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Protonic–Hydridic Bifunctionality: The Protonic (2-Aminoethyl)-dimethylphosphane Ligand in Nitrosyl Tungsten Hydride Complexes

Zilu Chen,[a] Ivan Timokhin,[a] Helmut W. Schmalle,[a] Thomas Fox,[a] Olivier Blacque,[a] and Heinz Berke*[a]

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The chemistry of nitrosyl tungsten hydrides bearing the (2-aminoethyl)dimethylphosphane ligand (edmp) with an acidic NH functionality was studied. Such complexes were targeted by applying the reaction of $WCl_3(NO)(CH_3CN)_2$ with edmp, which gave $[WCl_2(NO)(\eta^2\text{-edmp})_2][Cl]$ (**1a**) and $[WCl_2(NO)(\eta^2\text{-edmp})_2][BPh_4]$ (**1b**). Complex **1b** was treated with Zn to produce $[W(H)(Cl)(NO)(\eta^2\text{-edmp})_2][BPh_4]$ (**2b**). Subsequent attempts with the use of $WCl(NO)[P(OMe)_3]_4$ and edmp as starting materials produced $\{W(NO)(\eta^2\text{-edmp})_2[P(OMe)_3]\}[Cl]$ (**3a**) at 85 °C and $[W(H)(Cl)(NO)(\eta^2\text{-edmp})_2][Cl]$ (**2a**) at 120 °C. Substitution of the $P(OMe)_3$ ligand in $\{W(\eta^2\text{-edmp})_2(NO)[P(OMe)_3]\}[BPh_4]$ (**3b**) with CO afforded $[W(CO)(\eta^2\text{-edmp})_2(NO)][BPh_4]$ (**4b**). Complex **4b** was treated with $NaHBEt_3$, resulting in a dihydride product [W(CO)*trans*-$(\eta^1\text{-edmp})_2(H)_2(NO)$]Na (**4c**). The chlorido complexes containing one η^2-edmp ligand $WCl(NO)(\eta^2\text{-edmp})(PMe_3)_2$ (**5a**), $WCl(NO)(\eta^2\text{-edmp})(CO)(PMe_3)$ (**6a**), $WCl(NO)(\eta^2\text{-edmp})[P(OMe)_3]_2$ (**5b**), and $WCl(NO)(CO)(\eta^2\text{-edmp})[P(OMe)_3]$ (**6b**) were prepared and treated with $NaHBEt_3$ to obtain the corresponding hydride species $WH(NO)(\eta^2\text{-edmp})[P(OMe)_3]_2$ (**8b**), $WH(NO)(CO)(\eta^2\text{-edmp})(PMe_3)$ (**7a**), and $WH(NO)(CO)(\eta^2\text{-edmp})[P(OMe)_3]$ (**7b**). The initially formed $WH(NO)(\eta^2\text{-edmp})(PMe_3)_2$ (**8a**) was spontaneously transformed into the amide complex $W(NO)(CO)(NHCH_2CH_2PMe_2)(PMe_3)$ (**11a**) with loss of H_2. The anionic dihydride products $[W(H)_2(\eta^1\text{-edmp})(NO)L_2]$Na [L = PMe_3 (**9a**) and L = PMe_3 (**9b**)] were produced from **7a** and **7b** by the reaction with $NaHBEt_3$. Hydride **8b** turned out to be the most stable hydride complex in the given series. NMR spectroscopic experiments and deuterium labeling showed that **8b** coexists in equilibrium with corresponding dihydrogen amide complex **10b**. The structures of compounds **1a**, **2b**, **3a**, **4b**, **5b**, **6a**, and **6b** were studied by single-crystal X-ray diffraction.

Introduction

Transition–metal hydride complexes bearing NH functionalized ligands combine a hydridic and a protonic function, which together constitutes an H_2 equivalent and may be used for hydrogenations. Denoted as "ionic hydrogenations" or more general as "bifunctional molecular catalysis" they typically occur in the secondary coordination sphere through H^- and H^+ transfers. The bound and strongly polarized H atoms are prone to intra- or intermolecular dihydrogen bonding contacts ($-H^{\delta-}\cdots H^{\delta+}-$), which is assumed to appear in "ionic hydrogenations" of unsaturated molecules, such as olefins, ketones, and imines,[1–15] but their crucial involvement in such reaction courses is as yet not fully established. "Ionic hydrogenations" and also transfer hydrogenations with similar polar mechanistic background are presently mainly ruthenium and iridium based.[12–19] It is anticipated that related non-noble metal catalyses could principally work equally well, as the required hydride and proton transfers are reactions taking place in the secondary coordination sphere where the type of metal center is expected to play a less decisive role. In various earlier studies we had indeed established the hydridic character of W–H bonds in nitrosyl-substituted complexes and their propensity to undergo hydride-transfer reactions.[20–22] On the basis of this knowledge we still wanted to add a suitable ligand-contained acidic functionality "fitting" the hydridicities of the W–H bonds so that the spontaneous reaction of H^- and H^+ to give H_2 would not readily occur. NH acidities are enhanced upon metal coordination, but for the targeted (2-aminoethyl)dimethylphosphane (edmp) ligand the "metal-attached" pK_a was expected to fall into the feasible range of 7 to 10. Ruthenium catalysts with related P,N-chelating ligands were successfully applied in chiral hydrogenations and dehydrogenations.[23–28] Exploring now the potential of a middle transition element in protonic–hydridic reactivity the targeted edmp-substituted tungsten nitrosyl systems were thought to be varied in the ancillary ligand sphere allowing finetuning with subtle adjustment of the protonic–hydridic balance. We therefore set out to achieve synthetic access to NO/edmp hydride complexes variable in L^1 and L^2 as sketched in Figure 1.

[a] Department of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
Fax: +41-1-63-56-802
E-mail: hberke@aci.uzh.ch

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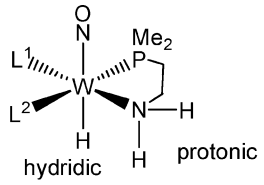


L^1L^2 = edmp; L^1 = L^2 = PMe_3 or $P(OMe)_3$
or L^1 = CO, L^2 = PMe_3 or $P(OMe)_3$

Figure 1. Structure of NO/edmp hydride complexes.

Results and Discussion

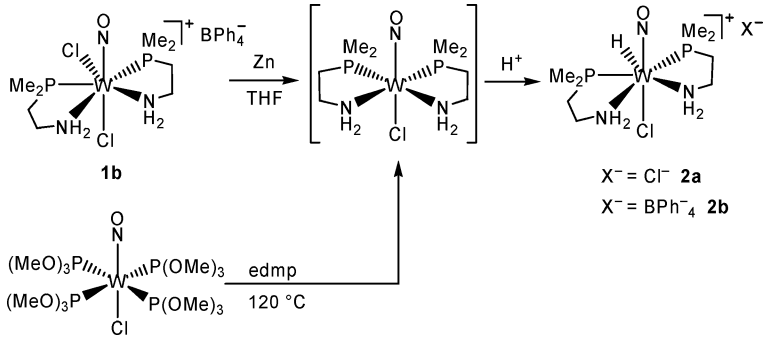
Attempted Synthesis of $WH(NO)(edmp)_2$

Using a hydride donor, the target complex $WH(NO)(edmp)_2$ was envisaged to be prepared by chloride replacement in $WCl(NO)(edmp)_2$.[29–32] Two preparative routes were considered to lead to $WCl(NO)(edmp)_2$. The first one was to introduce the edmp ligand(s) into the substitutionally labile complex $WCl_3(CH_3CN)_2(NO)$,[33] followed by subsequent reduction of the tungsten(II) species. Alternatively, starting from the tungsten(0) complexes $W(CO)_4(NO)(ClAlCl_3)$ or $WCl(NO)[P(OMe)_3]_4$, CO or $P(OMe)_3$ replacement was envisaged to result directly in the desired W^0 chlorides.

At room temperature, reaction of $WCl_3(CH_3CN)_2(NO)$ in thf with edmp led to immediate formation of a precipitate. The reaction was complete after 12 h, and the precipitate, the ionic complex $[WCl_2(NO)(edmp)_2][Cl]$ (**1a**), was separated off as an analytically pure, yellow powder. Complex **1a** was obtained in high yield (99%) and was identified by IR, NMR and MS spectroscopy and X-ray diffraction. The cation of **1a** displays a pentagonal bipyramidal structure with the two edmp ligands and one chlorido group in the pentagonal plane and a nitrosyl and one chlorido ligand in axial positions. The IR spectrum of **1a** in CH_2Cl_2 solution was in accord with the presence of an NO group displaying a strong ν(NO) band at 1634 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ showed several multiples appeared at 7.14, 5.05 ppm for the NH_2 group, at 3.84, 3.40 ppm for the NCH_2 group, at 2.25 ppm for the PCH_2 moieties and "filled-in" triplets ($^2J_{H,P}$ = 5.4 Hz) at 1.88, 1.77 ppm for the PCH_3 group. For the NH_2 or CH_2 protons, two sets of signals were found due to the chemically distinguished regions above and below the pentagonal plane. The PCH_2 resonance appeared broad, presumably as a result of the quite small chemical shift difference of the $H_{methylene}$ nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **1a** showed in $CDCl_3$ a singlet at 38.3 ppm with satellites ($^1J_{W,P}$ = 193 Hz), suggesting the chemical equivalence of the two equatorial P atoms. In accord with the ^1H NMR spectrum, the ^{13}C NMR spectrum of **1a** displayed two triplets for the Me_P units at 9.3 to 10.0 ppm, verifying that the two Me groups are chemically inequivalent. Another ^{13}C NMR resonance was found as a triplet at 29.0 ppm, belonging to the PCH_2 moiety. All of these triplet resonances are due to virtual $^{13}C,^{31}P$ coupling.

The solubility of **1a** turned out to be too low for proper subsequent reactivity. The solubility was sought to be improved by anion exchange of Cl^- with BPh_4^-. Indeed the $[W^{II}Cl_2(NO)(edmp)_2][BPh_4]$ complex (**1b**) turned out to be soluble in thf and CH_3CN. However, attempts to reduce **1b** to a $W^0Cl(NO)(edmp)_2$ complex failed. Applying a slight excess amount of sodium amalgam (1%) in thf resulted at room temperature in a mixture of several products that could not be identified. Magnesium and zinc powder in large excess amounts were then tried as alternative reducing agents. Both reacted with **1b**, but the zinc reaction turned out to be superior, causing less byproducts. A yellow product was obtained after extraction with CH_2Cl_2, which was identified to be the seven-coordinate hydride complex $[W(H)(Cl)(NO)(edmp)_2][BPh_4]$ (**2b**). As suggested in Scheme 1, **2b** could be envisaged to be produced by autoprotolysis of the transient target complex $[WCl(NO)(edmp)_2]$, leading additionally to the $[WCl(NO)(edmp)(HNCH_2CH_2PMe_2)]^-$ anion. This anionic amide complex is assumed to be unstable, decomposing with loss of the Cl^- and edmp ligands, and by this the autoprotolysis equilibrium is shifted totally to the **2b** side. However, the hydride ligand might also originate from trace amounts of water in the reaction mixture. Remarkably, several attempts with the use of "super" dried thf and zinc revealed the same yields so that the autoprotolysis seems to be the more probable reaction path for **2b**. Attempts to obtain $[WCl(NO)(edmp)_2]$ through deprotonation of **2b** failed. Presumably, deprotonation occurred at the edmp ligand, which might be, in the least, the kinetic site for deprotonation, if not the thermodynamic site. The reduction of **2b** with zinc to obtain the hydride complex $[WH(NO)(edmp)_2]$ resulted also in decomposition of the reaction mixture.

The IR spectrum of **2b** shows a strong ν(NO) band at 1600 cm^{-1}, at low wavenumbers not reflecting the cationic nature of the complex, but confirming extraordinarily strong electron back donation from the tungsten center. The ^1H NMR spectrum of **2b** revealed a triplet with satellites at 2.96 ppm, which became a singlet upon ^{31}P decoupling. This indicated that a hydride complex was formed ($^1J_{H,W}$ = 11 Hz) and confirmed that two phosphane ligands ($^2J_{H,P}$ = 72.7 Hz) are contained in the molecule. Further evidence for a hydride complex bearing two phosphane ligands was obtained from an NOE experiment. Upon irradiation of the signal of the Me_{edmp} groups, NOE enhancement was seen for the hydride triplet at ca. 3.0 ppm. The $^1H–^{31}P$ correlation spectrum additionally proved strong coupling between the hydride ligand and the chemically equivalent ^{31}P nuclei. The complex resonance patterns in the ^1H NMR spectrum were unraveled by $^1H–^{15}N$ correlation and long-range $^1H–^{13}C$ correlation experiments. $^1H,^{15}N$ coupling between the NO group and the hydride ligand proved their simultaneous presence in the complex. By this, **2b** was attributed a seven-coordinate structure related to that of **1b** by formal replacement of an equatorial Cl group with a hydride ligand. Another route to $WCl(NO)(edmp)_2$ or $WH(NO)(edmp)_2$ was then sought, utilizing the reaction of $W(CO)_4(NO)(ClAlCl_3)$



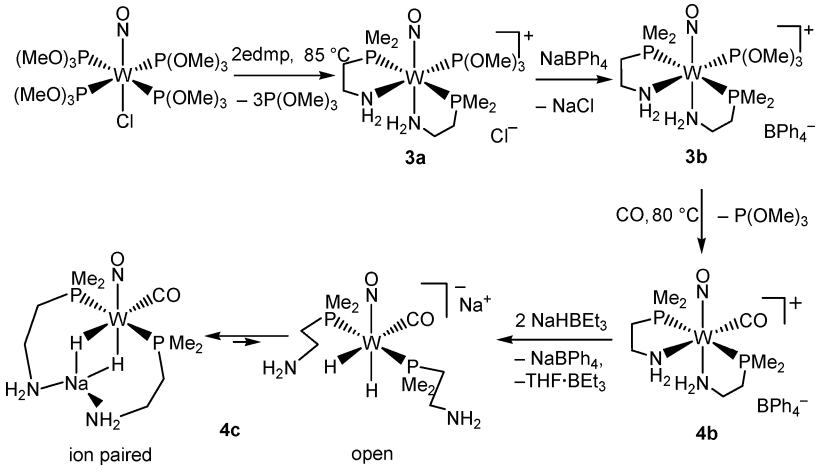
Scheme 1.

with edmp in thf, which however led to the formation of presumably ionic products completely insoluble in organic solvents.

