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Manganese and Rhenium Formyl Complexes of Diphosphanylborane Ligands: Stabilization of the Formyl Unit from Intramolecular B–O Bond Formation

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Several manganese(I) and rhenium(I) carbonyl complexes of the chelating diphosphanylborane ligands Ph₂PCH- $(PPh_2)CH_2B(C_8H_{14})$ (1) and $Ph_2PCH_2CH[B(C_8H_{14})]$ -PPh₂ (2) were prepared to study Lewis acid assisted stoichiometric CO reductions. The phosphanylborane complexes $fac,cis-Mn(CO)_3(1)(Br)$ (3a), $fac,cis-Re(CO)_3(1)(Br)$ (4a), $fac,cis-Mn(CO)_3(2)(Br)$ (5a), and $fac,cis-Re(CO)_3(2)(Br)$ (6a) were obtained from the reactions of Mn(CO)₅Br or Re(CO)₅-Br with diphosphanylborane ligands 1 and 2. Further treatment of all four complexes with one equivalent of $AgBF_4$ in CH_2Cl_2 in the dark followed by 1 atm of CO afforded the corresponding monocationic complexes $[Mn(CO)_4(1)][BF_4]$ (3b), $[Re(CO)_4(1)][BF_4]$ (4b), $[Mn(CO)_4(2)][BF_4]$ (5b), and [Re(CO)₄(2)](BF₄) [6b]. An X-ray diffraction study confirmed the expected molecular structure of 3b. In addition to NMR

Introduction

The conversion of homogeneous syngas (CO + H_2) to C₁-C₃ oxygenates or higher organics still poses a great challenge for research in academia and industry.[1] Although this field of research has been addressed for decades and even peaked after the first oil crisis, real progress has not been achieved yet. As the catalyst systems in a homogeneous process can readily be modified by changing the ligand environment to tune activities and selectivities.^[2] it seems attractive to revive basic research on transition-metal-catalyzed homogeneous CO reductions by utilizing newly established approaches. The key challenges associated with this chemistry, often denoted as homogeneous Fischer-Tropsch chemistry, are C-H and C-C bond formations, for which crucial reaction intermediates were obtained as mechanistic models mostly by the reaction of main group and transition-metal complexes.^[3] Recently, Bercaw et al.^[4a] and others^[4b] proposed that a dual system, consisting of a latetransition-metal hydrogen activator along with a relatively

lomepage: http://www.aci.uzh.ch/en/research-groups/emeriti/ berke-group/prof-dr-heinz-berke/?tx_wfqbe_pil and elemental analysis characterizations, the structures of these complexes could be unambiguously assigned based on two major v(CO) IR bands, which established the *cis*-(CO)₄ local ligand environment. The cationic complexes **3b**, **4b**, **5b**, and **6b** were tested for stoichiometric CO reductions by reaction with NaHBEt₃ in chlorobenzene. However, the reductions of the complexes **3b** and **4b** produced mixtures of formyl and hydride species. The reaction of complexes **5b** and **6b** led to the formation of the stable formyl derivatives [Mn(CHO)(CO)₃(**2**)] (**5c**) and [Re(CHO)(CO)₃(**2**)] (**6c**), which were isolated in pure form and characterized by spectroscopic means. In addition, **5c** could be characterized by a single-crystal X-ray study, which revealed the formyl structure and a stabilizing coordination of the pendant Lewis acidic B(C₈H₁₄) group to the formyl oxygen atom.

electrophilic metal carbonyl complex, could lead to catalytic conversion. This approach is based on a two-catalyst system, in which one metal complex acts as a scaffold for CO reduction and the other delivers the hydride anion and eventually also the proton as an H_2 equivalent. Such new approaches could thus be based on the chemistry of formal heterolysis of H_2 that has emerged in the last decade.

Ambiphilic phosphanylborane ligands are unique for this purpose because they contain nucleophilic phosphorus and electrophilic boron center connected by an organic spacer group.^[5] The pendant Lewis acidic borane moiety can assist in the delivery of a hydride ion to a metal-coordinated CO ligand and the subsequent formation of a C-C bond, (transiently) stabilize reaction intermediates by the affinity of the Lewis acidic groups with B-O bond formations, and eventually also function as a frustrated Lewis pair (FLP) in combination with an externally added bulky base to heterolytically cleave dihydrogen and deliver the hydride ion and the proton to metal-bound CO groups.[5c-5e] However, metal catalysts containing tethered Lewis acidic boron groups are often not viable for catalytic applications as they form strong B-O bonds, which are difficult to cleave and to release the organic product. Nevertheless, the boron-linked complexes are certainly important for obtaining models to provide insights into the key challenges in this process.



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From the work of Bercaw and co-workers, it became evident that both the number of phosphanylborane ligands in an electrophilic transition-metal carbonyl complex and the nature of the organic linker between the phosphorus and boron center have pronounced effects on the reduction chemistry.^[5c] To date, only monodentate monophosphanylborane ligands containing a straight chain linker (C₁–C₄) have been studied.^[5c–5e] The analogous bidentate diphosphanylborane ligands have not yet been reported.

As our group has longstanding interest in hydrogenation chemistry^[6] and metal-bound CO reduction, we became interested in new diphosphanylborane ligand systems. We recently reported the synthesis and coordination diphosphanylborane properties of the ligands $Ph_2PCH(PPh_2)CH_2B(C_8H_{14})$ (1) and $Ph_2PCH_2CH[B (C_8H_{14})$]PPh₂ (2, Figure 1) with relatively small bite angles.^[7] Both the diphosphanylborane ligands were obtained from the reaction of the corresponding diphosphoalkenes (Ph2P)2CHCH2 or Ph2PCHCHPPh2 with 9borabiyclo[3.3.1]nonane (9-BBN) under relatively drastic reaction conditions. These two ligands have monomeric open structures both in the free ligand form and in the metal complexes. Despite the large steric and ring strain factors, both ligands coordinate to tungsten centers in a chelated fashion through the formation of either a fivemembered (for 2) or a four-membered (for 1) chelate ring. The PPh₂ groups are involved in primary coordination to the metal center, whereas the Lewis acidic $B(C_8H_{14})$ group is present either as a free pendant in the secondary coordination sphere or involved in the secondary sphere coordination of a hydride ligand leading to a three-center, two-electron (3c-2e) bond. These results prompted us to explore the CO hydrogenation chemistry of cationic manganese and rhenium phosphanylborane (PB) complexes.



Figure 1. The diphosphanylborane ligands $Ph_2PCH(PPh_2)-CH_2B(C_8H_{14})$ (1) and $Ph_2PCH_2CH[B(C_8H_{14})]PPh_2$ (2).

