C1	94 (1)	C1–W–H3B	155 (3)
P1–W–B	89.3 (5)	H2B–W–H3B	64 (4)
P2–W–B	84.8 (5)	W–N–O1	172 (3)
N–W–B	139 (1)	W–C1–O2	178 (2)
C1–W–B	127 (2)	(W–P–C)$_{av}$	115 (1)
P1–W–H2B	96 (3)	(C–P–C)$_{av}$	104 (9)
P2–W–H2B	79 (3)		

like [Ph$_3$PNPPh$_3$]$^+$[M(η^2-BH$_4$)(CO)$_4$]$^-$ (M = Cr,[7] and Mo[8]), *fac*-FeH(η^2-BH$_4$)[MeC(CH$_2$PPh$_2$)$_3$],[9] and *mer*-RuH(η^2-BH$_4$)(PMe$_3$)$_3$:

Ph$_3$P=N$^+$=PPh$_3$ M = Cr, Mo
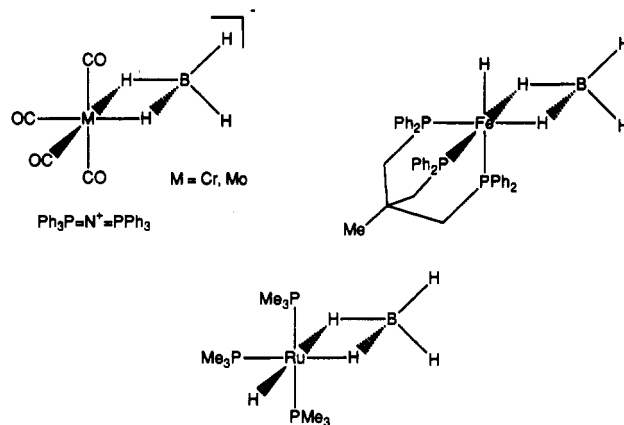
A striking feature of all these structures is that the boron atom is found slightly displaced from the axis bisecting the two opposing trans ligands, even in the symmetrical [Cr(η^2-BH$_4$)(CO)$_4$] anion.[7]

EHT calculations[11] on the model compound *trans*-W(η^2-BH$_4$)(CO)(NO)(PH$_3$)$_2$ show that an asymmetrical bonding mode of the η^2-BH$_4$ unit is indeed preferred. Consistent with the findings of the X-ray structure analysis on *trans*-W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$ a bending of the whole BH$_4$ moiety toward the CO group occurs. This may be explained by analyzing the binding abilities of the [W(CO)(NO)(PH$_3$)$_2$]$^+$ fragment, whose frontier orbitals can principally be derived from those of a C_{2v} ML$_4$ system.[12] The lowered symmetry in the C_s [W(CO)(NO)(PH$_3$)$_2$]$^+$ moiety does not change the fundamental "2 above 3" orbital situation of a C_{2v} ML$_4$ fragment; however, it induces perturbations with concomitant tilting of both of the high-lying "a$_1$" and "b$_2$" fragmental lobes toward the CO group, as sketched by the following schematic representation:


"a$_1$"   "b$_2$"
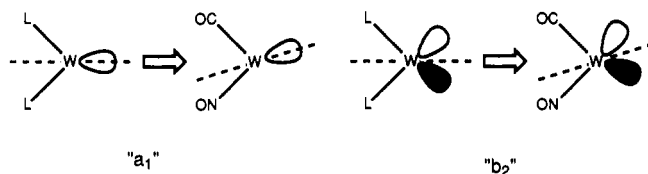
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Table VII. ^1H and ^{31}P NMR^a (ppm) and IR^b Data (cm^{-1}) for *trans,trans*-{W(S)(CO)$_2$(NO)[P(OiPr)$_3$]$_2$}{BH(C$_6$F$_5$)$_3$}

	^1H NMR				IR	
S	CH(CH$_3$)$_2$	CH(CH$_3$)$_2$	S	$^{31}P^c$ NMR	ν(CO)	ν(NO)
acetone	4.54 (m)	1.16 (d, 6.1)	1.85 (t, 1.1)^d	128.2 (444)	1977	1635
THF	4.43 (m)	1.11 (d, 6.2)	3.37 (m), 0.86 (m)	130.6 (447)	1973	1666
methanol	4.53 (m)	1.14 (d, 6.2)	3.31	131.7 (445)	1963	1642

^{a} In C$_6$D$_6$ at +24 °C. ^{b} Measured in S. ^{c} $^1J(^{31}P-^{183}W)$ (Hz) in parentheses. ^{d} $J(^1H-^{31}P)$ (Hz) in parentheses.