It was then anticipated that the easily accessible $WCl(NO)[P(OMe)_3]_4$ compound[34] could be used to generate the desired $WCl(NO)(edmp)_2$ by applying enforced conditions. The reaction of $W(Cl)(NO)[P(OMe)_3]_4$ with an excess amount of edmp was carried out in a closed vessel in toluene at 120 °C, which resulted however again in the formation of the cationic hydride complex $[W(H)(Cl)(NO)(edmp)_2][Cl]$ (**2a**) (Scheme 1). As a result of slow decomposition of the product at this temperature, the precipitate was separated every 2 d to obtain a quite pure product in an overall yield of 25%. Complex **2a** was characterized by NMR and IR spectroscopy, EA, MS and X-ray diffraction and revealed to consist of the same cation as **2b**. The cations of **2a** and **2b** showed practically the same NMR spectra. Minor deviations were due to the use of different solvents. In the ^1H NMR spectrum of **2a** in $CDCl_3$ the hydride resonance was found at 3.29 ppm split into a triplet with tungsten satellites. Similar to the formation of **2b**, the hydride ligand of **2a** was supposed to originate from autoprotolysis of the NH_2 protons or from protolysis with trace amounts of water in the solvent. The anion exchange of **2a** with $NaBPh_4$ led to **2b**.

Applying under milder conditions as for the preparation of **2a** starting from $WCl(NO)[P(OMe)_3]_4$[34] and edmp, we probed the possibility to obtain a substitutional intermediate still containing phosphite, thus also retaining proper solubility of a potential cationic species. Under relatively mild conditions, $WCl(NO)[P(OMe)_3]_4$ was treated with edmp at 85 °C in toluene for several days, which gave a precipitate corresponding to $\{W(NO)(edmp)_2[P(OMe)_3]\}[Cl]$ (**3a**) isolated in 88% yield (Scheme 2).

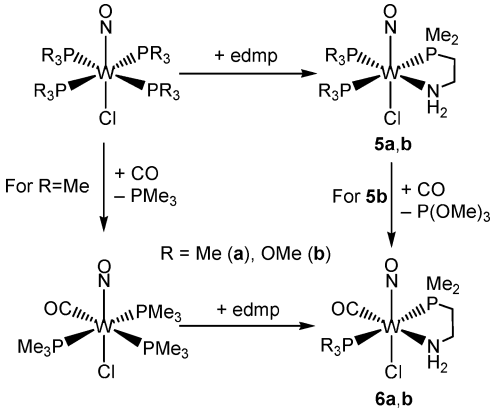
The IR spectrum of **3a** in CH_2Cl_2 revealed the presence of an NO group showing a strong absorption at 1540 cm^{-1}, apparently being strongly involved in back bonding. The $^{31}P\{^1H\}$ NMR spectrum of **3a** in $CDCl_3$ showed three groups of multiplets with tungsten satellites at 165.5, 16.0 and 13.5 ppm assigned to the $P(OMe)_3$ and the chemically inequivalent edmp ligands. The *trans* phosphorus nuclei are strongly coupled ($^2J_{P,P}$ = 128 Hz), whereas a smaller coupling to the $P(OMe)_3$ group (11 and 2 Hz) indicated their *cis* position to this ligand. The chemical shifts of the two P_{edmp} nuclei are characteristic for their binding in chelate rings. In the ^1H–^{15}N NMR correlation spectra of **3a**, one can find correlation between a multiplet resonance at 5.59 ppm in the ^1H NMR spectrum and a doublet resonance at –372.8 ppm in the ^{15}N NMR spectrum. Both signals are assigned to the NH_2 fragment located *trans* to the



Scheme 2.

$P(OMe)_3$ group. The doublet splitting of the ^{15}N NMR signal is anticipated to originate from coupling with the *trans* P atom. Another correlation was found between the NH_2 group *trans* to the NO group showing in the ^1H NMR spectrum a multiplet at 4.98 ppm and in the ^{15}N NMR spectrum a multiplet at –360.2 ppm. In the ^1H NMR and ^{13}C NMR spectra of **3a** further assignments were achieved by the ^{31}P–^1H correlation, ^1H COSY and long-range ^{13}C–^1H correlation spectra. Data gathered from elemental analysis, MS and NMR spectroscopy were also in accord with the given structure.

Considering the low solubility of compound **3a** and to allow for further reactions, the Cl^- anion was exchanged with BPh_4^- in thf at room temperature, leading to $\{W(NO)[P(OMe)_3](edmp)_2\}[BPh_4]$ (**3b**). Starting from this compound the replacement of $P(OMe)_3$ by CO in **3b** was attempted at 80 °C in a Young-tap Schlenk tube applying 2 bar of CO in thf (Scheme 3). The reaction was completed within 1 d accompanied by a color change from yellow to orange. *cis*-$[W(NO)(CO)(edmp)_2][BPh_4]$ (**4b**) was obtained in 98% yield by extraction with CH_2Cl_2.



Scheme 3.

The IR spectrum of **4b** confirmed the presence of CO and NO ligands, showing bands at 1893 and 1595 cm^{-1}. It is noteworthy that the ^1H NMR spectra of **4b** are very solvent dependent, in particular the NH_2 resonances, supposedly because the chelated edmp can open up establishing $\eta^2 \leftrightarrow \eta^1$ equilibria preferably in more donating solvents, where solvent molecules might support the process through intermediate coordination to the tungsten center. The formation of such coordination equilibria is supported further by the observation that **4b** shows completely different ^{31}P NMR spectra in CD_2Cl_2 and in $[D_8]$thf. In $[D_8]$thf the edmp ligands appear chemically more distinguished showing two groups of asymmetric doublets with satellites at 14.2, 12.8 ppm with a strong $^2J_{P,P}$ coupling constant of 134 Hz. It is anticipated that the NH_2 group *trans* to the NO group is kinetically more labile and opens more readily, as NO exerts the much stronger *trans* effect in comparison with the CO ligand. Practically no chemical shift difference was detectable for the two ^{31}P signals in CD_2Cl_2, which appear as singlets at 12.6 and 12.5 ppm possessing no $^2J_{P,P}$ coupling within the resolution of the NMR instrument. This observation is interpreted in terms of absence or almost absence of a $\eta^2 \leftrightarrow \eta^1$ equilibrium in CH_2Cl_2 making the edmp ligands chemically more similar.

Noteworthy is still a triplet in the ^{13}C NMR spectrum of **4b** appearing in CD_2Cl_2 at 237.9 ppm with $^2J_{C,P}$ = 3 Hz, which was attributed to the unique CO group. The full assignment of the spectra of **4b** was based on various NMR techniques, such as ^{31}P-decoupled NMR spectroscopy, ^{13}C–^1H correlation spectra, long-range ^{13}C–^1H correlation spectra, ^1H COSY and ^1H TOCSY.

Hydride complexes can advantageously be obtained from halo carbonyl complexes and hydride reagents, such as $LiHBEt_3$, $NaBH_4$ and Et_4NBH_4.[35–39] Whereas the direct halide/hydride exchange is kinetically often difficult to establish, CO-containing complexes are more easily attacked by hydride reagents to form short-lived formyl intermediates, which are expected to quickly decay into hydride complexes with liberation of CO and a halide anion. The reaction of **4b** was carried out with $NaHBEt_3$ (2 equiv.) in $[D_8]$thf first at –30 °C for 4 d, then another 6 d at –10 °C. No intermediates were detected, even not the targeted monohydride $[WH(NO)(edmp)_2]$. The only product we spectroscopically identified was the sodium-coordinated anionic dihydride complex **4c** with μ-edmp ligands bridging the tungsten center and the coordinated sodium cation (Scheme 2). Anionic hydride compounds frequently appear ion paired and the sodium cation is often the counterion enabling coordination to hydride ligands.[35a] In the ^1H NMR spectrum two doublet of triplet signals were observed at 1.07 ($^2J_{H,P}$ = 23.2 Hz, $^2J_{H,H}$ = 8.2 Hz, WH) and –2.88 ppm ($^2J_{H,P}$ = 24.4 Hz, $^2J_{H,H}$ = 8.3 Hz, WH) for two chemically distinct hydrides. In the $^{31}P\{^1H\}$ NMR spectrum a singlet appeared with satellites at –18.8 ppm for the phosphorus nuclei ($^1J_{P,W}$ = 285 Hz, edmp). There is coupling of the phosphorus nuclei to the hydrides, the P–CH_3, PCH_2 and the NH_2 protons stressing the structural vicinity of these atoms. The ^{13}C NMR spectrum showed a triplet signal at 249.3 ppm ($^2J_{C,P}$ = 6 Hz, CO), which indicated the presence of a carbonyl group and moreover scalar coupling of the $^{13}C_{CO}$ atom with the two hydrides was noticed. This structural assignment was further supported by IR, ^1H COSY, 1D ^1H TOCSY and the long-range ^{13}C–^1H correlation spectra. In the ^1H NMR spectrum scalar coupling was found between the chemically inequivalent NH protons at 3.92 and 5.40 ppm, between the NH_2 and the NCH_2 protons. Dipolar coupling could be traced between one of the hydrides (–2.88 ppm) and one of the NH protons (5.22 ppm), between the hydrides, and one of the hydrides (–2.88 ppm) and the Me_P groups. Particularly interesting is the fact that there are two distinct N*H* and NC*H* resonances, which would cope with the presence of a η^2-edmp or a μ-edmp, but principally contradicts the presence of a η^1-edmp, even though the chemical shift of the ^{31}P signal points to an open edmp structure. Therefore we assume sodium coordination to the anionic dihydride complex to form an ion pair: the two edmp ligands and the two hydrides pick the sodium cation in a chelating fashion. The sodium ion might fill its coordination sphere with a thf ligand. Sodium coordination is ex-

pected to be dynamic on the NMR timescale, but still the coordinated form should be thermodynamically more stable and respective sodium fixed conformations should determine the NMR picture. In the bridging form the edmp ligand has diastereotopic protons which cannot be interconverted even in the open form.

These spectra also provided evidence that both signals of the NH_2 protons at 3.92 and 5.40 ppm have no correlation with the ^{13}C signal at 15.7 ppm belonging to the $C_{methylene}$ atoms of the BEt_3 groups. This proves that the BEt_3 group is not NH_2 attached. Rather it is bonded to thf, as correlation was found between the thf protons and the ^{13}C signal at 15.7 ppm. Complex **4c** turned out to be too unstable to be isolated and other hydride products could structurally not be assigned, mainly because of too low concentrations of these components.

Preparation of $WCl(NO)(CO)_n(L)_{2-n}$(edmp) [L = $P(OMe)_3$ or PMe_3; n = 0, 1]

The ligand sphere can have pronounced influences on the hydridic character of a hydride ligand. For instance, in a CO, $P(OMe)_3$, PMe_3 ligand series it is expected to follow the order of CO < $P(OMe)_3$ < PMe_3. In contrast to this the acidity of hydride complexes with edmp containing the NH functions would be expected to decrease. Therefore a "tuning" series of complexes bearing only one edmp ligand was probed (Scheme 3).

The edmp monosubstituted compounds **5a** and **5b** can be prepared by the reactions of edmp with $WCl(NO)(PMe_3)_4$[40] and $WCl(NO)\{[P(OMe)_3]\}_4$,[34] respectively. In a subsequent reaction in thf, **5b** was transformed into **6b** by applying 2.5 bar of CO at 80 °C. Related species **6a** however could not be obtained by the reaction of **5a** with CO. It was eventually prepared starting from $WCl(NO)(PMe_3)_4$ and CO, generating first $WCl(NO)(CO)(PMe_3)_3$,[41] which was then converted into **6a** with edmp. It is noteworthy that both elevated temperatures and excessively large amounts of the edmp ligand lead to the formation of $[W(CO)(NO)(edmp)_2][Cl]$, a salt analogous to **4b**.

Complexes **5a**,**b** and **6a**,**b** were fully characterized by IR and NMR spectroscopy and elemental analysis. In addition, the structures of **5b** and **6a**,**b** were established by single-crystal X-ray diffraction. For all these derivatives the presence of NO groups was demonstrated by the appearance of strong ν(NO) bands in the IR spectra (CH_2Cl_2) appearing at 1494, 1536, 1591 and 1578 cm^{-1}, respectively. Furthermore, the IR spectra of **6a**,**b** in CH_2Cl_2 revealed strong bands at 1910 and 1891 cm^{-1}, confirming the presences of CO groups.

The ^{31}P NMR spectrum of **5a** in CD_3CN revealed one doublet resonance with tungsten satellites at 15.3 ppm ($^2J_{P,P}$ = 178 Hz), one singlet-like resonance with tungsten satellites at –12.1 ppm and one doublet of doublet resonance with tungsten satellites at –18.0 ppm ($^2J_{P,P_{trans}}$ = 179 Hz, $^2J_{P,P_{cis}}$ = 3 Hz). The former one was assigned to the edmp ligand, the latter two signals to the two PMe_3 ligands. On the basis of the ^1H COSY spectrum, it was possible to attribute the resonances at 4.27 and 2.83 ppm to the chemically inequivalent NH_2 protons and those at 3.09 and 2.55 ppm to the NCH_2 protons of the edmp ligand. The PCH_2 signals and the methyl resonance of the Me_{PMe_3} and Me_{edmp} groups overlapped in the range of 1.30–1.60 ppm.