To explore such transition-metal systems, we propose here to study CO hydrogenation chemistry by employing the PB ligands 1 and 2, which contain two P atoms, instead of one in all the earlier cases, and one boron center. We have prepared several cationic manganese and rhenium phosphanylborane complexes containing highly electrophilic CO groups and studied their reactivities towards the hydrogenation of metal-bound CO to formyl derivatives. The complexes were prepared from the reaction of commercially available metal carbonyl precursors $Mn(CO)_5Br$ and $Re(CO)_5Br$ with the diphosphanylborane ligands 1 and 2. It is expected that the chelating behavior of these two ligands would lead to the formation of *cis* complexes of the type $[M(L)(CO)_4]^+$ (M = Mn or Re, L = 1 or 2, two *cis* and two *trans* CO groups). These kinds of metal complexes were sought to act as new scaffolds for hydride transfer to CO as primary steps for CO hydrogenation, whereas NaHBEt₃ was anticipated to deliver the hydride ion for the reduction reactions.

Results and Discussion

Synthesis of Mn^I and Re^I Diphosphanylborane Complexes

The ligand exchange reactions of the commercially available metal carbonyl precursors Mn(CO)₅Br and Re(CO)₅Br with the diphosphanylborane ligands 1 or 2 were very much straightforward in tetrahydrofuran (THF), and the reactions were completed within a few hours at 80 °C (Scheme 1). When THF solutions containing an equimolar mixture of the metal precursor Mn(CO)₅Br or Re(CO)₅Br and the diphosphanylborane ligand 1 were heated to reflux at 80 °C for ca. three hours, we obtained the desired diphosphanylborane manganese and rhenium complexes fac, cis- $Mn(CO)_3(1)(Br)$ (3a) and $fac, cis-Re(CO)_3(1)(Br)$ (4a) through the expected chelate coordination of the ligand to the metal centers and the replacement of the two cis CO ligands. The isolated yields of the complexes were 86 and 93%, respectively. The ${}^{31}P{}^{1}H$ NMR signals were found at δ = 36.33 and -14.75 ppm, and the ¹¹B signals corresponding to the tethered Lewis acidic $B(C_8H_{14})$ group were found at $\delta = 58.3$ and 53.0 ppm for **3a** and **4a**, respectively. The elemental analyses were also satisfactory for these complexes. In such compounds, three v_{CO} bands in *facial* geometry and two v_{CO} bands in the *meridional* geometry are observed;^[8] the related examples are the bis(phosphane) complexes fac-[Re(CO)₃(PPh₃)₂Br] (2029, 1949, and 1906 cm⁻¹), *mer*-[Re(CO)₃(PPh₃)₂Br] (1949 and 1901 cm⁻¹), and *mer*- $[Mn(CO)_3(PPh_3)_2Br]$ (1948 and 1916 cm⁻¹). In the FTIR spectra, three v_{CO} bands were found at 2013, 1942, and 1901 cm⁻¹ for **3a** and at 2019, 1936, and 1895 cm⁻¹ for **4a** further confirming the formation of the fac, cis complexes through the formation of a four-membered chelate ring around the metal centers by the phosphanylborane ligand 1. In a similar procedure as above, the reaction of the diphosphanylborane ligand 2 with the metal precursors yielded the desired complexes fac, cis-[Mn(CO)₃-(2)(Br)] (5a) and fac, cis-[Re(CO)₃(2)(Br)] (6a, Scheme 1). The ³¹P{¹H} NMR signals for **5a** were observed at δ = 67.20 and 86.49 ppm as two doublets with ${}^{3}J_{\rm P,P} = 22.7$ Hz. The presence of the tethered Lewis acidic B(C8H14) group was confirmed from the broad ¹¹B NMR signal at δ = 51.3 ppm. The chelate coordination of the diphosphanylborane ligand 2 in 5a was confirmed by the three characteristic v_{CO} bands in the FTIR spectra at 2010 (vs), 1940 (vs), and 1911 (vs) cm⁻¹. The isolated yield of the complex was found to be 78%. For the rhenium complex 6a, two diastereomers formed as indicated by the appearance of two sets of doublets in the ${}^{31}P{}^{1}H$ NMR spectrum [major (63%): δ = 26.14 (d, ${}^{3}J_{P,P}$ = 8 Hz, 1 P), 48.55 (d, ${}^{3}J_{P,P}$ = 8 Hz, 1 P) ppm; minor (37%): δ = 30.37 (d, ${}^{3}J_{PP}$ = 16 Hz,

1 P), 44.82 (d, ${}^{3}J_{P,P} = 16$ Hz, 1 P) ppm]. The formation of two diastereomers (as for ligand **2**) was also observed previously in the tungsten complexes^[7] and could be explained on the basis of the two possible stereochemical positions of the boryl group and Br ligands, which could either be *cis* or *trans* to each other in this case. However, only one isomer was detected in the ${}^{31}P{}^{1}H$ NMR spectrum of the analogous manganese complex **5a** containing the same PB ligand. Three v_{CO} bands were observed in the FTIR spectrum of **6a** at 2021 (vs), 1938 (vs), and 1897 (vs) cm⁻¹ in the expected region. The ${}^{11}B$ NMR signal was observed at $\delta = 56.1$ ppm. Details of the synthetic procedure and characterizations are provided in the Experimental Section.



Scheme 1. Synthesis of the manganese and rhenium phosphanylborane complexes.

Synthesis of the Cationic Manganese and Rhenium Carbonyl Complexes

The phosphanylborane complexes 3a, 4a, 5a, and 6a, containing a bromide ligand, were further reacted with one equivalent of AgBF₄ in dichloromethane in the dark in the presence of 1 atm CO. The bromide abstraction by Ag⁺ followed by the coordination of a new CO ligand gave the desired monocationic carbonyl complexes [Mn(CO)₄(1)]- $[BF_4]$ (3b), $[Re(CO)_4(1)][BF_4]$ (4b), $[Mn(CO)_4(2)][BF_4]$ (5b), and $[Re(CO)_4(2)][BF_4]$ (6b, Scheme 2) in analytically pure form. As the reactions of the rhenium complexes were light sensitive, all the reactions were manipulated under complete darkness, and the reactions of the manganese complexes were also performed in darkness to avoid the possibility of the formation of mixtures of decomposition products. It must be also noted that diastereomeric mixtures of the complex 6a yielded complex 6b containing only a single isomer, as supported by the ³¹P{¹H} NMR signals at δ = 29.63 (br., 1 P) and 46.12 (br., 1 P) ppm. In addition to the shifted ¹H and ³¹P{¹H} NMR signals, new singlet ¹⁹F NMR signals between $\delta = -153$ and -156 ppm confirmed the presence of a BF₄⁻ counteranion for all complexes. One sharp singlet ¹¹B NMR resonance between $\delta = -0.6$ and 3.6 ppm was also observed for the boron atom of the BF_4^- counteranion.