Scheme II

Solvent = acetone, THF, methanol
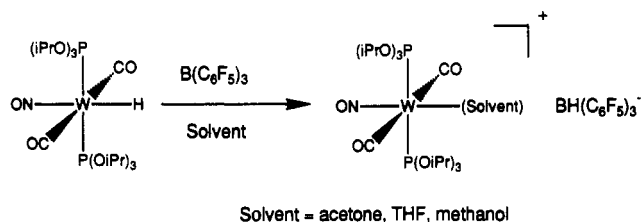
Intuitively, it is somewhat surprising that "a$_1$" and "b$_2$" get polarized in such a way that they both turn the same direction. The unexpected behavior in rotation is the one of "a$_1$". In {W-(CO)(NO)(PH$_3$)$_2$}$^+$, "a$_1$" is found to be preferentially mixed with an in-plane π^* combination of the π acceptor ligands, which also contains some d and p orbital character of the tungsten center. The direction of the rotation is set by the tendency to minimize antibonding contact between orbital character at the tungsten and the stronger π acceptor ligand, which carries quite pronounced orbital coefficients. The η^2-[BH$_4$]$^-$ ligand may be viewed as a single-faced π-donor offering two filled orbitals for interaction with "a$_1$" and "b$_2$". For maximum interaction, the BH$_4$ unit has to seek a position rotated in the same directiuon as "a$_1$" and "b$_2$".

The X-ray structures of W(η^2-BH$_4$)(CO)(NO)(PMe$_3$)$_2$ and of the starting compound WH(CO)$_2$(NO)(PMe$_3$)$_2$^{2} show the following differences: (1) Both the W-N and W-C distances are ca. 0.1 Å shorter in the borohydride complex. This is because the substitution of one of three π-accepting ligands through a σ-donating H atom in the W(CO)$_2$(NO)H plane causes a more efficient distribution of π-electron density to the remaining two CO and NO ligands. On the other hand the W–P, C–O, and N–O bond lengths are similar in the two structures. (2) In the tungsten hydride the phosphine ligands are bent toward the hydride atom ($\angle$P–W–P = 164.4 (1)°), while in the borohydride they are only slightly bent toward the boron atom ($\angle$P–W–P = 174.0 (1)°).

Reaction of WH(CO)$_2$(NO)(PR$_3$)$_2$ with Other Homoleptic Boron Compounds. No reaction was observed of WH(CO)$_2$-(NO)(PR$_3$)$_2$ with the weaker Lewis acids BEt$_3$, B(OMe)$_3$, and BPh$_3$. The stronger Lewis acid B(C$_6$F$_5$)$_3$ reacted with the tungsten hydride (only investigated for the P(OiPr)$_3$ derivative), with abstraction of the hydride atoms and production of a solvated tungsten cation (Scheme II).

The product *trans,trans*-{W(S)(CO)$_2$(NO)[P(OiPr)$_3$]$_2$}{BH-(C$_6$F$_5$)$_3$} was found to be stable and isolable only when the reaction was conducted in a coordinating solvent, like acetone, THF, or methanol. The ^1H and ^{31}P NMR data for these cations are listed in Table VII. Strong coordination of solvent molecules is anticipated because of (1) slow exchange of coordinated and free solvent molecules (NMR) and (2) the observation of a ^{31}P triplet coupling (1.1 Hz) of the acetone hydrogens in the {W(acetone)(CO)$_2$(NO)[P(OiPr)$_3$]$_2$} cation.

The same cations could be obtained by reaction of WH-(CO)$_2$(NO)[P(OiPr)$_3$]$_2$ with either Ph$_3$CPF$_6$, HPF$_6$, HBF$_4$, or BF$_3$·Et$_2$O.