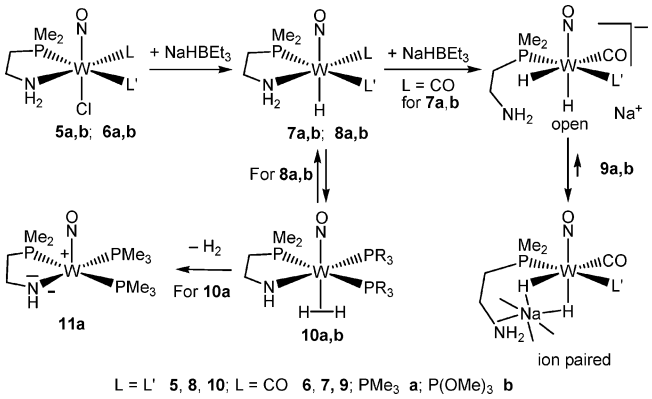
The ^{31}P NMR spectrum of **5b** revealed in CD_3CN two characteristic doublet of doublet resonances at 14.5 and 163.1 ppm, which were assigned to the edmp ligand ($J_{P,W}$ = 294 Hz) and the $P(OMe)_3$ ligand ($J_{P,W}$ = 505 Hz)[42,43] *trans* to the edmp PMe_2 moiety, respectively. Furthermore, a triplet at 179.5 ppm was assigned to the $P(OMe)_3$ ligand ($J_{P,W}$ = 606 Hz)[42,43] *cis* to the former two. Similar to **5a** the ^1H NMR spectrum of **5b** showed two multiplets at 4.36 and 2.89 ppm for the NH_2 group and two multiplets at 1.59 and 2.89 ppm for the NCH_2 unit. In addition two doublets were seen at 3.62 and 3.54 ppm for the $P(OMe)_3$ ligands and one multiplet at 2.59 ppm for the PCH_2 moiety and furthermore a multiplet at ca. 1.5 ppm for the PMe_2 residue. In the ^{13}C NMR spectrum the NCH_2 moiety appeared at 45.6 ppm as a doublet of doublet of doublet resonance due to the coupling with three chemically different phosphorus nuclei. For the PCH_2 moiety a doublet of doublet signal was found at 31.2 ppm, possessing coupling with only two phosphorus nuclei; the coupling with the other phosphorus nucleus is apparently too small to be resolved.

The structures of **6a** and **6b**, in particular the *trans* phosphane arrangement, followed from the $^{31}P\{^1H\}$ NMR spectra revealing two doublet resonances at 14.1 and –17.4 ppm ($^2J_{P,P}$ = 174 Hz) for **6a** and at 157.0 ppm ($^2J_{P,P}$ = 261 Hz, $^1J_{P,W}$ = 485 Hz) and 11.6 ppm ($^2J_{P,P}$ = 260 Hz, $^1J_{P,W}$ = 295 Hz) for **6b**. A ^1H COSY spectrum of **6a** was recorded in CD_3CN to unravel the complicated resonance pattern of the 1D spectrum. One of the NH_2 signals at 2.70 ppm was found to overlap with the resonance of one of the NCH_2 groups, and in the range of 1.40–1.60 ppm the PCH_2 resonance overlapped with the methyl signals of the edmp and PMe_3 ligands. The resonances at 4.16, 3.30 and 1.71 ppm were assigned to the other NH and NCH and the PCH_2 protons, respectively, thus establishing the η^2-binding mode for the edmp moiety. Complex **6b** possesses a geometry related to **6a** with a η^2-edmp ligand, as supported by the ^1H NMR spectrum of **6b**, which revealed besides the resonances for the η^2-edmp ligand [4.16 (NH), 3.24 (NCH), 2.74 (NH and NCH) and 1.66 ppm (PCH_2)] one doublet resonance at 3.68 ppm with a $^2J_{H,P}$ coupling constant of 11 Hz attributed to the $P(OMe)_3$ moiety. In the ^{13}C NMR spectra of **6a** and **6b** the size of the coupling of the ^{13}CO resonance (t, $^2J_{C,P}$ = 3 and 5 Hz for **6a** and **6b**, respectively) suggested that this ligand is located *cis* to the two *trans* phosphorus atoms.

Solution NMR Spectroscopic Studies and Attempted Isolation of $WH(NO)(CO)_n(L_{2-n})$(edmp) Complexes [L = $P(OMe)_3$ or PMe_3; n = 0, 1]

The targeted hydride $WH(NO)(CO)_n(L_{2-n})$(edmp) complexes were expected to possess hydridic character in the

W–H bond. If, like for **4c**, η^1-edmp ligands were to be formed, these complexes would be expected to be capable of generating intra- or intermolecular WH···HN dihydrogen bonding contacts. Attempts to prepare complexes **7a**,**b** and **8a**,**b** were carried out by utilizing in situ NMR pursuit of the reactions of chlorido complexes **5a**,**b** and **6a**,**b** and $NaHBEt_3$ at –30 °C. In the cases of CO-substituted complexes, subsequent reaction steps led to anionic dihydride species **9a**,**b** as presented in Scheme 4.



Scheme 4.

The preparation of hydride **7a** was attempted through the reaction of $WCl(CO)(NO)(PMe_3)(edmp)$ (**6a**) by applying $NaHBEt_3$ (2 equiv.) in [D8]thf at –30 °C. The reaction monitored by ^{31}P NMR spectroscopy was complete after 2 d. Two doublets appeared at 10.8 (edmp) and –18.9 ppm (PMe_3) ($^2J_{P,P}$ = 117 Hz). The ^1H–^{31}P correlation spectrum proved ^{31}P correlation with the proton resonance at 3.84 ppm (t, $^2J_{H,P}$ = 24.8 Hz, $J_{H,W}$ = 73 Hz), suggesting it to be the hydride resonance. The position at low field is typical for a *trans* NO arrangement. When a [D8]thf solution of **7a** was kept at –30 °C for 8 d no apparent change was observed. All attempts to isolate **7a** at low temperature failed. When the reaction solution was warmed to 4 °C or to room temperature it began to react further with $NaHBEt_3$ to form anionic dihydride compound **9a** prevailing in the reaction mixture at this temperature (Scheme 4). The NH_2 arm of the edmp ligand was thus replaced by another hydride substituent generating a η^1 edmp open form of **9a**. In the ^{31}P NMR spectrum at –40 °C two resonances appeared at –19.3 and –22.8 ppm (d, $^2J_{P,P}$ = 89 Hz), which were attributed to the edmp and the PMe_3 ligands. The P_{edmp} resonance appeared at a chemical shift comparable to that of **4c** (and of **9b**), but is considerably shifted upfield by about 30 ppm with respect to **7a** suggesting an open edmp chelate ring. Complex **9a** was further characterized in solution by ^1H NMR, ^1H COSY and ^{31}P–^1H correlation spectra. In contrast to **9b** both hydride signals of **9a** showed strong correlation with the ^{31}P NMR signals indicating their simultaneous presence in the coordination sphere. At –40 °C the two hydride ligands $H(CO_{trans})$ and $H(NO_{trans})$ were assigned to two ^1H NMR multiplets at –3.03 and 1.05 ppm, respectively, and broad multiplet resonances at 1.98/2.04 and 2.72/2.82 ppm were assigned to the PCH_2/NCH_2 groups. Despite the η^1 binding of the edmp ligand, the PCH_2/NCH_2 moieties show, like in **4c**, separate apparently diastereotopic methylene ^1H NMR signals as expected for complexes with chelating η^2 edmp ligands. The broadness of these signals might point to slow dynamics between several conformers caused by fixation of the edmp geometry in the ion-paired, sodium-containing form with coordination to the NH_2 and the two hydride ligands[35] (Scheme 4). Furthermore, the NH_2 protons were attributed two triplets at 5.57 and 4.42 ppm ($^3J_{H,H}$ = 12.5 Hz), which also supports the idea of their fixation through coordination. In this context, it is maybe also noteworthy that the appearance of two relatively sharp signals for the NH_2 protons contradicts attachment to a BEt_3 group. Rather, we have to assume attachment of BEt_3 to a [D8]thf solvent molecule as confirmed by the appearance of two [D8]thf triplets at 4.42 and 5.57 ppm (cf. **4c**).

Complex **7a** was too unstable for isolation and we therefore anticipated that further ligand tuning, retaining the edmp ligand but replacing the PMe_3 group with the more π-accepting $P(OMe)_3$ ligand could lend these systems more stability. We thus attempted the preparation of $WH(CO)(NO)(edmp)[P(OMe)_3]$ (**7b**) from chloride **6b** by addition of $NaHBEt_3$ (2 equiv.) to a [D8]thf solution of $WCl(CO)(NO)(edmp)[P(OMe)_3]$ (**6b**) at –30 °C, which initiated a very slow conversion to **7b** (Scheme 4). In the ^{31}P NMR spectrum two doublet resonances were detected possessing satellites at 176.6 ppm [$^2J_{P,P}$ = 185 Hz, $^1J_{P,W}$ = 480 Hz, $P(OMe)_3$] and 9.0 ppm ($^2J_{P,P}$ = 185 Hz, $^1J_{P,W}$ = 290 Hz, edmp). However two intermediate doublet signals with satellites were detected: one at 173.1 ppm [$^2J_{P,P}$ = 179 Hz, $^1J_{P,W}$ = 490 Hz, $P(OMe)_3$] and the other one at 11.3 ppm ($^2J_{P,P}$ = 179 Hz, $^1J_{P,W}$ = 297 Hz, edmp). These signals could belong to a formyl species formed prior to the appearance of hydride **7b**. In comparison with **6a**, the CO group of **6b** has to be assigned a more electrophilic character, resulting in an increased lifetime of the corresponding formyl species, whereas no such intermediate was observable in the reaction of **6a** with $NaHBEt_3$.

After 3 d at –30 °C subsequent reaction was noticed in the presence of an excess amount of $NaBHEt_3$, transforming **7b** further into anionic dihydride compound **9b**, revealing in the ^{31}P NMR spectrum another pair of doublets with tungsten satellites appearing at 182.1 ppm [$^2J_{P,P}$ = 158 Hz, $^1J_{P,W}$ = 461 Hz, $P(OMe)_3$] and –22.3 ppm ($^2J_{P,P}$ = 158 Hz, $^1J_{P,W}$ = 278 Hz, edmp). These signals remained even after the temperature was raised to –10 °C for 9 d in order to drive the reaction to completion. The ^1H NMR spectrum then revealed a doublet of triplet resonances at –0.48 ppm ($^2J_{H,P}$ = 24.3 Hz, $^2J_{H,H}$ = 10 Hz, WH) and a doublet of doublet of doublet signal at –4.05 ($^2J_{H,P}$ = 24 Hz, $^2J_{H,P}$ = 33.9 Hz, $^2J_{H,H}$ = 9.6 Hz, WH) for the two chemically different hydride ligands, indicating a pseudo-octahedral structure as proposed in Scheme 4. Complex **9b** thus possesses unique CO, NO and $P(OMe)_3$ π-acceptor ligands, the *trans* σ donors: one η^1-edmp ligand and two hydrides (for sodium coordination), makes up for the valence saturated 18e⁻ complex. The tungsten center has no vacancy

left to accommodate the amino group, which seems to be temporarily fixed to the sodium ion, giving rise to two NH triplets at 4.97 and 4.12 ppm ($^3J_{H,H}$ = 11.9 Hz), two NCH multiplets at 2.84 and 2.92 ppm and a PCH_2 multiplet at 2.06 ppm. Like for **9a**, we assume also for **9b** a dynamic process between the open and the ion-paired form operating fast on the NMR timescale, however, with preference for the ion-paired state. In Scheme 4 a sodium ion with only three ligands is shown, which means that this coordination center would lack ligands. It is suggested that the "missing" ligand positions are either taken by the solvent molecules or that a higher adduct of the formula $\{[W(CO)(NO)(H)_2(\eta^1\text{-edmp})P(OMe)_3]_2Na\}^-$ is generated.

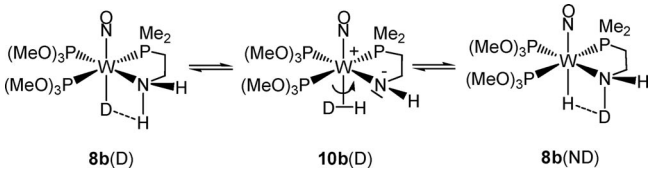
When the reaction solution was warmed to 4 °C for a few hours or kept at –10 °C for a longer period of time, **9b** decomposed into some other yet unidentified products. In order to further support the structure of **9b**, **6b** was then treated again with $NaHBEt_3$ at –30 °C for 11 d and the reaction was pursued with a 500 MHz NMR instrument using more sophisticated NMR techniques including 1D ^1H NOE, ^{31}P-decoupled ^1H and ^1H–^{31}P COSY spectra. The ^1H NOE spectrum revealed with irradiation at the Me_{edmp} groups enhancement of the H (NO_{trans}) triplet signal at 3.20 ppm ($^2J_{H,P}$ = 27.8 Hz) revealed the presence of monohydride **7b**, which became a singlet upon $\{^{31}P\}$ decoupling and showed correlation in the ^1H–^{31}P COSY spectrum with the ^{31}P NMR resonances at 176.2 ppm of the $P(OMe)_3$ moiety and at 10.2 ppm of the edmp ligand. In addition it could be shown that the hydride signals of **9b** appearing as doublet of triplet resonances at –0.60 ppm ($^2J_{P,H}$ = 23.9 Hz, $^2J_{H,H}$ = 9.6 Hz) and the doublet of doublet of doublet resonance at –4.24 ppm ($^2J_{P,H}$ = 27.9 Hz, $^2J_{P,H}$ = 23.6 Hz, $^2J_{H,H}$ = 9.6 Hz) in the ^1H NMR spectrum became doublets when they were $\{^{31}P\}$ decoupled. The $^2J_{P,H}$ coupling constants of the chemically distinguished hydride ligands fall into the range of *cis* couplings for both hydride ligands and are therefore expected to be *cis* to the phosphorus ligands. The ^1H–^{31}P COSY spectrum gave further evidence to the structure of **9b**, revealing correlation of these hydride signals with the ^{31}P NMR resonances at –20.8 ppm (edmp), suggesting that all these ligands belong to the same molecule and are coordinated to tungsten. These studies on hydride complexes **7a**,**b** revealed that these less-electron-rich carbonyl derivatives can be further stabilized by addition of another hydride ligand to form anionic dihydride species **9a**,**b** through NH_2 lability of the edmp chelate, causing ring opening to a η^1-edmp moiety with a pending amino ethylene group.