However, the typical broad ¹¹B NMR resonance corresponding to the trialkyl boron group was also observed. All these complexes were fully characterized by NMR spectroscopy and also provided satisfactory elemental analyses (see Experimental Section). The identity of these complexes was further supported by the FTIR spectra of 3b, 4b, 5b, and **6b**, which exhibited two intense v_{CO} bands at 2091 (vs) and 1987 (vs) cm⁻¹ for **3b**, 2108 (vs) and 1982 (vs) cm⁻¹ for **4b**, 2092 (vs) and 2001 (vs) cm⁻¹ for **5b**, and at 2110 (vs) and 2001 (vs) cm^{-1} for **6b**. The frequencies are much higher than those of the previously reported bis(phosphane) cationic complexes^[9] trans-[Re(CO)₄(PPh₃)₂][BF₄] (2000 cm⁻¹), *trans*-[Mn(CO)₄(PPh₃)₂][BF₄] (2090, 2040, and 1996 cm⁻¹), and the bis(monophosphanylborane) cationic complexes^[10,5c] $trans-[Mn(CO)_4{Ph_2P(CH_2)_2B(C_8H_{14})}_2][BF_4]$ $(1995 \text{ cm}^{-1}), \text{ trans-}[\text{Re}(\text{CO})_4 \{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{B}(\text{C}_8\text{H}_{14})\}_2][\text{BF}_4]$ $(1999 \text{ cm}^{-1}),$ trans-[Re(CO)₄{Ph₂PCH₂B(C₈H₁₄)}₂]- $[B(C_6F_5)_4]$ (1998 cm⁻¹), and *trans*- $[Re(CO)_4]$ Ph₂PCH₂B- $(C_8H_{14})_2$ [B(C₆F₅)₄] (1998 cm⁻¹). This implies that the CO ligands in 3b, 4b, 5b, and 6b are much more electrophilic (labile) than the previously reported trans analogs and, consequently, these cationic metal carbonyl complexes should be suitable for metal-coordinated CO hydrogenations.



Scheme 2. Synthesis of the cationic manganese and rhenium phosphanylborane complexes.

Single crystals of **3b** suitable for X-ray diffraction (XRD) study were obtained from slow diffusion of pentane into a saturated dichloromethane solution at -25 °C. The structure analysis showed the expected chelate coordination of the diphosphanylborane 1 to the manganese center and substitution of the bromide ion by a CO ligand to form the monocationic tetracarbonyl manganese complex. The complex cation adopts a distorted octahedral geometry owing to the coordination of two PPh₂ groups with a relatively small bite angle $[P1-Mn1-P2 = 71.53(3)^\circ]$ and the coordination of four CO ligands. Two cis CO ligands and two trans CO ligands are present in the structure. The trans C-O bond lengths are 1.130(4) and 1.128(4) Å, and the two cis-C-O bond lengths are 1.127(4) and 1.134(4) Å. The Mn–P bond lengths are 2.313(1) and 2.305(1) Å for Mn1– P1 and Mn1-P2, respectively. As coordinating solvents were



avoided throughout the synthesis of **3b**, the pendant Lewis acidic boron center is tricoordinated and is not involved in any intra- or intermolecular interactions. The presence of the BF_4^- counteranion confirmed that the complex contains a cationic Mn^I center. The thermal ellipsoid plot of the structure is represented in Figure 2. Selected bond lengths and angles are provided in Table 1. It is anticipated that the structure of the remaining three complexes **4b**, **5b**, and **6b** have similar coordination geometry, as indicated by the exemplary X-ray structure of **3b**.



Figure 2. Thermal ellipsoid plot of the crystal structure obtained from the single-crystal X-ray measurements of $[Mn(CO)_4(1)][BF_4]$ - CH₂Cl₂ (**3b**·CH₂Cl₂). Phenyl rings on phosphorus atoms and all the hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for 3b.

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Bond	Length	Bonds	Angle
Mn1–P1	2.313(1)	P1-Mn1-P2	71.53(3)
Mn1–P2	2.305(1)	P1–Mn1–C2	98.54(10)
C101	1.130(4)	P2–Mn1–C4	96.38(10)
C2–O2	1.127(4)	C2–Mn1–C4	93.61(14)
C3–O3	1.128(4)	C3–Mn1–C1	178.18(13)
C4–O4	1.134(4)		

Reactions of $[Mn(CO)_4(1)][BF_4]$ (3b) and $[Re(CO)_4(1)][BF_4]$ (4b) with NaHBEt₃

When a $[D_5]$ chlorobenzene solution of **3b** (50 mg, 0.065 mmol) was treated dropwise with NaHBEt₃ (1 M solu-

tion in toluene, 64.75 µL) at room temperature, the pale yellow solution immediately turned deep red and cloudy owing to the precipitation of NaBF₄. An in situ measured ¹H NMR spectrum (Figure 3) showed no evidence for the formation of a formyl species. Rather, two triplet hydride resonances were found in the ¹H NMR spectra at $\delta = -4.96$ $(^{2}J_{P,H} = 40.10 \text{ Hz})$ and $-5.66 \text{ ppm} (^{2}J_{P,H} = 44.02 \text{ Hz})$ with coupling of the hydride nuclei with both of the phosphorus atoms of the diphosphanylborane ligand 1. This suggested that the η^2 -binding of the diphosphanylborane ligand 1 in the complex 3b remains intact in the in situ generated hydride complexes. Owing to the occurrence of two hydride resonances, we assumed that two isomers of the hydride complex Mn(H)(CO)₃(1) are present in solution with the hydride ligand either cis or trans to the ring position of the boryl group. The ³¹P{¹H} NMR spectra revealed the appearance of several other unidentified decomposition products in addition to these two hydride species. The same reaction was then repeated at -25 °C and monitored by ¹H and ³¹P{¹H} NMR spectroscopy with a 300 MHz spectrometer. The reaction was very fast even at low temperature and the color change observed was the same as that of the room temperature reactions. The ¹H NMR spectrum measured immediately after the addition of NaHBEt₃ solution (1 M in toluene) at -25 °C is shown in Figure 4. In addition to the hydride species detected at room temperature, a new formyl proton resonance was observed in the expected downfield region ($\delta = 13.28$ ppm) in the ¹H NMR spectra. However, the formyl signal disappeared upon warming the reaction mixture to room temperature, which demonstrates the instability of the "room temperature" formyl species. As no significant changes in the chemical shifts of the hydride species were observed, it is believed that the hydride species formed at room temperature and at -25 °C are same.

The reaction mixture was then transferred to a glove box, filtered through a celite bed, and the solvents were removed completely. Recrystallization of the solid mixture of compounds from a chlorobenzene/pentane solution produced few yellow single crystals suitable for X-ray diffraction studies. The hydride complex *fac*,*cis*-[Mn(H)(CO)₃(1)] (3c) crystallizes in the triclinic $P\bar{1}$ space group. The hydride atom was located in a difference Fourier map and freely refined. All other hydrogen positions were calculated after each cycle of refinement by using a riding model. The thermal ellipsoid plot of the crystal structure is given in Figure 5. As expected from the in situ measured ³¹P{¹H}spectrum, the



Figure 3. ¹H NMR spectrum (C_6D_5Cl , 400 MHz, room temp., in situ) measured immediately after mixing a C_6D_5Cl solution of **3b** (50 mg, 0.065 mmol) with NaHBEt₃ (1 M solution in toluene, 64.75 μ L) at room temperature.





Figure 4. ¹H NMR spectrum (C₆D₅Cl, 300 MHz, -25 °C, in situ) measured immediately after mixing a C₆D₅Cl solution of **3b** (50 mg, 0.065 mmol) with NaHBEt₃ (1 M solution in toluene, 64.75 µL) at -25 °C.

diphosphanylborane ligand **1** is present as a chelator to the manganese center, and one of the labile CO groups (*trans* to each other) was replaced by a hydride ligand. Two CO groups remain *cis* to each other and *trans* to the phosphane groups, and another CO ligand and the H_{Mn} are *trans*. The



Figure 5. Thermal ellipsoid plot of the crystal structure obtained from the single-crystal X-ray measurements of fac,cis-[Mn(H)-(CO)₃(1)] (3c). Phenyl rings on phosphorus atoms and all the hydrogen atoms except the hydride ligand are omitted for clarity.

 H_{Mn} atom is *cis* to the phosphane groups. The Mn1–H bond length is 1.54 Å, and the Mn1–P1 and Mn1–P2 bond lengths are 2.2639(4) and 2.2557(4) Å, respectively. The P1–Mn1–P2 bite angle is 73.05(2)°, which is very close to that in the crystal structure of the cationic complex **3b**. The tethered Lewis acidic B(C₈H₁₄) group was found to be intact in the complex, and remains free in the coordination sphere without involvement in intra- or intermolecular interactions. Selected bond lengths and angles are provided in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for 3c.

Bond	Length	Bonds	Angle
Mn1–P1 Mn1–P2 C1–O1 C2–O2 C3–O3 Mn1–H	2.2639(4) 2.2557(4) 1.148(2) 1.142(2) 1.146(2) 1.54(2)	P1-Mn1-P2 C2-Mn1-C3 P1-Mn1-C2 P2-Mn1-C3 C1-Mn1-H	73.05(2) 92.52(8) 94.84(6) 96.19(6) 175.2(9)

In a similar way, when a C_6D_5Cl solution of **4b** (50 mg, 0.055 mmol) was treated with NaHBEt₃ (1 M solution in



Figure 6. ¹H NMR spectrum (C_6D_5Cl , 400 MHz, room temp., in situ) measured immediately after mixing a C_6D_5Cl solution of **4b** (50 mg, 0.055 mmol) with NaHBEt₃ (1 M solution in toluene, 55.34 μ L) at room temperature.



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toluene, 55.34 μ L) at room temperature, the colorless solution immediately turned yellow, which indicated the formation of a new species in solution. An in situ ¹H NMR spectra showed a singlet resonance at $\delta = 13.59$ ppm corresponding to a metal formyl species $[Re(CHO)(CO)_3(1)]$ and a triplet hydride resonance at $\delta = -3.68 \text{ ppm} (^2J_{\text{P,H}} =$ 26.4 Hz) corresponding to a rhenium hydride complex $[Re(H)(CO)_3(1)]$ analogous to the previously discussed manganese complex fac, cis-[Mn(H)(CO)₃(1)] (3c). The ¹H NMR spectrum obtained from the reaction mixture is shown in Figure 6. The hydride species could be formed either by decarbonylation of the formyl species or by substitution of one of the labile CO ligands from 4b by a hydride ion from the NaHBEt3 source. In addition to the mentioned formyl and hydride species, several other unidentified decomposition products were detected in the ³¹P{¹H} NMR spectrum. After one day at room temperature, the ¹H NMR spectrum of the reaction mixture showed the presence of both the formyl and the hydride species in solution and additional new decomposition products. The reaction at -25 °C gave similar products including the metal formyl and metal hydride species. Unfortunately, neither the formyl species nor the hydride species could be isolated from the reaction mixture and analyzed further.

Stoichiometric Reduction of $[Mn(CO)_4(2)][BF_4]$ (5b) and $[Re(CO)_4(2)][BF_4]$ (6b) with NaHBEt₃

In a Young NMR tube, a NaHBEt₃ solution (1 m in toluene, 135.66 µL, 0.135 mmol) was added dropwise to a C_6D_5Cl solution (0.5 mL) of [Mn(CO)₄(2)][BF₄] (5b, 100 mg, 0.135 mmol), and the mixture was shaken vigorously. From the in situ monitoring by ¹H NMR, the stoichiometric conversion to a single formyl species [Mn(CHO)(CO)₃(2)] (5c, Scheme 3) was observed in addition to the precipitation of the NaBF₄ salt. The downfield-shifted broad singlet ¹H NMR resonance at δ = 14.59 ppm was assigned to the formyl proton of the expected manganese formyl species 5c (Figure 7). In addition, the absence of a ¹⁹F NMR signal indicated the formation of a neutral formyl species and the removal of the BF₄⁻



Scheme 3. Reduction of $[Mn(CO)_4(2)](BF_4)$ (5b) and $[Re(CO)_4(2)](BF_4)$ (6b) with NaHBEt₃ (1 M solution in toluene) at room temperature.

counteranion to form NaBF₄, which precipitated in chlorobenzene solution. The in situ reaction monitored by ¹H and ³¹P{¹H} NMR over a few days at room temperature showed no evidence for decomposition products. As the formyl species was stable in solution over a few days, the reaction mixture was filtered through a celite bed, all the solvents were removed completely under reduced pressure, and the obtained solid was washed several times with pentane. The analytically pure formyl complex could be isolated and stored at $-25 \,^{\circ}\text{C}$ for at least a few weeks. The ${}^{31}\text{P}{}^{1}\text{H}{}$ NMR signals of **5b** were shifted to $\delta = 87.89$ (d, ${}^{3}J_{\rm PP} =$ 22.7 Hz) and 88.69 ppm (d, ${}^{3}J_{P,P} = 22.7$ Hz) upon hydride transfer to the CO ligand. A typical ¹¹B NMR signal was found at $\delta = 43.6$ ppm [br., B(C₈H₁₄)]. The shift of ca. 40 ppm with respect to the freely pendant boron group in **5b** $[\delta(^{11}B) = 87.10 \text{ ppm}]$ clearly indicates a tetrahedral boron atom and coordination of the boron center to the formyl group.

The crystal structure of **5c** was also determined (thermal ellipsoid plot shown in Figure 8). The single crystals for X-ray diffraction were grown from the diffusion of pentane into a saturated chlorobenzene solution of **5c** at room temperature. The structural analysis revealed the identity of the neutral manganese formyl complex, which contains the chelating diphosphanylborane ligand **2**, two CO ligands (*cis* to each other and *trans* to the PPh₂ groups), and another CO ligand and the formyl group (*trans* to each other). As expected, one of the *trans* CO ligands was found to be converted into the formyl group and remained attached to the metal center as a ligand. The distance between the formyl carbon atom and the manganese center (Mn1–C4) is



Figure 7. ¹H NMR spectrum (C_6D_5Cl , 400 MHz, room temp., formyl region) of the manganese formyl complex [Mn(CHO)(CO)₃(2)] (5c).