Access to the trisphosphorus donor substituted complexes $W(H)(edmp)(NO)(PMe_3)_2$ (**8a**) and $W(H)(edmp)(NO)[P(OMe)_3]_2$ (**8b**) was then attempted by reaction of chlorides **5a** and **5b** with $NaHBEt_3$. The reaction of **5a** with $NaHBEt_3$ in $[D_8]$thf carried out at –30 °C and was pursued by ^1H NMR spectroscopy; the reaction proceeded sluggishly with residual starting material present at all stages of the reaction. The reaction course was complicated, showing three resonances for distinct hydride species: two resonances at –1.14 and –0.40 ppm belonged to unassigned hydride complexes. Prevailing hydride **8a** was identified by a triplet resonance at 4.29 ppm ($^2J_{P,H}$ = 35.5 Hz and $J_{W,H}$ = 61.9 Hz), which seems to be in equilibrium with the "tautomeric" dihydrogen complex **10a** indicated by the appearance of a broad resonance at 1.21 ppm. The reaction mixture of **8a** with $NaHBEt_3$ quickly transforms into the pentacoordinate complex **11a** with H_2 evolution [^1H NMR ($[D_8]$thf, 293 K): δ = 4.54 ppm] presumably via dihydrogen complex **10a** as the crucial intermediate as depicted in Scheme 4. As a result of the complexity of the reaction mixture, the assignment of the ^1H NMR signals, like those, for instance, of the edmp NH_2 and CH_2 protons, seemed difficult and could not be made in confidence. However, the ^{31}P NMR spectrum of **11a** provided clear evidence for three chemically distinct phosphorus ligands [δ = 13.7 (dd, PMe_3), –21.8 (dd, PMe_3), 9.3 ppm (dd, edmp)], which were anticipated to be arranged in a square-pyramidal coordination sphere.

The related chemistry of substituted complex **8b** seemed grossly similar to that of **8a**. It could be studied in greater detail, as the **8b** and **10b** species appearing in solution were more stable. Monitored by NMR spectroscopy, **8b** was obtained through the reaction of $WCl(edmp)(NO)[P(OMe)_3]_2$ (**5b**) with $NaHBEt_3$ in $[D_8]$thf. A very slow reaction was initiated at –30 °C; therefore, the temperature was raised to 4 °C, and the reaction to **8b** went to completion within 6 h. Prolonged reaction time produced then complex **10b** in increasing amounts, which indeed revealed to be fairly stable in solution even at room temperature for a period of 2 d. After a longer period of time at room temperature and attempts to isolate **8b** or **10b**, decomposition of the products was noticed. The relatively stable nature of the neutral monohydride complex was emphasized further by the fact that subsequent reactions with $NaHBEt_3$ related to the cases of **7a**,**b** did not occur, leading to the related anionic dihydride species. Complexes **8b** and **10b** turned out to be the most stable hydride or hydrogen-containing complexes within the given series. Complexes **8b** or **10b** are in slow equilibrium, which at the end of the reaction resides almost totally on the side of dihydrogen complex **10b**. At 273 K, both complexes are characterized by one ^{31}P NMR spectrum. Three doublet of doublet resonances appear at 182 ($^2J_{P,P}$ = 179 Hz, $^2J_{P,P}$ = 7 Hz), 178.1 ($^2J_{P,P}$ = 17 Hz, $^2J_{P,P}$ = 7 Hz) and 9.3 ppm ($^2J_{P,P}$ = 179 Hz, $^2J_{P,P}$ = 17 Hz) typical for the meridionally arranged P-donor ligands with two chemically different *cis* phosphites and the P atom of the η^2 edmp moiety. Their binding to the tungsten center was further substantiated by the appearance of appropriate tungsten satellites with $J_{P,W}$ coupling constants of 499 [$P(OMe)_3$], 450 [$P(OMe)_3$] and 278 Hz (PMe_2). In the ^1H NMR spectrum of the reaction solution at 273 K only the resonances for the hydride and the H_2 ligand could be separated. A quartet resonance at 2.42 ppm ($^2J_{H,P}$ = 28 Hz) was assigned to the hydride ligand of **8b**. It collapsed to a singlet upon ^{31}P decoupling, which demonstrated that this signal has coupling with all three phosphorus nuclei with practically the same coupling constant. The ^{31}P–^1H COSY spectrum confirmed that this resonance originated from hydride

8b, and on the basis of the ^{31}P NMR spectra **8b** could be assigned a pseudo-octahedral *trans* NO/H structure as given in Scheme 4. In addition to the hydride resonance of **8b** a peculiar broadened resonance was found in the high-field range of the ^{1}H NMR spectrum at –2.35 ppm, which was eventually attributed to H_2 complex **10b**. In order to analyze this resonance further ^{31}P–^{1}H COSY, long-range ^{13}C–^{1}H COSY and ^{1}H COSY spectra were recorded, but apparently no coupling partner could be identified. Then 1D NOE spectra were additionally recorded at 293 K with irradiation of one methyl group of the edmp ligand, but expectedly for such ligands with a large T_1 relaxation time, no NOE enhancement was detected for this signal at –2.35 ppm. Thus, this resonance was attributed to the unique H_2 ligand of **10b**.

The hydride and NH_2 resonances of **8b** were found to be in exchange and it was presumed that this would occur through a prototropic equilibrium involving **10b**. Deuterium labeling and ^{2}H spectroscopy of the reaction of $WCl(NO)(edmp)[P(OMe)_3]_2$ (**5b**) with $LiDBEt_3$ in thf at –30 °C revealed after 2 h resonances related to the ^{1}H NMR spectrum with one W–D quartet at 2.57 ppm and one multiplet at –2.36 ppm for the HD ligand as the main deuterium signals, which were anticipated to result from a WD/NH scrambling process initiated by intramolecular W–D···H–N dihydrogen contact and formation of a mixture of isotopomers of **10b**(D) and **8b**(ND) as sketched in Scheme 5.



Scheme 5.

The exchange process of non-deuterated complexes **8b** and **10b** related to Scheme 5 can partially be pursued in the ^{1}H NMR spectra. The exchanging resonances of the hydride of **8b** and all the NH protons of **8b/10b** are hidden under the very intense signals of the CH protons. The low-field signal of the H_2 ligand of **10b** appeared however well isolated with increase in broadening from 193 up to 233 K (Figure 2). At 253 K this signal underwent coalescence in the exchange with the hydride and the NH proton of **8b**. In the high-temperature and fast-exchange regime, the 273 and 293 K spectra showed the collapsed signal of the averaging NH, H_W and H_2 protons, confirming the conclusion from the deuterium labeling experiment. Dihydrogen complexes are often susceptible to H_2 exchange. Thus, for **10b** exchange with D_2 (1 bar) was anticipated. However, no such reaction could be traced for **8b** in the presence of D_2 at various temperatures followed by ^{2}H NMR spectroscopy. The prototropic reactions of **8a**,**b** seemed to be supported by the general observation of acidified α-amine hydrogens occurring upon coordination. The conjugate bases resulting from deprotonation are amide ligands, which are strongly π-donating ligands capable of labilizing the H_2 ligand through the *cis* labilization effect. In addition to this the amide ligand should be labile by itself through repulsion of its π-donating electron pair with the metal d electrons. This pathway, if thermodynamically feasible, may be the cause of the instability of protonic–hydridic bifunctional transition metal systems like **8a**,**b**. This seems to be particularly true for **10a**, which deliberately releases H_2, whereas for **10b** the π acceptor $P(OMe)_3$ is prone to take over charge from the *trans* π donor, lending the system higher stability. Transient stability for protonic–hydridic bifunctional molecules is however crucial to their H transfer function in hydrogenation and transfer hydrogenation catalyses.[44]

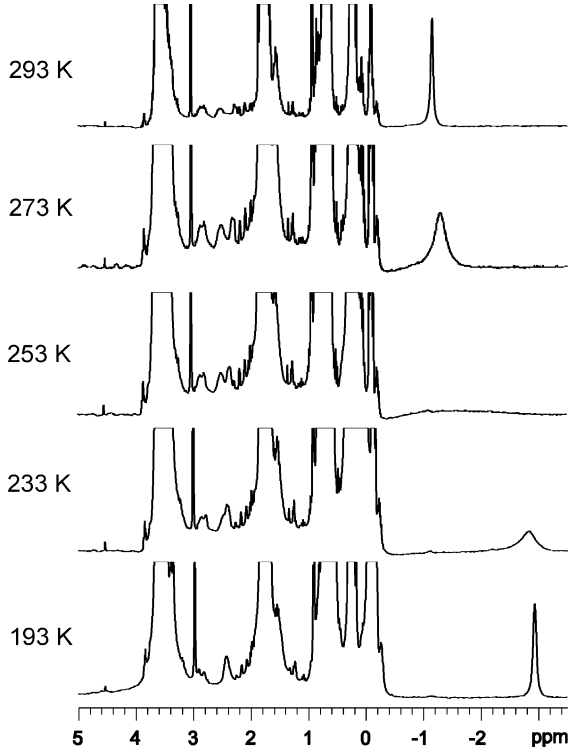


Figure 2. ^{1}H NMR spectra in $[D_8]$thf for the **8b/10b** mixture at various temperatures.

X-ray Crystal Structures of 1a, 2b, 3a, 4b, 5b, 6a and 6b

Crystals of **1a** suitable for X-ray diffraction study were obtained by cooling a CH_2Cl_2 solution to –30 °C for several days. The structure model of **1a** is shown in Figure 3. Selected bond lengths and angles are listed in Table 1. The tungsten center possesses a pentagonal bipyramidal geometry with two chelating edmp ligands in the pentagonal plane and the nitrogen atoms in neighboring positions. The two chloride atoms are equatorial and axial and the nitrosyl ligand is axial. There is an almost linear Cl–W–N–O [N11–W1–Cl14 176.7(3)°, W1–N11–O11 178.5(12)°] with nitrosyl and chlorido ligands disordered. The equatorial N–M–P angles are close to the ideal valence angle 72° of the pentagonal plane [N1–W1–P1 73.64(13)° and N2–W1–P2

73.92(13)°], much smaller than those reported for pseudo-octahedron.[45–48] A third chloride exists as a counterion to the cationic complex.

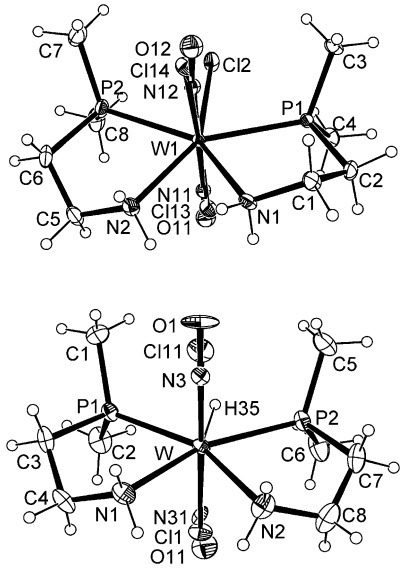


Figure 3. ORTEP plot of the cations of **1a** (top) and **2b** (bottom). Anions and solvate molecules are omitted. The displacement ellipsoids are drawn with 30% probability.

Table 1. Selected bond lengths [Å] and angles [°] of **1a** and **2b**.

1a		**2b**	
W1–N2	2.236(5)	W–N1	2.263(3)
W1–N1	2.258(5)	W–N2	2.265(3)
W1–P1	2.5255(15)	W–Cl1	2.442(3)
W1–Cl2	2.4990(15)	W–P2	2.4445(10)
W1–P2	2.5237(16)	W–P1	2.4458(10)
N11–W1–Cl14	176.7(3)	W–H35	1.7399(11)
N2–W1–Cl14	93.06(16)	N3–W–Cl1	179.1(3)
N2–W1–P2	73.92(13)	N2–W–P2	77.76(9)
Cl2–W1–P2	70.79(5)	N1–W–P1	76.50(9)
O11–N11–W1	178.5(12)	P2–W–H35	57.9(17)
N1–W1–P1	73.64(13)	P1–W–H35	68.0(17)
Cl2–W1–P1	71.16(5)	O1–N3–W	176.5(10)

Crystals of **2b** suitable for X-ray diffraction were prepared by diffusion of pentane and ether into a CH_3CN solution of **2b** over several days at –30 °C. The structure of **2b** is shown in Figure 3. It is related to that of **1a**, possessing a pentagonal bipyramidal coordination around the tungsten center with disordered *trans* disposed Cl and NO groups. Selected bond lengths and angles are listed in Table 1. The hydride ligand is located in the pentagonal plane between the two phosphorus atoms. Apparently, as a result of the smaller size of the H atom with respect to Cl, the H–W–P angles [H35–W–P1 68.0(17)° and H35–W–P2 57.9(17)°] are considerably smaller than the corresponding Cl–W–P angles in **1a**.

Crystals of **3a** suitable for X-ray diffraction were obtained by evaporation of a CH_3CN solution at ambient temperature. A structural model is shown in Figure 4. Selected bond lengths and angles are listed in Table 2. Complex **3a** reveals distorted octahedral coordination at the tungsten center with the $P(OMe)_3$ and the NO ligand in *cis* positions and the two chelating edmp ligands are arranged with *trans* P atoms so that one of the NH_2 groups is located *trans* to the NO group with a practical linearity in the N–W–N–O unit following the principal tendency for π acceptors and non-π acceptors to arrange *trans* [N1–W1–N3 179.38 Å, W1–N1–O1 177.0(4) Å]. The two *trans* phosphorus atoms of the edmp ligands are diastereotopic, causing the complex ^{31}P NMR spectrum.