1.988(1) Å, which is comparable to that of the previously reported neutral manganese formyl complex trans-[Mn- $(PPh_3)_2(CO)_3(CHOB\{C_6F_5\}_3)^{[10]}$ [Mn-C4 = 1.994(2) Å] with an intermolecular B-O interaction in the secondary sphere. Also in the present case, the tethered Lewis acidic $B(C_8H_{14})$ group is involved in intramolecular coordination from the formyl oxygen atom to the Lewis acidic boron center of the tethered $B(C_8H_{14})$ group. The B1–O4 distance is 1.599(2) Å. The related distance for the above reported complex was 1.593 Å. The formyl C4–O4 bond length is 1.265(2) Å, which is much longer than the C \equiv O triple bond of a CO group. The C1-O1 bond length trans to the formyl group is 1.140(2) Å, and the C2–O2 and C3–O3 bond lengths are 1.143(2) and 1.134(2) Å, respectively. The diphosphanylborane ligand 2 showed a tridentate type chelation through the phosphorus atoms and the coordinated boron atom, which led to a five-membered, a six-membered, and a seven-membered chelate ring. The P1-Mn1-P2 bite angle is 84.57(1)°, the Mn1-C4-O4 angle is 135.61(10)°, the C4–O4–B1 angle is 133.02(11)°, and the C4-Mn1-C1 angle is 175.70(7)°. All selected bond lengths and angles are given in Table 3.



Figure 8. Thermal ellipsoid plot of the crystal structure obtained from the single-crystal X-ray measurements of $[Mn(CHO)(CO)_3(2)]$ -0.5(C₆H₅Cl) [**5c**·0.5(C₆H₅Cl)]. The solvent molecule C₆H₅Cl, the phenyl rings on the phosphorus atoms, and all hydrogen atoms except the formyl H atom are omitted for clarity.

The addition of one equivalent of NaHBEt₃ (1 m in toluene) to a C₆D₅Cl solution of [Re(CO)₄(2)][BF₄] (**6b**, Scheme 3) led to the appearance of a new ¹H NMR resonance at $\delta = 15.06$ (Figure 9) and ³¹P NMR resonances at $\delta = 40.67$ and 45.93 ppm, in addition to the precipitation of NaBF₄. The downfield-shifted ¹H NMR resonance at δ = 15.06 ppm was attributed to the proton of the expected rhenium formyl species [Re(CHO)(CO)₃(2)] (**6c**). The formyl complex is stable in solution over a few weeks. Following a workup procedure similar to that for **5c**, the analytically pure rhenium formyl complex **6c** was obtained. A

Table 3. Bond lengths [Å] and angles [°] for 5c.

Bond	Length	Bonds	Angle
Mn1–C4	1.988(1)	P1–Mn1–P2	87.19(4)
Mn1–C1	1.839(2)	C2-Mn1-C3	89.61(7)
Mn1–C2	1.813(2)	P1-Mn1-C2	93.94(5)
Mn1–C3	1.813(2)	P2-Mn1-C3	91.86(5)
Mn1–P1	2.2860(4)	Mn1-C4-O4	135.61(10)
Mn1–P2	2.2876(4)	C4O4B1	133.02(11)
C4–H4	1.027(16)	C17-B1-O4	109.41(10)
C4–O4	1.265(2)	C4–Mn1–P1	83.33(4)
C1O1	1.140(2)	C4–Mn1–P2	87.19(4)
C3–O3	1.134(2)	C4–Mn1–C1	175.70(7)
C2–O2	1.143(2)		
O4–B1	1.599(2)		

broad ¹¹B NMR signal was found at $\delta = 51.2$ ppm for the 9-boranorbornyl group B(C₈H₁₄), which indicates a freely pendant boron Lewis acid not coordinated to the formyl group. This observation emphasizes the importance of an exact match of the ring size to establish the coordination of the boron center to the formyl group. Several attempts to crystallize the formyl species **6c** and characterize it by Xray diffraction remained unsuccessful because of the oily consistence of the precipitate from chlorobenzene/pentane solutions.



Figure 9. Formyl region of the ¹H NMR spectrum (C_6D_5Cl , 400 MHz, room temperature) of the rhenium formyl complex [Re-(CHO)(CO)₃(**2**)] (**6c**).

Conclusions

This work is the first report on the synthesis, characterization, and reactivity of manganese(I) and rhenium(I) carbonyl complexes with chelating diphosphanylborane ligands. The *cis*-enforcing nature of the diphosphanylborane ligands makes the metal-bound CO ligands even more labile in comparison to those in the complexes of monodentate



phosphane ligands. The cationic complexes 3b, 4b, 5b, and **6b** containing highly electrophilic CO groups (v_{CO}) $\approx 2100 \text{ cm}^{-1}$) were prepared and fully characterized. All four cationic complexes were tested for stoichiometric hydride transfer to metal-bound CO by reacting them with NaHBEt₃. The reduction of the manganese complex **3b** and rhenium complex 4b gave mixtures of products that included formyl species and hydride species. The corresponding formyl complexes were unstable, apparently because of a lack of stabilization either from the metal center or by intramolecular attachment of the boron Lewis acid to the formyl group. In accord with general observations on formyl complexes, the heavy metal rhenium formyl complexes appear to be more stable than the manganese formyl complexes, and parallel to this, the four-membered MPCP ring seemed to be too rigid to allow the boron center to reach the formyl group in the corresponding formyl complexes and to achieve additional stabilization. However, reduction of **5b** and **6b** produced the stable formyl species **5c** and **6c** upon treatment with NaHBEt₃. The structural analysis of 5c revealed that one of the trans CO groups in 5b and 6b was attacked by the hydride reagent to build up a formyl group, which is further stabilized by a strong intramolecular B-O bond formation. The backbone of the coordinated PB ligand 1 is too rigid and it does not support formyl formation, whereas ligand 2 with a more flexible backbone in the metal-coordinated form was suited to the stabilization of the manganese and rhenium formyl unit through a correct fit of its structure, which enabled the coordination of the formyl oxygen atom to the Lewis acidic boron center.

Experimental Section

General Considerations: All experiments were performed under an atmosphere of nitrogen by using either dry glove box or Schlenk techniques. Reagent grade solvents were dried with sodium benzophenone (tetrahydrofuran, diethyl ether, and pentane) and calcium hydride (dichloromethane and chlorobenzene) and distilled prior to use under a N2 atmosphere. Deuterated solvents were dried with sodium benzophenone ketyl ([D₈]THF) or calcium hydride (C_6D_5Cl, CD_2Cl_2) and distilled by a freeze-pump-thaw cycle prior to use. NaHBEt₃ (1 M toluene solution), 9-borabicyclo[3.3.1]nonane (0.5 M solution), Mn(CO)₅Br, and Re(CO)₅Br were purchased from commercially available sources and used without further purifications. NMR spectra were measured with Varian Gemini-300 (300 MHz for ¹H and 96.28 MHz for ¹¹B) and Bruker DRX 400 spectrometers (400.1 MHz for 1 H, 162.0 MHz for 31 P). All 1 H chemical shifts are expressed in ppm relative to tetramethylsilane (TMS), ${}^{31}P{}^{1}H$ chemical shifts are relative to 85% H₃PO₄, and ¹¹B chemical shifts are relative to BF₃·OEt₂ as an external standard. Signal patterns are as follows: s singlet, d doublet, t triplet, q quartet, m multiplet. IR spectra were obtained either by attenuated total reflectance (ATR) or KBr methods with a Bio-rad FTS-45 instrument. Elemental analyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich.