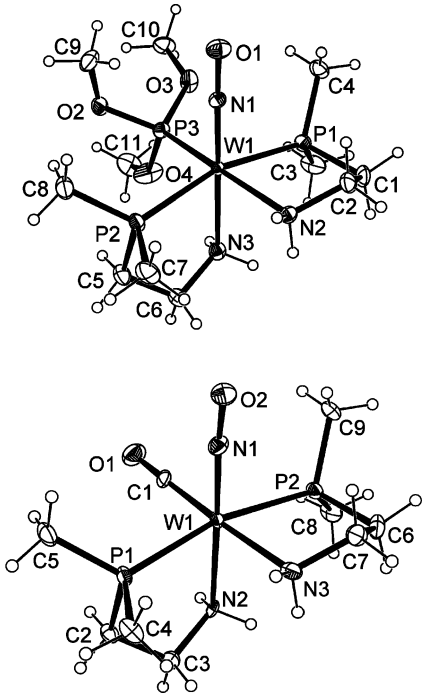


Figure 4. Structures of the cations of **3a** (top) and **4b** (bottom). The anions are omitted. The displacement ellipsoids are drawn with 30% probability.

Table 2. Selected bond lengths [Å] and angles [°] of **3a** and **4b**.

3a		**4b**	
W1–N1	1.787(5)	W1–N1	1.821(7)
W1–N2	2.272(4)	W1–C1	1.959(10)
W1–N3	2.295(5)	W1–N3	2.266(8)
W1–P3	2.3547(14)	W1–N2	2.312(7)
W1–P1	2.4391(15)	W1–P1	2.460(2)
W1–P2	2.4467(14)	W1–P2	2.467(2)
N1–W1–N3	179.38(18)	C1–W1–N3	175.1(3)
N2–W1–P3	169.32(14)	N1–W1–N2	177.8(3)
N1–W1–P1	91.68(15)	O1–C1–W1	176.7(8)
N1–W1–P2	101.52(15)	O2–N1–W1	175.8(7)
O1–N1–W1	177.0(4)		

Crystals of **4b** suitable for X-ray diffraction were obtained within 1 d by diffusion of pentane and ether into a CH_3CN solution at ambient temperature. The structure is shown in Figure 4. Selected bond lengths and angles are listed in Table 2. Substitution of $P(OMe)_3$ by CO did not induce much structural difference for compound **4b** in comparison with **3a**. Pseudo-octahedral **4b** possesses a related ligand arrangement around the tungsten center with *trans*

phosphorus atoms and a practically linear ON–W–N arrangement [O2–N1–W1 175.8(7)°, N1–W1–N2 177.8(3)°].

Crystals suitable for X-ray diffraction were obtained for **5b**, **6a** and **6b** by cooling an ether solution to –30 °C (for **5b**), by diffusion of hexane into a thf solution at ambient temperature over 4 d (for **6a**) and by slow evaporation of the thf solution at room temperature (for **6b**). Their structures are shown in Figures 5 and 6. Selected bond lengths and angles are listed in Table 3.

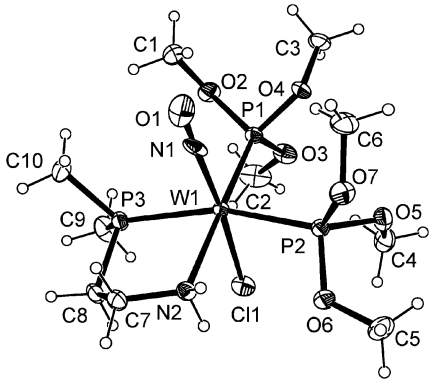


Figure 5. ORTEP plot of the structure of **5b**. The displacement ellipsoids are drawn with 30% probability.

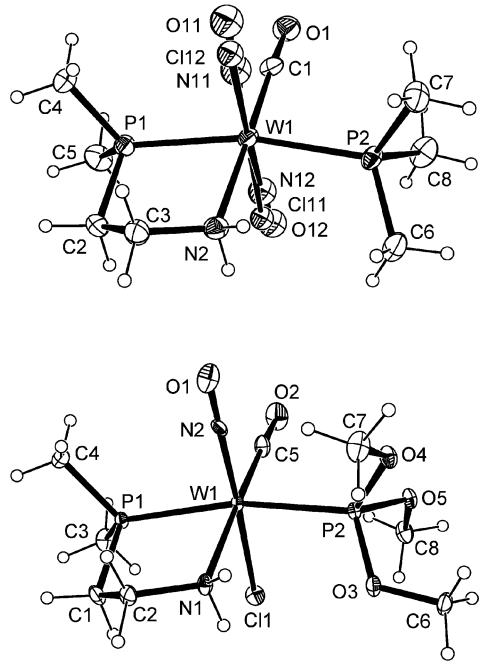


Figure 6. ORTEP plots of the structure of **6a** (top) and **6b** (bottom). The displacement ellipsoids are drawn with 30% probability.

The X-ray crystal structures of **5b**, **6a** and **6b** reveal that the tungsten centers of these complexes have a distorted octahedral coordination geometry with almost linear *trans* nitrosyl and chlorido ligands, which are disordered in the structure of **6a**.

In the structure of **5b**, the P2–W1–P3 angle [163.08(4)°] is considerably narrowed, presumably as a consequence of angular constraints imposed by the edmp chelate with a relatively narrow bite angle of around 78° in octahedral environment and the general tendency to avoid "genuine" *trans* positions of different kinds of strong donors, whereas the P1–W1–N2 angle [176.20(10)°] of a strong and a weaker donor is kept almost linear. The W1–P1 distance [2.3742(11) Å] is shorter than the W1–P2 distance [2.4204(13) Å], suggesting a weaker binding and a *trans* influence of the NH_2 compared with the PMe_2 unit.

Table 3. Selected bond lengths [Å] and angles [°] of **5b**, **6a** and **6b**.

5b			
W1–P1	2.3742(11)	W1–P3	2.4725(13)
W1–P2	2.4204(13)	W1–Cl1	2.4881(13)
N2–W1–P2	85.87(11)	P2–W1–P3	163.08(4)
P1–W1–P2	95.39(4)	N1–W1–Cl1	174.99(13)
N2–W1–P3	78.16(11)	O1–N1–W1	175.5(4)
P1–W1–P3	100.20(4)	N2–W1–P1	176.20(10)
6a			
W1–N2	2.282(5)	W1–P2	2.4729(17)
W1–Cl12	2.393(5)	W1–P1	2.4728(17)
C1–W1–N2	178.9(2)	C1–W1–P1	101.1(2)
C1–W1–P2	92.2(2)	N2–W1–P1	77.79(15)
N2–W1–P2	88.83(15)	P2–W1–P1	166.03(6)
6b			
W1–N2	1.846(6)	W1–P2	2.4339(15)
W1–N1	2.272(5)	W1–P1	2.4848(15)
P2–W1–P1	167.31(5)	C5–W1–P2	90.81(19)
C5–W1–N1	173.8(3)	N1–W1–P2	90.51(13)
N1–W1–P1	78.14(13)	O1–N2–W1	178.4(5)
C5–W1–P1	99.87(19)	O2–C5–W1	178.6(7)

In both complexes **6a** and **6b** the CO ligands are located *cis* to two phosphorus atoms and *trans* to the NH_2 moieties of the edmp ligand. Similar to **5b** their corresponding P1–W1–P2 angles [166.03(6)° for **6a** and 167.31(5)° for **6b**] deviate significantly from linearity for reasons given in the discussion of **5b**. No apparent difference in the W1–P1 and W1–P2 bond lengths was found. Both bond lengths in **6a** and **6b** are however a little longer than those of compound **4b**.

Conclusions

Synthetic access to nitrosyl tungsten chloride/hydride complexes bearing the P,N-ligating edmp moiety was studied. The edmp disubstituted species $W(Cl,H)(NO)(edmp)_2$ could not be obtained. It was proposed that $WCl(NO)(edmp)_2$ – very electron rich at the tungsten center, but protic at the amine function – undergoes autoprotolysis or accepts a proton from supposedly water. Access to $[WH(NO)(edmp)_2]$ was prevented by two factors: strong CO binding from the CO-containing starting materials gave preference to alternative chemical pathways. The general tendency of such systems for edmp chelate opening supported the formation of very basic (hydridic) anionic dihydrides as in the complex $[W(H)_2(CO)(NO)(\eta^1\text{-edmp})_2]^-$ (**4c**). Further tuning of the residual ligand sphere keeping one edmp ligand and replacing the other one by L^1 and L^2 furnished hydride complexes of the type

[WH(NO)(edmp)(L^1)(L^2)] (L^1, L^2 = phosphorus donor or CO; **7a**,**b** and **8a**,**b**). The specific protonic–hydridic character of the phosphorus donor trisubstituted complexes **8a**,**b** provoked formation of the tautomeric dihydrogen complexes **10a**,**b** existing in proton transfer equilibria, which play an important role in "ionic hydrogenations" and transfer hydrogenations. Subtle balance of the hydridicity of the WH bond in relation to the acidity of the NH protons gave enhanced stability in solution to the phosphite disubstituted monohydride species **8b**. Further hydride addition to the CO-containing monohydride species furnished related anionic dihydrides [WH_2(NO)(edmp)(L^1)(L^2)]Na **9a**,**b** with L^1 = PMe_3 or $P(OMe)_3$ and L^2 = CO, which were attributed relatively strong $H_{NH_2}\cdots H_W$(*trans* NO) dihydrogen bonding, suggesting an extraordinary hydridicity for the anionic dihydride.

Experimental Section

General Considerations: All reactions and manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques or a glove box. Solvents were dried by standard methods and freshly distilled before use. Reagents of commercial quality were obtained from commercial suppliers and used as received. NMR spectra were recorded with the following spectrometers: Varian Gemini-300 instrument; ^{1}H at 300.08 MHz, ^{13}C at 75.46 MHz, ^{19}F at 282.33 MHz, ^{31}P at 121.47 MHz. Bruker DRX-500 instrument; ^{1}H at 500.13 MHz, ^{13}C at 125.23 MHz, ^{31}P at 202.51 MHz. Chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ relative to $SiMe_4$, $\delta(^{31}P)$ relative to 85% H_3PO_4. IR spectra: Biorad FTS-45 instrument and FTS-3500 instruments. Raman spectra: Renishaw Labram Raman microscope. Mass Spectra: Finnigan-MAT-8400 spectrometer. FAB spectra in 3-nitrobenzyl alcohol matrix. Elemental analyses: Leco CHN(*S*)-932 instrument.

[WCl_2(NO)(edmp)$_2$][Cl] (1a): To a powdery sample of $WCl_3(NO)(CH_3CN)_2$ (2.0100 g, 5 mmol) was added a solution of edmp (1.1600 g, 11.04 mmol) in thf at ambient temperature. The resulting mixture was stirred for 12 h, filtered and washed with thf (4 × 10 mL) and ether (4 × 10 mL). The powdery product was then dried in vacuo to give yellow **1a** as an analytically pure sample. Yield: 2.6200 g (99%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1634 (NO) cm^{-1}. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 7.14 (m, 2 H, NH), 5.05 (m, 2 H, NH), 3.84 (m, 2 H, NCH), 3.40 (m, 2 H, NCH), 2.33 (m, 2 H, PCH_2), 2.25 (m, 2 H, PCH_2), 1.88 (t, $^2J_{H,P}$ = 5.1 Hz, 6 H, PCH_3), 1.77 (t, $^2J_{H,P}$ = 5.4 Hz, 6 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = 38.3 (s with satellites, $^1J_{W,P}$ = 193 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 44.5 (m, NCH_2), 29.0 (t, $^1J_{C,P}$ = 12 Hz, PCH_2), 10.0 (t, $^1J_{C,P}$ = 19 Hz, PCH_3), 9.3 (t, $^1J_{C,P}$ = 19 Hz, PCH_3) ppm. $C_8H_{24}Cl_3N_3OP_2W$ (530.44): calcd. C 18.11, H 4.56, N 7.92; found C 18.07, H 4.34, N 7.90. MS (FAB): *m*/*z* = 495 [M$^+$].

[WCl_2(NO)(edmp)$_2$][BPh_4] (1b): To a solid mixture of [WCl_2(NO)(edmp)$_2$][Cl] (0.2130 g, 0.40 mmol) and $NaBPh_4$ (0.1400 g, 0.41 mmol) was added thf (10 mL). The suspension was stirred overnight and filtered, and the solvent was removed in vacuo. Extraction with CH_2Cl_2, concentration and subsequent crystallization was followed by addition of ether and cooling to –30 °C, which afforded compound **1b**. The formation of [WCl_2(NO)(edmp)$_2$][BPh_4] was confirmed by both the formation of a white insoluble compound and the presence of phenyl resonances in the ^{1}H NMR spectrum. Yield: 0.3070 g (94%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1634 (NO) cm^{-1}. ^{1}H NMR (300.1 MHz, [D_8]thf): δ = 7.37 (m, 8 H, Ph), 6.95 (t, $^3J_{H,H}$ = 7.2 Hz, 8 H, Ph), 6.79 (t, $^3J_{H,H}$ = 7 Hz, 4 H, Ph), 4.25 (m, 2 H, NH), 3.69 (m, 2 H, NH), 3.17 (m, 2 H, NCH), 3.02 (m, 2 H, NCH), 2.04 (m, 2 H, PCH_2), 1.93 (m, 2 H, PCH_2), 1.77 (m, 6 H, PCH_3), 1.64 (m, 6 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [D_8]thf): δ = 37.9 (s with satellites, $^1J_{P,W}$ = 196 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, [D_8]thf): δ = 165.4 (m, Ph), 137.1 (m, Ph), 126.3 (m, Ph), 122.5 (m, Ph), 45.0 (m, NCH_2), 29.5 (t, $^1J_{C,P}$ = 12 Hz, PCH_2), 9.7 (t, $^1J_{C,P}$ = 20 Hz, PCH_3), 8.9 (t, $^1J_{C,P}$ = 20 Hz, PCH_3) ppm. $C_{32}H_{44}BCl_2N_3OP_2W$ (814.21): calcd. C 47.20, H 5.45, N 5.16; found C 47.15, H 5.45, N 5.17.