Crystal Structure Determination: The data collection and structurerefinement data for **3b**, **3c**, and **5c** are presented in Table 4. Singlecrystal X-ray diffraction data were collected at 183(2) K with an Xcalibur diffractometer (Agilent Technologies, Ruby CCD detector) by using a single wavelength Enhance X-ray source with Mo- K_{α} radiation ($\lambda = 0.71073$ Å).^[11] The selected suitable single crystals were mounted by using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction, and analytical absorption corrections^[12] were performed with the CrysAlis^{Pro} program suite.^[11] The crystal structures were solved with SHELXS97^[13] by using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL97.^[13] All programs used during the crystal structure determination process are included in the WINGX software.^[14] PLATON^[15] was used to check the result of the X-ray analyses.

CCDC-929474 (for **3b**), -929475 (for **3c**), and -929476 (for **5c**) 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.

General Procedure for the Synthesis of 3a, 4a, 5a, and 6a: A weighed quantity of $Mn(CO)_5Br$ or $Re(CO)_5Br$, an equimolar amount of diphosphanylborane ligand 1 or 2, and THF were placed in sealed tubes under a nitrogen atmosphere. The reaction mixtures were heated to reflux for ca. 3 h at 80 °C. The sealed tubes were cooled to room temperature and transferred to the glove box. All solvents were removed under vacuum to obtain yellow (for manganese complexes) and white solids (for rhenium complexes). The obtained solids were extracted several times with diethyl ether. The combined ether extracts were concentrated to minimum volume and kept at -25 °C to obtain crystals. The crystals obtained from four different reactions were characterized by ¹H, ³¹P, ¹¹B NMR, and IR spectroscopy and elemental analyses.

fac,cis-Mn(CO)₃[Ph₂PCH(PPh₂)CH₂B(C₈H₁₄)](Br) (3a): Yield 86%. FTIR (solid, ATR): $\tilde{v} = 2013$ (vs, v_{CO}), 1942 (vs, v_{CO}), 1901 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): $\delta = 36.33$ (s, PPh₂) ppm. ¹¹B NMR ([D₈]THF, 96.28 MHz): $\delta = 58.3$ [br., B(C₈H₁₄)] ppm. ¹H NMR ([D₈]THF, 400 MHz): $\delta = 7.36-7.66$ (m, 20 H, PhH), 2.25 (m, 1 H, CH), 2.14 (m, 2 H, CH₂), 1.78–1.83 [m, 14 H, B(C₈H₁₄)] ppm. C₃₇H₃₇BBrMnO₃P₂ (737.29): calcd. C 60.27, H 5.06; found C 60.38, H 5.17.

fac,cis-Re(CO)₃[Ph₂PCH(PPh₂)CH₂B(C₈H₁₄)](Br) (4a): Yield 93%. FTIR (solid, ATR): $\tilde{v} = 2019$ (vs, v_{CO}), 1936 (vs, v_{CO}), 1895 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): $\delta = -14.75$ (s) ppm. ¹¹B NMR ([D₈]THF, 96.28 MHz): $\delta = 53.0$ [br., B(C₈H₁₄)] ppm. ¹H NMR ([D₈]THF, 400 MHz): $\delta = 7.37-7.67$ (m, 20 H, PhH), 2.19 (m, 1 H, CH), 2.01 (m, 2 H, CH₂), 1.54–1.82 [m, 14 H, B(C₈H₁₄)] ppm. C₃₇H₃₇BBrO₃P₂Re (868.56): calcd. C 51.16, H 4.29; found C 51.38, H 4.21.

fac,cis-Mn(CO)₃{Ph₂PCH₂CH[B(C₈H₁₄)]PPh₂}(Br) (5a): Yield 78%. FTIR (solid, ATR): $\tilde{v} = 2010$ (vs, v_{CO}), 1940 (vs, v_{CO}), 1911 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): $\delta = 67.20$ (d, ³*J*_{P,P} = 22.7 Hz, 1 P), 86.49 (d, ³*J*_{P,P} = 22.7 Hz, 1 P) ppm. ¹¹B NMR ([D₈]THF, 96.28 MHz): $\delta = 51.3$ [br., B(C₈H₁₄)] ppm. ¹H NMR ([D₈]THF, 400 MHz): $\delta = 6.95$ -8.05 (m, 20 H, PhH), 3.62 (m, 1 H, CH), 3.22 (m, 2 H, CH₂), 1.32–1.84 [m, 14 H, B(C₈H₁₄)] ppm. C₃₇H₃₇BBrMnO₃P₂ (737.29): calcd. C 60.27, H 5.06; found C 59.98, H 4.93.

fac,cis-Re(CO)₃{Ph₂PCH₂CH[B(C₈H₁₄)]PPh₂}(Br) (6a): Yield 96%. FTIR (solid, ATR): $\tilde{v} = 2021$ (vs, v_{CO}), 1938 (vs, v_{CO}), 1897 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR ([D₈]THF, 162 MHz): Major (63%): $\delta = 26.14$ (d, ³*J*_{PP} = 8 Hz, 1 P), 48.55 (1P, d, ³*J*_{PP} = 8 Hz); minor (37%): $\delta = 30.37$ (d, ³*J*_{PP} = 16 Hz, 1 P), 44.82 (d, ³*J*_{PP} = 16 Hz, 1 P) ppm. ¹¹B NMR ([D₈]THF, 96.28 MHz): $\delta = 56.1$ [br., B(C₈H₁₄)] ppm. ¹H NMR ([D₈]THF, 400 MHz): $\delta = 7.13-7.85$ (m, 20 H,

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	3b	3c	5c
Empirical formula	$C_{38}H_{37}B_2F_4MnO_4P_2\cdot CH_2Cl_2$	C ₃₇ H ₃₈ BMnO ₃ P ₂	$(C_{38}H_{38}BMnO_4P_2)_2 \cdot C_6H_5Cl$
Formula weight /g mol ⁻¹	857.10	658.36	1485.30
Temperature /K	183(2)	183(2)	183(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	triclinic, P1	triclinic, PĪ
a /Å	10.6759(4)	9.8427(5)	8.6414(2)
b /Å	35.1572(8)	9.9301(4)	10.5320(2)
c /Å	11.8633(5)	18.8448(6)	21.0251(5)
a /°	90	98.206(3)	81.103(2)
β /°	116.535(5)	95.053(3)	87.009(2)
γ /°	90	110.305(4)	74.356(2)
Volume /Å ³	3983.7(3)	1690.84(12)	1820.35(7)
Z, density (calcd.) $/Mgm^{-3}$	4, 1.429	2, 1.293	1, 1.355
Abs. coefficient /mm ⁻¹	0.604	0.520	0.529
<i>F</i> (000)	1760	688	774
Crystal size /mm	$0.50 \times 0.45 \times 0.28$	$0.38 \times 0.35 \times 0.29$	$0.50 \times 0.26 \times 0.15$
θ range /°	3.01-30.51	2.83-30.51	2.94-30.51
Reflections collected	52370	31391	33454
Unique reflections	$12120/R_{\rm int} = 0.0418$	$10292/R_{\rm int} = 0.0406$	$11072/R_{\rm int} = 0.0407$
Completeness to $\theta / \%$	99.7	99.9	99.7
Absorption correction	analytical	analytical	analytical
Max. and min. transmission	0.896 and 0.808	0.900 and 0.866	0.917 and 0.773
Data/restraints/parameters	10000/36/515	8616/0/401	9318/0/455
Goodness-of-fit on F^2	1.088	1.034	1.046
Final R_1 and wR_2 indices $[I > 2\sigma(I)]^{[a]}$	0.0770, 0.1861	0.0429, 0.1129	0.0387, 0.0992
R_1 and wR_2 indices (all data)	0.0919, 0.1966	0.0529, 0.1208	0.0481, 0.1060
Largest diff. peak and hole /e Å ⁻³	1.116, -0.729	0.666, -0.305	0.546, -0.363

[a] The unweighted R factor is $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$ and the weighted R factor is $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

PhH), 3.09 (m, 2 H, CH₂), 2.63 (m, 1 H, CH), 1.63–1.75 [m, 14 H, $B(C_8H_{14})$] ppm. $C_{37}H_{37}BBrO_3P_2Re$ (868.56): calcd. C 51.16, H 4.29; found C 51.53, H 4.48.

General Procedure for the Synthesis of Cationic Manganese and Rhenium Complexes 3b, 4b, 5b, and 6b: A Teflon-stoppered J. Young Schlenk tube was charged with the bromide precursor, AgBF₄ (1 equiv.), a stirbar, and CH₂Cl₂ (50 mL). The vessels were sealed and removed from the glove box. The reaction mixtures were immediately frozen in liquid nitrogen, evacuated to degas, and 1.5 atm CO was introduced to the vessels. After the injection of CO gas, the vessels were covered with aluminum foil to protect the reaction mixtures from light. After 30 min, the vellow solution became colorless (for manganese complexes) and precipitation of AgBr occurred, and then the mixtures were stirred overnight at room temperature. The reaction mixtures were boil-degassed to remove excess CO and filtered through a small celite bed to afford a pale yellow (manganese complexes) or colorless (rhenium complexes) solution. The filtrates were dried in vacuo to afford the desired white or pale yellow cationic manganese tetracarbonyl or white cationic rhenium tetracarbonyl complexes.

[Mn(CO)₄{Ph₂PCH(PPh₂)CH₂B(C₈H₁₄)}][BF₄] (3b): Yield 73%. FTIR (solid, ATR): $\tilde{v} = 2091$ (vs, v_{CO}), 1987 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): $\delta = 31.68$ (s, PPh₂) ppm. ¹¹B NMR (CD₂Cl₂, 96.28 MHz): $\delta = 87.0$ [br., B(C₈H₁₄)], 3.6 (s, BF₄) ppm. ¹H NMR (CD₂Cl₂, 400 MHz): $\delta = 7.41-7.73$ (m, 20 H, PhH), 1.90 (m, 1 H, CH), 2.12 (m, 2 H, br., CH₂), 1.36–1.86 [m, 14 H, B(C₈H₁₄)] ppm. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz): $\delta = -156.03$ (s, BF₄) ppm. C₃₈H₃₇B₂F₄MnO₄P₂ (772.20): calcd. C 59.10, H 4.83; found C 58.94, H 4.93.

[Re(CO)₄{Ph₂PCH(PPh₂)CH₂B(C₈H₁₄)}][BF₄] (4b): Yield 71%. FTIR (solid, KBr): $\tilde{v} = 2108$ (vs, v_{CO}), 1982 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): $\delta = -20.95$ (s, PPh₂) ppm. ¹¹B NMR (CD₂Cl₂, 300 MHz): $\delta = 86.7$ [br., B(C₈H₁₄)], 0.99 (s, BF₄) ppm. ¹H NMR (CD₂Cl₂, 400 MHz): $\delta = 7.29-8.44$ (m, 20 H, PhH), 2.74 (m, 3 H, CH and CH₂), 1.27-1.73 [m, 14 H, B(C₈H₁₄)] ppm. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz): $\delta = -153.03$ (s, BF₄) ppm. C₃₈H₃₇B₂F₄O₄P₂Re (903.47): calcd. C 50.52, H 4.13; found C 50.38, H 4.13.

[Mn(CO)₄{Ph₂PCH₂CH{B(C₈H₁₄)}PPh₂}][BF₄] (5b): Yield 84%. FTIR (solid, KBr): $\tilde{v} = 2092(vs, v_{CO}), 2001(vs, v_{CO}) \text{ cm}^{-1}. {}^{31}P{}^{1}H}$ NMR (CD₂Cl₂, 162 MHz): $\delta = 74.14$ (br s, 1 P, PPh₂), 87.58 (br s, 1 P, PPh₂) ppm. {}^{11}B NMR (CD₂Cl₂, 96.28 MHz): $\delta = 87.10$ [br., B(C₈H₁₄)], -0.62 (s, BF₄) ppm. {}^{19}F NMR (CD₂Cl₂, 376.5 MHz): $\delta = -153.01$ (s) ppm. {}^{1}H NMR (CD₂Cl₂, 400 MHz): $\delta = 7.43-7.62$ (m, 20 H, PhH), 3.91 (m, 1 H, CH), 2.86 (m, 2 H, CH₂), 1.45-1.82 [m, 14 H, B(C₈H₁₄)] ppm. C₃₈H₃₇B₂F₄MnO₄P₂ (772.20): calcd. C 59.10, H 4.83; found C 59.18, H 4.71.

[Re(CO)₄{Ph₂PCH₂CH{B(C₈H₁₄)}PPh₂}][BF₄] (6b): Yield 68%. FTIR (solid, ATR): $\tilde{v} = 2110$ (vs, v_{CO}), 2001 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ = 29.63 (br., 1 P), 46.12 (br., 1 P) ppm. ¹¹B NMR (CD₂Cl₂, 96.28 MHz): δ = 64.7 [br., B(C₈H₁₄)], 0.41 (BF₄) ppm. ¹H NMR (CD₂Cl₂, 400 MHz): δ = 7.47-7.71 (m, 20 H, PhH), 3.28 (m, 1 H, CH), 2.75 (m, 2 H, CH₂), $1.43 - 1.65 \ [m, \ 14 \ H, \ B(C_8H_{14})] \ ppm. \ ^{19}F \ NMR \ (CD_2Cl_2,$ 188.14 MHz): = δ -152.69 BF_4) (s, ppm. $C_{38}H_{37}B_2F_4O_4P_2Re \cdot CH_2Cl_2$ (903.47 + 84.9): calcd. C 47.35, H 3.98; found C 47.18, H 3.73.