[W(Cl)(H)(NO)(edmp)$_2$][Cl] (2a): $WCl(NO)[P(OMe)_3]_4$ (1.3600 g, 1.82 mmol) was dissolved in toluene (30 mL) and the solution was transferred into a Young tap Schlenk tube, to which was subsequently added edmp (0.7700 g, 7.29 mmol). The resulting mixture was heated to 120 °C. During the reaction a precipitate was formed, which was separated off every 4 d. After 12 d, the reaction was nearly complete. The combined precipitates were extracted with CH_2Cl_2 and the solution cooled in the fridge to –30 °C to give yellow crystals. Yield: 0.3690 g (37%). An analytically pure sample of **2a** suitable for elemental analysis could not be obtained. IR (toluene): $\tilde{\nu}$ = 1600 (NO) cm^{-1}. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ = 7.16 (m, 2 H, NH_2), 4.08 (m, 2 H, NH_2), 3.78 (m, 2 H, NCH_2), 3.29 (t, $^2J_{H,P}$ = 73.1 Hz, 1 H, WH), 3.10 (m, 2 H, NCH_2), 2.25 (m, 2 H, PCH_2), 1.94 (m, 2 H, PCH_2), 1.85 (d, $^2J_{H,P}$ = 10.6 Hz, 6 H, PCH_3), 1.81 (d, $^2J_{H,P}$ = 10.2 Hz, 6 H, PCH_3) ppm. ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ = 33.7 (s with satellites, $^1J_{P,W}$ = 198 Hz, PMe) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ = 43.7 (m, NCH_2), 29.6 (dd, $^1J_{C,P}$ = 25 Hz, $^3J_{C,P}$ = 5 Hz, PCH_2), 14.8 (d, $^1J_{C,P}$ = 42 Hz, PCH_3), 12.6 (d, $^1J_{C,P}$ = 41.3 Hz, PCH_3) ppm. MS (EI): *m*/*z* = 459 [M$^+$ – H], 421 [M$^+$ – 2Cl – 4H], 352 [M$^+$ – edmp – 3H], 325 [M$^+$ – edmp – NO], 310 [M$^+$ – edmp – NO – CH_3].

[W(Cl)(H)(NO)(edmp)$_2$][BPh_4] (2b): [WCl_2(NO)(edmp)$_2$][BPh_4] (0.0860 g, 0.106 mmol) was dissolved in thf (10 mL) and a large excess of zinc powder was added. The resulting mixture was stirred overnight and then filtered, and the solvent was evaporated to dryness under high vacuum. Subsequent extraction with CH_2Cl_2 and removal of the solvent afforded an analytically pure product. Yield: 0.0730 g (89%). IR (thf): $\tilde{\nu}$ = 1600 (NO) cm^{-1}. ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ = 7.50 (m, 8 H, Ph), 7.13 (t, $^3J_{H,H}$ = 7.6 Hz, 8 H, Ph), 6.96 (pseudo-t, $^3J_{H,H}$ = 7.2 Hz, 4 H, Ph), 2.96 (t, $^2J_{H,P}$ = 72.7 Hz, $^1J_{H,W}$ = 11 Hz, 1 H, WH), 2.90 (m, 2 H, NCH_2), 2.69 (m, 2 H, NCH_2), 1.90 (m, 4 H, PCH_2 and NH_2), 1.72 (d, $^2J_{H,P}$ = 10.6 Hz, 14 H, PCH_3 and PCH_2), 1.49 (m, 2 H, NH_2) ppm. ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 34.0 (s with satellites, $^1J_{P,W}$ = 207 Hz, PMe_2) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 164.5 (m, Ph), 135.9 (s, Ph), 126.8 (m, Ph), 123.0 (s, Ph), 43.7 (m, NCH_2), 30.0 (dd, $^1J_{C,P}$ = 21.2 Hz, $^3J_{C,P}$ = 2 Hz, PCH_2), 14.2 (d, $^1J_{C,P}$ = 41 Hz, PCH_3), 12.2 (d, $^1J_{C,P}$ = 41 Hz, PCH_3) ppm. $C_{32}H_{45}BClN_3OP_2W$ (779.77): calcd. C 49.28, H 5.82, N 5.39; found C 49.11, H 6.18, N 5.39. MS (EI): *m*/*z* = 459 [M$^+$ – H], 324 [M$^+$ – edmp NO – H], 319 [BPh_4].

{W(NO)[P(OMe)$_3$](edmp)$_2$}[Cl] (3a): To the solution of WCl(NO)-$[P(OMe)_3]_4$ (4.7600 g, 6.39 mmol) in toluene (40 mL) in a Young tap Schlenk tube was added edmp (1.7800 g, 16.92 mmol). The resulting mixture was heated at 85 °C. After 3 d a precipitate was formed. It was separated, washed with toluene (3 × 15 mL) and ether (4 × 15 mL) and then dried under high vacuum to give product **3a** (1.8300 g). The filtrate was dried to remove the $P(OMe)_3$ formed in the reaction. To the residue was added edmp (1.6800 g, 15.98 mmol) and toluene (25 mL). After another reaction time of 7 d at 85 °C, an additional amount of product (1.27 g) was col-

lected again. Overall yield: 3.1000 g (88%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1540 (NO) cm^{-1}. ^1H NMR (500.2 MHz, $CDCl_3$): δ = 5.59 (m, 1 H, NH_2), 4.98 (m, 1 H, NH_2), 3.81 (m, 1 H, NCH_2), 3.69 [d, $^3J_{H,P}$ = 10.4 Hz, $P(OMe)_3$], 3.66 (m, 1 H, NH_2), 3.09 (m, 1 H, NCH_2), 2.75 (m, 1 H, NCH_2), 2.55 (m, 1 H, NCH_2), 2.26 (m, 1 H, PCH_2), 1.94 (m, 1 H, PCH_2), 1.81 (d, $^2J_{H,P}$ = 8.7 Hz, 3 H, PCH_3), 1.70 (d, $^2J_{H,P}$ = 8.7 Hz, 4 H, NH_2 and PCH_3), 1.57 (m, 7 H, 2PCH_3 and 1PCH_2) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 165.5 [d with satellites, $^2J_{P,P_{trans}}$ = 11 Hz, $^1J_{P,W}$ = 612 Hz, $P(OMe)_3$], 16.0 (dd with satellites, $^2J_{P,P_{cis}}$ = 11 Hz, $^2J_{P,P_{trans}}$ = 129 Hz, $^1J_{P,W}$ = 309 Hz, PMe), 13.5 (dd with satellites, $^2J_{P,P_{cis}}$ = 2 Hz, $^2J_{P,P_{trans}}$ = 128 Hz, $^1J_{P,W}$ = 329 Hz, PMe) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = 52.6 [d, $^2J_{C,P}$ = 6 Hz, $P(OMe)_3$], 47.2 (dd, $^2J_{C,P}$ = 8 Hz, $^3J_{C,P}$ = 5 Hz, NCH_2), 42.1 (dd, $^2J_{C,P}$ = 10 Hz, $^3J_{C,P}$ = 7 Hz, NCH_2), 31.9 (d, $^1J_{C,P}$ = 25 Hz, PCH_2), 29.8 (dd, $^1J_{C,P}$ = 23 Hz, $^3J_{C,P}$ = 3 Hz, PCH_2), 19.3 (d, $^1J_{C,P}$ = 28.1 Hz, PCH_3), 15.4 (d, $^1J_{C,P}$ = 21 Hz, PCH_3), 14.4 (dd, $^1J_{C,P}$ = 25 Hz, $^3J_{C,P}$ = 2 Hz, PCH_3), 13.1 (d, $^1J_{C,P}$ = 29 Hz, PCH_3) ppm. $^{15}N\{^1H\}$ NMR (50.7 MHz, $CDCl_3$): δ = 372.8 [d, $^2J_{N,P}$ = 21 Hz, NH_2 *trans* to $P(OMe)_3$], 360.2 (m, NH_2 *trans* to NO) ppm. $C_{11}H_{33}ClN_3O_4P_3W$ (583.61): calcd. C 22.64, H 5.70, N 7.20; found C 22.76, H 5.81, N 7.24. MS (EI): *m*/*z* = 547 [M^+ – H], 458 [M^+ – 4Me – NO], 422 [M^+ – 2H – $P(OMe)_3$], 378 [M^+ – H – $P(OMe)_3$ – 3Me].

{W(NO)(edmp)$_2$[P(OMe)$_3$]}[BPh$_4$] (3b): A thf suspension of {W(NO)(edmp)$_2$[P(OMe)$_3$]}[Cl] (0.2130 g, 0.364 mmol) was stirred overnight with an excess amount of $NaBPh_4$ (0.3662 g, 1.07 mmol). The reaction mixture was filtered, the solvent removed and the residue extracted with CH_2Cl_2 to give compound **3b** as an orange powder. Yield: 0.3110 g (98%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1556 (NO) cm^{-1}. ^1H NMR (300.1 MHz, $CDCl_3$): δ = 7.45 (m, 8 H, Ph), 7.07 (t, $^3J_{H,H}$ = 7.4 Hz, 8 H, Ph), 6.93 (t, $^3J_{H,H}$ = 7.1 Hz, 4 H, Ph), 3.61 [d, $^3J_{H,P}$ = 10.4 Hz, 9 H, $P(OMe)_3$], 2.75 (m, 1 H, NH_2), 2.52 (m, 1 H, NCH_2), 2.19 (m, 2 H, PCH_2 and NCH_2), 1.65 (d, $^2J_{H,P}$ = 8.8 Hz, 3 H, PMe), 1.61 (m, 1 H, PCH_2), 1.54 (d, $^2J_{H,P}$ = 8.8 Hz, 3 H, PMe), 1.41 (m, 2 H, PCH_2 and NCH_2), 1.29 (d, $^2J_{H,P}$ = 6.8 Hz, 3 H, PCH_3), 1.27 (d, $^2J_{H,P}$ = 6.4 Hz, 3 H, PCH_3), 1.19 (m, 1 H, NH_2), 1.10–0.90 (br. m, 3 H, NH_2, NCH_2 and PCH_2), 0.12 (m, 1 H, NH_2) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 163.8 [d with satellites, $^2J_{P,P_{trans}}$ = 12 Hz, $^1J_{P,W}$ = 630 Hz, $P(OMe)_3$], 17.3 (dd with satellites, $^2J_{P,P_{cis}}$ = 12 Hz, $^2J_{P,P_{trans}}$ = 131 Hz, $^1J_{P,W}$ = 310 Hz, PMe), 13.5 (d with satellites, $^2J_{P,P_{trans}}$ = 131 Hz, $^1J_{P,W}$ = 330 Hz, PMe) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 164.2 (m, $^1J_{CB}$ = 49.8 Hz, Ph), 136.1 (s, Ph), 126.0 (s, Ph), 122.2 (s, Ph), 52.7 [d, $^2J_{C,P}$ = 7 Hz, $P(OMe)_3$], 46.8 (m, NCH_2), 42.3 (m, NCH_2), 30.7 (d, $^1J_{C,P}$ = 24 Hz, PCH_2), 30.1 (d, $^1J_{C,P}$ = 21 Hz, PCH_2), 18.9 (d, $^1J_{C,P}$ = 30 Hz, PCH_3), 15.7 (d, $^1J_{C,P}$ = 20 Hz, PCH_3), 14.0 (dd, $^1J_{C,P}$ = 25 Hz, $^3J_{C,P}$ = 3 Hz, PCH_3), 12.4 (d, $^1J_{C,P}$ = 30 Hz, PCH_3) ppm. $C_{35}H_{53}BN_3O_4P_3W$ (867.38): calcd. C 48.46, H 6.16, N 4.84; found C 48.24, H 6.32, N 4.71. MS (EI): *m*/*z* = 422 [M^+ – 2H – $P(OMe)_3$], 392 [M^+ – 2H – $P(OMe)_3$ – 2Me], 318 [M^+ – H – $P(OMe)_3$ – edmp].

[W(NO)(CO)(edmp)$_2$][Cl] (4a): A thf solution (20 mL) of $WCl(CO)(NO)[PMe_3]_3$ (0.4560 g, 0.90 mmol) and edmp (0.2113 g, 2.01 mmol) was stirred at 70 °C for 3 d. A precipitate was formed. The precipitate was separated, washed with thf (3 × 5 mL) and ether (3 × 5 mL) and then dried under high vacuum to give an analytically pure orange-red powder. Yield: 0.4000 g, (91%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1890 (CO), 1592 (NO) cm^{-1}. ^1H NMR (300.1 MHz, $CDCl_3$): δ = 6.03 (m, 1 H, NH), 5.48 (m, 1 H, NH), 3.71 (m, 1 H), 3.33 (m, 2 H), 2.66 (m, 2 H), 2.12 (m, 2 H), 1.96 (m, 1 H), 1.83 (d, $^2J_{H,P}$ = 7.2 Hz, 3 H, PMe), 1.74 (d, $^2J_{H,P}$ = 7.5 Hz, 3 H, PMe), 1.64 (d, $^2J_{H,P}$ = 5.7 Hz, 6 H, PMe) ppm, other two proton resonances are overlapped by the methyl resonances. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 13.1 (s with satellites, $^1J_{P,W}$ = 311 Hz, edmp), 13.0 (s with satellites, $^1J_{P,W}$ = 316 Hz, edmp) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 241.3 (t, $^2J_{C,P}$ = 4 Hz, CO), 45.5 (t, $^{2,3}J_{C,P}$ = 7 Hz, NCH_2), 43.8 (t, $^{2,3}J_{C,P}$ = 8 Hz, NCH_2), 30.3 (dd, $^1J_{C,P}$ = 19 Hz, $^3J_{C,P}$ = 7 Hz, PCH_2), 29.4 (dd, $^1J_{C,P}$ = 18 Hz, $^3J_{C,P}$ = 7 Hz, PCH_2), 17.4 (dd, $^1J_{C,P}$ = 23 Hz, $^3J_{C,P}$ = 7 Hz, PCH_3), 14.4 (dd, $^1J_{C,P}$ = 18 Hz, $^3J_{C,P}$ = 7 Hz, PCH_3), 13.9 (dd, $^1J_{C,P}$ = 20 Hz, $^3J_{C,P}$ = 9 Hz, PCH_3), 13.1 (dd, $^1J_{C,P}$ = 22 Hz, $^3J_{C,P}$ = 7 Hz, PCH_3) ppm. $C_9H_{24}ClN_3O_2P_2W$ (487.54): calcd. C 22.17, H 4.96, N 8.62; found C 22.32, H 5.13, N 8.80.