Reduction of $[Mn(CO)_4{Ph_2PCH(PPh_2)CH_2B(C_8H_{14})}][BF_4]$ (3b) with NaHBEt₃: NaHBEt₃ (1 M solution in toluene, 64.75 µL, 0.065 mmol) was added to a Young NMR tube containing a solution of 3b (50 mg, 0.065 mmol) in C₆D₅Cl (ca. 0.5 mL), and the mixture was stirred vigorously before the NMR measurements. Immediately after mixing, the pale yellow solution turned deep red and conversion to two hydride species was observed in addition to



several other unidentified products. Two triplet hydride resonances were found at $\delta = -4.96$ and -5.66 ppm in the in situ measured ¹H NMR spectrum. The hydride species were identified as two isomers of the manganese complex $[Mn(H)(CO)_3(1)]$, in which the hydride ligand can either be *cis* or *trans* to the ring position of the boryl group. A formyl resonance was also observed along with the two triplet hydride resonances when the same reaction was repeated at -25 °C. However, only the formyl resonance disappeared upon warming of the reaction mixture to room temperature. After filtration through a small celite bed followed by removal of the solvents, the reaction mixture gave a red solid mixture of compounds. The solid mixture was then recrystallized from a chlorobenzene/ pentane solution to obtain a few red single crystals of the manganese hydride complex fac, cis-[Mn(H)(CO)₃(1)] (3c) suitable for single-crystal X-ray diffraction studies. However, all the other products formed could not be isolated and analyzed separately. Some selected in situ measured NMR values are reported here. ¹H NMR (C₆D₅Cl, 400 MHz, reaction at room temperature): $\delta = -4.96$ (t, ${}^{2}J_{P,H}$ = 40.10 Hz, hydride), -5.66 (t, ${}^{2}J_{P,H}$ = 44.02 Hz, hydride) ppm. ³¹P{¹H} NMR (C₆D₅Cl, 162 MHz, reaction at room temperature): $\delta = 74.00, 58.04, 56.42$ (major), 52.28, 40.77, 39.14, 4.28, -0.61 (major), -8.44 and -8.69 ppm. ¹H NMR (C₆D₅Cl, 300 MHz, reaction at -25 °C): $\delta = 13.28$ (d, J = 20.7 Hz, formyl species), -4.50 (t, ${}^{2}J_{PH}$ = 40.8 Hz, hydride species), -5.70 (t, ${}^{2}J_{PH}$ = 45.6 Hz, hydride species) ppm.

Reduction of $[Re(CO)_4{Ph_2PCH(PPh_2)CH_2B(C_8H_{14})}](BF_4)$ (4b) with NaHBEt₃: To a Young NMR tube containing a solution of 4b (50 mg, 0.055 mmol) in C₆D₅Cl (са. 0.5 mL), NaHBEt₃ (1 м solution in toluene, 55.34 µL, 0.055 mmol) was added, and the mixture was stirred vigorously before the NMR measurements. The colorless solution immediately turned yellow, and conversion to a formyl {likely to be [Re(CHO)(CO)₃(1)]} and a hydride species was observed in addition to other unidentified decomposition products. The triplet hydride resonance confirmed the presence of the diphosphanylborane ligand 1 in the hydride complex. Therefore, the hydride species was identified as the rhenium hydride complex $[Re(H)(CO)_3(1)]$, analogous to the manganese hydride complex fac, cis-[Mn(H)(CO)₃(1)] (3c). However, the products formed in the reaction mixture could not be isolated and analyzed separately. Selected in situ measured data: ¹H NMR (C₆D₅Cl, 400 MHz, reaction at room temperature): $\delta = 13.59$ (s, formyl species), -3.68 (t, ${}^{2}J_{P,H}$ = 26.4 Hz, hydride species) ppm. ${}^{31}P{}^{1}H$ NMR (C₆D₅Cl, 162 MHz, reaction at room temperature): δ = 37.33, 32.52, 29.60, -2.79, -6.33, -7.45, -11.04, -13.79, -17.01, -18.99, -43.25 (major) ppm.

Reduction of $[Mn(CO)_4]Ph_2PCH_2CH(B\{C_8H_{14}\})PPh_2\}[BF_4]$ (5b) with NaHBEt₃: In a Young NMR tube, 5b (100 mg, 0.135 mmol) was dissolved in C₆D₅Cl (0.5 mL). NaHBEt₃ (1 м solution in toluene, 135.66 µL, 0.135 mmol) was added dropwise, and the mixture was stirred vigorously. The in situ measured ¹H and ³¹P{¹H} NMR spectra indicated the stoichiometric conversion to the desired formyl complex $[Mn(CHO)(CO)_3(2)]$ (5c). The formyl complex was stable in solution over a few weeks. The reaction mixture was transferred to the glove box, filtered through a small celite bed, and all the solvents were removed to obtain a yellow color solid. The solid was washed several times with pentane and dried under reduced pressure. The complex was recrystallized several times from a chlorobenzene/pentane solution to obtain the pure formyl complex 5c, yield 51%. FTIR (solid, ATR): $\tilde{v} = 2013$ (vs, v_{CO}), 1947 (vs, v_{CO}), 1920 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR (C₆D₅Cl, 162 MHz): δ = 87.89 (d, ${}^{3}J_{P,P} = 22.7$ Hz, 1 P), 88.69 (d, ${}^{3}J_{P,P} = 22.7$ Hz, 1 P) ppm. ${}^{11}B$ NMR (C₆D₅Cl, 96.28 MHz): δ = 43.6 [br., B(C₈H₁₄)] ppm. ¹H NMR (C₆D₅Cl, 400 MHz): δ = 14.59 (s, 1 H, formyl), 7.03–7.54

(m, 20 H, PhH), 3.16–3.39 (m, 3 H, CH and CH₂), 1.50–1.88 [m, 14 H, B(C₈H₁₄)] ppm. C₃₈H₃₇BF₄MnO₄P₂ (761.15): calcd. C 59.91, H 4.90; found C 61.05, H 5.41.

Reduction of $[Re(CO)_4]Ph_2PCH_2CH(B\{C_8H_{14}\})PPh_2\}[BF_4]$ (6b) with NaHBEt₃: In a Young NMR tube, complex 6b (100 mg, 0.111 mmol) was dissolved in C₆D₅Cl (0.5 mL). NaHBEt₃ (1 M solution in toluene, 110.68 µL, 0.135 mmol) was added dropwise, and the mixture was stirred vigorously. The in situ measured ¹H and ³¹P{¹H} NMR spectra indicated the stoichiometric conversion to the desired formyl complex [Re(CHO)(CO)₃(2)] (6c). The formyl complex is stable in solution over a few weeks. The workup was performed in a similar procedure as for 5c to obtain analytically pure rhenium formyl complex 6c, yield 68%. FTIR (solid, ATR): $\tilde{v} = 2001$ (vs, v_{CO}), 1905 (vs, v_{CO}), 1860 (vs, v_{CO}) cm⁻¹. ³¹P{¹H} NMR (C₆D₅Cl, 162 MHz): δ = 40.67 (s, 1 P, PPh₂), 45.93 (s, 1 P, PPh₂) ppm. ¹¹B NMR (C₆D₅Cl, 96.28 MHz): δ = 51.2 [br., B(C₈H₁₄)] ppm. ¹H NMR (C₆D₅Cl, 400 MHz): δ = 15.06 (s, 1 H, formyl), 7.25-7.47 (m, 20 H, PhH), 2.65 (m, 2 H, CH₂), 3.12 (m, 1 H, CH), 1.60-2.08 [m, 14 H, B(C8H14)] ppm. C38H38BO4P2Re (817.43): calcd. C 55.78, H 4.68; found C 55.62, H 4.53.

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