[W(NO)(CO)(edmp)$_2$][BPh$_4$] (4b): {W(NO)(edmp)$_2$[P(OMe)$_3$]}-[BPh_4] (0.0930 g, 0.107 mmol) was dissolved in thf (20 mL) in a Young tap Schlenk tube, which was subsequently pressurized with 2 bar of CO. After stirring for 1 d at 80 °C, the mixture was dried under high vacuum and extracted with CH_2Cl_2 to give a pure orange product after drying. Yield: 0.0810 g (98%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1893 (CO), 1595 (NO) cm^{-1}. ^1H NMR (500.2 MHz, CD_2Cl_2): δ = 7.46 (m, 8 H, Ph), 7.07 (t, $^3J_{H,H}$ = 7.6 Hz, 8 H, Ph), 6.93 (pseudo-t, $^3J_{H,H}$ = 7.2 Hz, 4 H, Ph), 2.69 (m, 1 H, NH_2), 2.45 (m, 2 H, NCH_2 and NH_2), 2.18 (m, 1 H, NCH_2), 1.86 (m, 1 H, NCH_2), 1.72 (m, 3 H, PCH_3), 1.62 (m, 3 H, PCH_3), 1.58 (m, 1 H, PCH_2), 1.40 (m, 3 H, PCH_2), 1.35 (m, 3 H, PCH_3), 1.32 (m, 3 H, PCH_3), 1.08 (m, 1 H, NH_2), 0.18 (m, 1 H, NH_2), –0.45 (m, 1 H, NH_2) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ = 12.6 (s with satellites, $^1J_{P,W}$ = 310 Hz, PMe_2), 12.5 (s with satellites, $^1J_{P,W}$ = 307 Hz, PMe_2) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 237.9 (t, $^2J_{C,P}$ = 3 Hz, CO), 164.5 (m, Ph), 136.1 (m, Ph), 126.5 (m, Ph), 122.5 (m, Ph), 46.3 (t, $^{2,3}J_{C,P}$ = 7 Hz, NCH_2), 45.2 (t, $^{2,3}J_{C,P}$ = 8 Hz, NCH_2), 29.9 (dd, $^1J_{C,P}$ = 17 Hz, $^3J_{C,P}$ = 10 Hz, PCH_2), 29.5 (dd, $^1J_{C,P}$ = 16 Hz, $^3J_{C,P}$ = 8 Hz, PCH_2), 17.1 (dd, $^1J_{C,P}$ = 21 Hz, $^3J_{C,P}$ = 11 Hz, PCH_3), 14.4 (dd, $^1J_{C,P}$ = 15 Hz, $^3J_{C,P}$ = 9 Hz, PCH_3), 14.1 (dd, $^1J_{C,P}$ = 18 Hz, $^3J_{C,P}$ = 11 Hz, PCH_3), 13.0 (dd, $^1J_{C,P}$ = 21 Hz, $^3J_{C,P}$ = 10 Hz, PCH_3) ppm. ^1H NMR (500.2 MHz, [D_8]thf): δ = 7.30 (m, 8 H, Ph), 6.89 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H, Ph), 6.75 (pseudo-t, $^3J_{H,H}$ = 7.2 Hz, 4 H, Ph), 4.35 (m, 1 H, NH_2), 3.05 (m, 1 H, NH_2), 2.60–2.94 (br., 4 H, NH_2 and NCH_2), 2.36 (m, 1 H, NCH_2), 2.01 (m, 1 H, NH_2), 1.75 (d, $^2J_{H,P}$ = 8.7 Hz, 3 H, PCH_3), 1.66 (d, $^2J_{H,P}$ = 8.5 Hz, 4 H, 3H from PCH_3 and 1 H from PCH_2), 1.57 (m, 3 H, PCH_2), 1.46 (d, $^2J_{H,P}$ = 7 Hz, 3 H, PCH_3), 1.43 (d, $^2J_{H,P}$ = 7.3 Hz, 3 H, PCH_3) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D_8]thf): δ = 14.2 (d with satellites, $^2J_{P,P}$ = 134 Hz, $^1J_{P,W}$ = 306 Hz, PMe), 12.8 (d with satellites, $^2J_{P,P}$ = 134 Hz, $^1J_{P,W}$ = 315 Hz, PMe) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, [D_8]thf): δ = 239.8 (t, $^2J_{C,P}$ = 3.4 Hz, CO), 165.3 (m, Ph), 137.2 (m, Ph), 126.0 (m, Ph), 122.1 (m, Ph), 45.7 (dd, $^2J_{C,P}$ = 9 Hz, $^3J_{C,P}$ = 6 Hz, NCH_2), 44.0 (dd, $^2J_{C,P}$ = 9 Hz, $^3J_{C,P}$ = 7 Hz, NCH_2), 31.4 (dd, $^1J_{C,P}$ = 24 Hz, $^3J_{C,P}$ = 3 Hz, PCH_2), 30.9 (dd, $^1J_{C,P}$ = 22 Hz, $^3J_{C,P}$ = 2 Hz, PCH_2), 16.8 (d, $^1J_{C,P}$ = 32 Hz, PCH_3), 13.5 (dd, $^1J_{C,P}$ = 20 Hz, $^3J_{C,P}$ = 3 Hz, PCH_3), 13.0 (dd, $^1J_{C,P}$ = 23 Hz, $^3J_{C,P}$ = 4 Hz, PCH_3), 12.6 (dd, $^1J_{C,P}$ = 29 Hz, $^3J_{C,P}$ = 1 Hz, PCH_3) ppm. $C_{33}H_{44}BN_3O_2P_2W$ (771.32): calcd. C 51.39, H 5.75, N 5.45; found C 51.28, H 5.88, N 5.07.

Reaction of [W(NO)(CO)(edmp)$_2$][BPh$_4$] (4b) with NaHBEt$_3$: [W(NO)(CO)(edmp)$_2$][BPh_4] (**4b**) (0.0180 g, 0.023 mmol) was treated with $NaHBEt_3$ (3 equiv.) in [D_8]thf first at –30 °C for 4 d, then another 6 d at –10 °C to give dihydride **4c**. Attempts to separate **4c** from solution by various methods resulted in its decomposition. Complex **4c** was identified spectroscopically. IR (thf): $\tilde{\nu}$ = 1869 (CO), 1580 (NO) cm^{-1}. ^1H NMR (500.2 MHz, [D_8]thf): δ = 1.05 (dt, $^2J_{H,P}$ = 23.2 Hz, $^2J_{H,H}$ = 8.2 Hz, 1 H, WH), –2.90 (dt, $^2J_{H,P}$ = 24.4 Hz, $^2J_{H,H}$ = 8.3 Hz, 1 H, WH) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D_8]thf): δ = –19.7 (s, $^1J_{P,W}$ = 285 Hz, edmp) ppm.

^{13}C NMR (125.8 MHz, [D$_8$]thf): δ = 249.9 (t, $^2J_{C,P}$ = 6 Hz, CO) ppm.

WCl(NO)(PMe$_3$)$_2$(edmp) (5a): A toluene solution (20 mL) of WCl(NO)(PMe$_3$)$_4$ (0.565 g, 1.02 mmol) and edmp (0.1090 g, 1.04 mmol) was stirred at 35–40 °C for 2 d. After removal of P(OMe)$_3$ under vacuo, another toluene (20 mL) solution of edmp (0.1020 g, 0.97 mmol) was added. The resulting mixture was heated further to 35–40 °C for another 3 d. Then, the solvent was removed, and the residue was washed with diethyl ether (3 × 5 mL). Further purification was carried out by diffusion of hexane into its thf solution to give yellow crystals suitable for X-ray crystallographic analysis. Yield: 0.3950 g (77%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1494 (NO) cm^{-1}. ^1H NMR (300.1 MHz, CD_3CN): δ = 4.27 (m, 1 H, NH), 3.09 (m, 1 H, NCH), 2.83 (m, 1 H, NH), 2.55 (m, 1 H, NCH), 1.30–1.60 (m, 24 H, PCH_2 and PMe) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 15.3 (d, $^2J_{P,P}$ = 178 Hz, $^1J_{P,W}$ = 315 Hz, edmp), –12.1 (s, $^1J_{P,W}$ = 404 Hz, PMe$_3$), –18.0 (dd, $^2J_{P,P_{trans}}$ = 179 Hz, $^2J_{P,P_{cis}}$ = 3 Hz, $^1J_{P,W}$ = 333 Hz, PMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 46.7 (m, NCH_2), 33.8 (d, $^1J_{C,P}$ = 21 Hz, PCH_2), 24.7 (d, $^1J_{C,P}$ = 25 Hz, PMe$_3$), 18.9 (d, $^1J_{C,P}$ = 23 Hz, PMe$_3$), 13.2 (dt, $^1J_{C,P}$ = 22 Hz, $^3J_{C,P}$ = 2 Hz, PMe from edmp), 12.8 (d, $^1J_{C,P}$ = 25 Hz, PMe from edmp) ppm. $C_{10}H_{30}ClN_2OP_3W$ (506.57): calcd. C 23.71, H 5.97, N 5.53; found C 24.05, H 5.96, N 5.83.

WCl(NO)(edmp)[P(OMe$_3$)$_2$] (5b): WCl(NO)[P(OMe$_3$)]$_4$ (3.13 g, 4.2 mmol) was dissolved in thf (30 mL) in a Young tap Schlenk tube and edmp (0.538 g, 5.12 mmol) was added. After the mixture was heated to 55 °C for 1 d, the solvent, the excess amount of edmp and the P(OMe)$_3$ formed in the reaction were removed under vacuum to give an analytically pure product. Yield: 2.50 g (99%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1536 (NO) cm^{-1}. ^1H NMR (300.1 MHz, CD_3CN): δ = 4.36 (m, 1 H, NH), 3.62 [d, $^3J_{H,P}$ = 10.8 Hz, 9 H, P(OMe$_3$)], 3.54 [d, $^3J_{H,P}$ = 10.8 Hz, 9 H, P(OMe$_3$)], 3.21 (m, 1 H, NCH), 2.89 (m, 1 H, NH), 2.59 (m, 1 H, NCH), 1.59 (m, 2 H, PCH_2), 1.50 (m, 6 H, PCH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 179.5 [t with satellites, $^2J_{P,P}$ = 11 Hz, $^1J_{P,W}$ = 607 Hz, P(OMe$_3$) *trans* to NH_2], 163.1 [dd with satellites, $^2J_{P,P_{trans}}$ = 254 Hz, $^2J_{P,P_{cis}}$ = 9 Hz, $^1J_{P,W}$ = 505 Hz, P(OMe$_3$) *trans* to PCH_3], 14.5 (dd with satellites, $^2J_{P,P_{trans}}$ = 254 Hz, $^2J_{P,P_{cis}}$ = 13 Hz, $^1J_{P,W}$ = 294 Hz, PCH_3) ppm. $^{13}C\{^1H\}$NMR (75.5 MHz, CD_3CN): δ = 52.2 [m, P(OMe$_3$)], 45.6 (m, NCH_2), 31.2 (dd, $^1J_{C,P}$ = 22 Hz, $^3J_{C,P}$ = 3 Hz, PCH_2), 11.1 (m, PCH_3), 10.8 (m, PCH_3) ppm. $C_{10}H_{30}ClN_2O_7P_3W$ (602.56): calcd. C 19.93, H 5.02, N 4.65; found C 20.11, H 5.13, N 4.64.

[WCl(CO)(NO)(PMe$_3$)(edmp)] (6a): A thf solution (15 mL) of WCl(CO)(NO)(PMe$_3$)$_3$ (0.5110 g, 1.0 mmol) and edmp (0.1550 g, 1.47 mmol) was stirred at 55 °C for 10 d to give an orange solution, which was filtered off and dried. The crude product was recrystallized by diffusion of hexane into a thf solution to give **6a** as orange crystals. Yield: 0.4010 g (87%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1891 (CO), 1591 (NO) cm^{-1}. ^1H NMR (300.1 MHz, CD_3CN): δ = 4.16 (m, 1 H, NH), 3.30 (m, 1 H, NCH), 2.70 (m, 2 H, NH and NCH), 1.71 (br. m, 2 H, PCH_2), 1.40–1.60 (m, 15 H, PMe) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 14.1 (d, $^2J_{P,P}$ = 174 Hz, $^1J_{P,W}$ = 301 Hz, edmp), –17.4 (d, $^2J_{P,P}$ = 174 Hz, $^1J_{P,W}$ = 313 Hz, PMe$_3$) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 247.2 (t, $^2J_{C,P}$ = 3 Hz, CO), 45.2 (dd, $^2J_{C,P}$ = 9 Hz, $^3J_{C,P}$ = 6 Hz, NCH_2), 30.6 (d, $^1J_{C,P}$ = 23 Hz, PCH_2), 16.4 (d, $^1J_{C,P}$ = 26.6 Hz, PMe$_3$), 12.0 (d, $^1J_{C,P}$ = 28 Hz, PMe), 11.6 (dd, $^1J_{C,P}$ = 27 Hz, $^3J_{C,P}$ = 1 Hz, PMe) ppm. $C_8H_{21}ClN_2O_2P_2W$ (458.50): calcd. C 20.96, H 4.62, N 6.11; found C 21.02, H 4.71, N 6.30.

WCl(CO)(NO)(edmp)[P(OMe$_3$)] (6b): A thf solution (15 mL) of WCl(NO)(edmp)[P(OMe$_3$)]$_2$ (0.3840 g, 0.64 mmol) was placed in a Young tap Schlenk tube and was frozen by immersion into liquid N_2. After evacuation, 2.5 bar of CO gas was allowed to fill the tube, then it was closed and warmed to room temperature. The solution was stirred at 80 °C for 4 d. The pressure in the tube was released, the solvent was evaporated in vacuo and the residue was washed with cold ether (–30 °C; 3 × 5 mL) and pentane (3 × 5 mL) to give pure yellow **6b**. Yield: 0.2580 g (80%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1910 (CO), 1578 (NO) cm^{-1}. ^1H NMR (300.1 MHz, [D$_8$]thf): δ = 4.60 (m, 1 H, NH), 3.24 (m, 1 H, NCH), 2.74 (m, 2 H, NH and NCH), 1.66 (m, 2 H, PCH_2), 3.68 [d, $^3J_{H,P}$ = 11.1 Hz, 9 H, P(OMe)$_3$], 1.59 (m, 6 H, PMe) ppm. $^{31}P\{^1H\}$NMR (121.5 MHz, [D$_8$]thf): δ = 157.0 [d, $^2J_{P,P}$ = 261 Hz, $^1J_{P,W}$ = 485 Hz, P(OMe$_3$)], 11.6 (d, $^2J_{P,P}$ = 260 Hz, $^1J_{P,W}$ = 295 Hz, edmp) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, [D$_8$]thf): δ = 238.1 (t, $^2J_{C,P}$ = 5 Hz, CO), 52.2 [d, $^2J_{C,P}$ = 2 Hz, P(OMe$_3$)], 44.3 (dd, $^2J_{C,P}$ = 9 Hz, $^3J_{C,P}$ = 6 Hz, NCH_2), 30.5 (d, $^1J_{C,P}$ = 23 Hz, PCH_2), 10.4 (d, $^1J_{C,P}$ = 27 Hz, PCH_3), 10.0 (dd, $^1J_{C,P}$ = 27 Hz, $^3J_{C,P}$ = 2 Hz, PCH_3) ppm. $C_8H_{21}ClN_2O_5P_2W$ (506.51): calcd. C 18.97, H 4.18, N 5.53; found C 19.07, H 4.21, N 5.54.

Reaction of 6a with NaHBEt$_3$ To Obtain WH(NO)(CO)(PMe$_3$)(edmp) (7a): To a [D$_8$]thf solution of WCl(NO)(CO)(PMe$_3$)(edmp) (**6a**) was added NaHBEt$_3$ (2 equiv.) in [D$_8$]thf at –30 °C, and the reaction was monitored by NMR spectroscopy. Product **7a** formed after 2 d at –30 °C. Data for **7a**: ^1H NMR (500.2 MHz, [D$_8$]thf, 233 K): δ = 3.84 (t, $^2J_{H,P}$ = 24.8 Hz, $^1J_{H,W}$ = 73 Hz, 1 H, WH), 1.76 [d, PMe(edmp)], 1.66 [d, $^2J_{H,P}$ = 8 Hz, PMe(edmp)], 1.62 (d, $^2J_{H,P}$ = 8 Hz, PMe$_3$) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_8$]thf, 233 K): δ = 10.8 (d with satellites, $^2J_{P,P}$ = 117 Hz, $^1J_{P,W}$ = 296 Hz, edmp), –18.9 (d with satellites, $^2J_{P,P}$ = 117 Hz, $^1J_{P,W}$ = 299 Hz, PMe$_3$) ppm. Warming of the reaction mixture to 4 °C or room temperature led to the formation of **9a**. Data for **9a**: ^1H NMR (500.2 MHz, [D$_8$]thf, 233 K): δ = 5.75 (t, $^3J_{H,H}$ = 12.5 Hz, NH_2), 4.42 (t, $^3J_{H,H}$ = 12.5 Hz, NH_2), 2.82 [br. m, NCH_2], 2.72 [br. m, NCH_2], 2.04 [br. m, PCH_2],1.98 [br., PCH_2], 1.52 (d, $^2J_{H,P}$ = 7 Hz, PMe$_3$), 1.05 [m, 1 H, WH(*trans* CO)], –3.03 [m, 1 H, WH(*trans* NO)] ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_8$]thf, 233 K): δ = –19.3 (d, $^2J_{P,P}$ = 89 Hz, $^1J_{P,W}$ = 296 Hz, edmp), –22.8 (d, $^2J_{P,P}$ = 89 Hz, $^1J_{P,W}$ = 299 Hz, PMe$_3$) ppm.

Reaction of 6b with NaBHEt$_3$ To Afford WH(CO)(NO)(edmp)[P(OMe$_3$)] (7b): To a [D$_8$]thf solution of complex **6b** (0.0260 g, 0.051 mmol) placed in an NMR tube was added NaBHEt$_3$ (3 equiv.) in [D$_8$]thf at –30 °C, and the slowly proceeding reaction was monitored by ^1H NMR and ^{31}P NMR spectroscopy. After 11 d at –30 °C, WH(CO)(NO)(edmp)[P(OMe$_3$)] (**7b**) was formed as the main product. Another 9 d at –10 °C caused the formation of **9b** as the main product together with a small amount of other unidentified compounds. Complex **9b** decomposed slowly upon warming to 4 °C for some time. Compounds **7b** and **9b** could not be isolated and were spectroscopically identified. Data for **7b**: ^1H NMR (500.2 MHz, [D$_8$]thf, 243 K): δ = 3.20 (t, $^2J_{H,P}$ = 27.8 Hz, 1 H, WH) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_8$]thf, 243 K): δ = 176.6 [d with satellites, $^2J_{P,P}$ = 184.5 Hz, $^1J_{P,W}$ = 477 Hz, P(OMe$_3$)], 10.2 (d, $^2J_{P,P}$ = 183 Hz, $^1J_{P,W}$ = 286.5 Hz, edmp) ppm. Data for **9b**: ^1H NMR (500.2 MHz, [D$_8$]thf, 243 K): δ = –0.60 (dt, $^2J_{H,P}$ = 23.9 Hz, $^2J_{H,H}$ = 9.6 Hz, 1 H, WH), –4.24 (ddd, $^2J_{H,P}$ = 23.6 Hz, $^2J_{H,P}$ = 23.6 Hz, $^2J_{H,H}$ = 9.6 Hz, 1 H, WH) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_8$]thf, 243 K): δ = 181.6 [d, $^2J_{P,P}$ = 157 Hz, $^1J_{P,W}$ = 461 Hz, P(OMe$_3$)], –20.8 (d, $^2J_{P,P}$ = 157 Hz, $^1J_{P,W}$ = 278 Hz, edmp) ppm.

W(H$_2$)(NO)(NHCH$_2$CH$_2$PMe$_2$)(PMe$_3$)$_2$ (11a): To a [D$_8$]thf solution of compound **5a** (0.030 g, 0.055 mmol) was added NaBHEt$_3$ (2 equiv.) in [D$_8$]thf at –30 °C, and the reaction was monitored by

^{1}H and ^{31}P NMR spectroscopy. The reaction was complete after 2 d. ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]thf, 293 K): δ = 13.7 (dd with satellites, $^2J_{P,P_{cis}}$ = 9 Hz, $^2J_{P,P_{cis}}$ = 2 Hz, $^1J_{P,W}$ = 307 Hz, PMe_3), –21.8 (dd with satellites, $^2J_{P,P_{cis}}$ = 9 Hz, $^2J_{P,P_{trans}}$ = 164 Hz, $^1J_{P,W}$ = 316 Hz, PMe_3), 9.3 (dd with satellites, $^2J_{P,P_{cis}}$ = 2 Hz, $^2J_{P,P_{trans}}$ = 164 Hz, $^1J_{P,W}$ = 292 Hz, edmp) ppm.

Mixture of WH(NO)(edmp)[P(OMe)$_3$]$_2$ (8b) and W(H$_2$)(NO)-(NHCH$_2$CH$_2$PMe$_2$)[P(OMe)$_3$]$_2$ (10b): To a [D$_8$]thf solution of compound **5b** (0.0330 g, 0.055 mmol) was added $NaBHEt_3$ (2 equiv.) in [D$_8$]thf at –30 °C, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. The resulting mixture of **8b** and **10b** was kept at –10 °C for 6 h and then at 4 °C for 6 h and finally at room temperature overnight. The reaction was then complete and there was no further change even if the reaction solution was left at room temperature for another 2 d with prevailing presence of **10b**, but any attempt to separate **8b** and **10b** from the reaction mixture led to their decomposition. Data for the mixture **8b/10b**: ^{1}H NMR (500.2 MHz, [D$_8$]thf, 273 K): δ = 3.64, 3.58 [d, $^3J_{H,P}$ = 11 Hz, P(OMe)$_3$], 2.85, 2.53 (m, 1 H, NCH_2), 2.44 (q., $^2J_{H,P}$ = 28 Hz, 1 H, WH), 2.35, 1.59 (m, 1 H, PCH_2), 1.89 (d, $^2J_{H,P}$ = 8.8 Hz, 3 H, PCH_3), 1.70 (d, $^2J_{H,P}$ = 8.0 Hz, 3 H, PCH_3), 2.09, 1.81 (m, 1 H, NH_2), –2.35 [br., W(H$_2$)] ppm. ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]thf, 273 K): δ = 181.9 [dd with satellites, $^2J_{P,P_{trans}}$ = 179 Hz, $^2J_{P,P_{cis}}$ = 7 Hz, $^1J_{P,W}$ = 499 Hz, P(OMe)$_3$], 178.1 [dd with satellites, $^2J_{P,P_{cis}}$ = 17 Hz, $^2J_{P,P_{cis}}$ = 7 Hz, $^1J_{P,W}$ = 450 Hz, P-(OMe)$_3$], 9.3 (dd with satellites, $^2J_{P,P_{trans}}$ = 179 Hz, $^2J_{P,P_{cis}}$ = 17 Hz, $^1J_{P,W}$ = 278 Hz, edmp) ppm.

X-ray Data Collection and Structure Refinement: Single crystals of **1a**, **2b**, **3a**, **4b**, **5b**, **6a** and **6b** were mounted on top of a glass fiber using polybutene oil as protecting agent and immediately transferred to the diffractometer. There the crystals were cooled to 183(2) K by an Oxford cryogenic system. The determination of the unit cell parameters and the collection of intensity data were performed with an image plate detector system (Stoe IPDS diffractometer) with graphite monochromated Mo-K_a radiation using the Stoe IPDS software.[49] A total of 200, 143, 200, 275, 243, 200 and 240 images were exposed at constant times of 2.50, 2.50, 3.00, 3.00, 1.40, 2.00 and 1.60 min image^{-1} for compounds **1a**, **2b**, **3a**, **4b**, **5b**, **6a** and **6b**, respectively. The crystal-to-image distances were set to 50.0 mm, except for compounds **1a** and **4b**, which had a necessary larger distance of 54.0 and 60.0 mm, respectively. The corresponding θ_{max} values were 29.28, 30.37, 30.30, 28.00, 30.43, 30.20 and 30.37°, respectively. ϕ-Oscillation (**1a**, **3a**, **4b**) or rotation scan modes (**2b**, **5b**, **6a**, **6b**) were selected for the ϕ increments of 1.0, 1.2, 0.8, 1.4, 1.4, 1.2 and 1.5° per exposure in each case. Total exposure times for the six compounds were 22, 16, 24, 33, 17, 21 and 23 h in the order of complexes **1a**, **2b**, **3a**, **4b**, **5b**, **6a** and **6b**. After integrations and corrections for Lorentz and polarization effects, a total of 8000, 8000, 8000, 7998, 7998, 7997 and 7997 reflections for complexes **1a**, **2b**, **3a**, **4b**, **5b**, **6a** and **6b**, respectively, were selected out of the whole limiting sphere for the cell parameter refinements. A total of 47409, 10586, 29505, 25237, 21942, 19936 and 33957 reflections were collected, of which 12316, 10586, 6288, 8042, 5957, 4344 and 4557 reflections were unique (R_{int} = 0.0900, 0.0352, 0.0655, 0.1518, 0.0784, 0.1037 and 0.0688); data reduction and numerical absorption correction used 12, 13, 6, 18, 11, 18 and 18 indexed crystal faces. All of the structures were solved by direct methods using the Program SHELXS-97[50] and they were refined by the full-matrix least-squares methods on all F^2 data with SHELXL-97.[50] The program PLATON[51] was used to check the result of the X-ray analysis and the program ORTEP[52] used to give a representation of the structures. Structures **1a**, **2b** and **6a** exhibited Cl/N=O positional disorder with 0.50:0.50, 0.39:0.61 and 0.48:0.52 ratios. The hydride atom in compound **2b** was located and freely refined. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C–H or N–H distances in the range 0.90–0.98 Å and their isotropic displacement parameters constrained to 1.2 or 1.5 times the value of U_{eq} of the atom it binds to.

CCDC-729437 (for **1a**), -729438 (for **2b**), -729439 (for **3a**), -729440 (for **4b**), -729441 (for **5b**), -729442 (for **6a**) and -729443 (for **6b**) 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.

Supporting Information (see footnote on the first page of this article): Tables of crystal data and structure refinement parameters for compounds **1a**, **2b**, **3a**, **4b**, **5b**, **6a** and **6b**.

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