Synthesis and Characterization of Hydrido Carbonyl Molybdenum and Tungsten PNP Pincer Complexes

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Supporting Information

ABSTRACT: In the present study the Mo(0) and W(0) complexes [M(PNP)(CO)₃] as well as seven-coordinate cationic hydridocarbonyl Mo(II) and W(II) complexes of the type [M(PNP)(CO)₃H]⁺, featuring PNP pincer ligands based on 2,6-diaminopyridine, have been prepared and fully characterized. The synthesis of Mo(0) complexes [Mo(PNP)(CO)₃] was accomplished by treatment of [Mo(CO)₃(CH₃CN)₃] with the respective PNP ligands. The analogous W(0) complexes were prepared by reduction of the bromocarbonyl complexes [W(PNP)(CO)₃Br]⁺ with NaHg. These intermediates were obtained from the known dinuclear complex [W(CO)₄(μ-Br)Br]₂, prepared in situ from W(CO)₆ and stoichiometric amounts of Br₂. Addition of HBF₄ to [M(PNP)(CO)₃] resulted in clean protonation at the molybdenum and tungsten centers to generate the Mo(II) and W(II) hydride complexes [M(PNP)(CO)₃H]⁺. The protonation is fully reversible, and upon addition of NEt₃ as base the Mo(0) and W(0) complexes [M(PNP)(CO)₃] are regenerated quantitatively. All heptacoordinate complexes exhibit fluxional behavior in solution. The mechanism of the dynamic process of the hydrido carbonyl complexes was investigated by means of DFT calculations, revealing that it occurs in a single step. The structures of representative complexes were determined by X-ray single-crystal analyses.

INTRODUCTION

Tridentate PNP ligands in which the central pyridine-based ring donor contains −CH₂PR₂ substituents in the two ortho positions are widely utilized ligands in transition-metal chemistry (e.g., Fe, Ru, Rh, Ir, Pd, Pt).¹−¹⁴ As part of our effort to create tridentate PNP pincer-type ligands in which the steric, electronic, and stereochemical properties can be easily varied, we have recently described the synthesis of a series of modularly designed PNP ligands based on N-heterocyclic diamines and R₂PCl which contain both bulky and electron-rich dialkylphosphines as well as various P−O bond containing achiral and chiral phosphate units.¹¹ In these PNP ligands the central pyridine ring contains −NR₂PR₂ (R = H, alkyl, R = alkyl, aryl) substituents in the two ortho positions. This methodology was first developed for the synthesis of NN′ bis(diphenylphosphino)-2,6-diaminopyridine (PNPPh).¹²

With these types of PNP ligands, we have thus far studied their reactivity toward different transition-metal fragments, which resulted in the preparation of a range of new pincer transition-metal complexes, including several new square-planar Ni(II), Pd(II), and Pt(II) PNP complexes,¹³ various iron complexes acting as CO sensors¹⁴ and catalysts for the coupling of aromatic aldehydes with ethyldiazoacetate,¹⁵ and several pentacoordinated nickel complexes.¹⁶ Surprisingly, as far as group 6 PNP complexes are concerned, only a few examples have been described in the literature. A few years ago Haupt and co-workers reported the synthesis of [M(PNP-Ph)(CO)₃] (M = Cr, Mo, W),¹⁷ while Walton and co-workers described the synthesis of the dinuclear molybdenum complex [Mo₂(PNP)(μ-H)(PCy₂)₂Cl₂] (PNP = 2,6-bis-(dicyclohexylphosphinomethyl)pyridine).¹⁸ Most recently, Templeton and co-workers described the synthesis of a series of hydrido carbonyl and halo carbonyl tungsten pincer complexes featuring the silazane-based PNP
pincer-type ligand HN(SiMe₂CH₂PPh₂)₂. In a preliminary study we have prepared cationic seven-coordinate halo carbonyl molybdenum pincer complexes of the type [Mo(PNP-iPr)(CO)₃]⁺ and [Mo(PNP-iPr)(CO)₃(CH₃CN)]⁺. Here we report on the synthesis, characterization, and reactivity of a series of new hydrido carbonyl molybdenum(II) and tungsten(II) PNP pincer complexes.

■ RESULTS AND DISCUSSION

Molybdenum(0) and Tungsten(0) Complexes. We have recently reported the synthesis of molybdenum tricarbonyl complexes of the type [Mo(PNP)(CO)₃], prepared in situ by reacting [Mo(CO)₆] in CH₃CN for 4 h, with the PNP ligands PNP-Ph, PNP-iPr, and PNP-tBu (1c) in 74−90% isolated yields. The same procedure was followed with the N-methylated PNP ligand PNPMe-Ph (1d), affording [Mo(PNPMe-iPr)(CO)₃] (2d) in 80% yield (Scheme 1). The new complex [W(CO)₅(μ-Br)Br]₂,2⁻ prepared in situ from W(CO)₆ and stoichiometric amounts of Br₂ in CH₂Cl₂ at −70 °C, afforded the analogous seven-coordinate tungsten(II) complexes [W(PNP)(CO)₃Br]Br (3a−c) in 60−80% yields (Scheme 3).

It has to be noted that the reaction of PNP ligands with [Mo(CO)₅(μ-Br)Br]₂,2⁻ prepared in situ from Mo(CO)₆ and Br₂ in CH₂Cl₂ at −70 °C, affords the analogous seven-coordinate molybdenum complexes [Mo(PNP)(CO)₃Br]Br. This has been demonstrated for the synthesis of [Mo(PNP-Ph)(CO)₃Br]Br (4a) and [Mo(PNP-iPr)(CO)₃Br]Br (4b), as illustrated in Scheme 3.

The solid-state structures of 3a and 4b were determined by single-crystal X-ray diffraction. Molecular views of 3a and 4b are depicted in Figures 1 and 2, respectively, with selected bond distances and angles reported in the captions. While the Mo-bonded bromide in 4b was clearly in an axial position, the bromide in the tungsten complex 3a adopted an axial position at about 86% occupancy (Br1 in Figure 1), while the remaining 14% exchanged places with the carbonyl group C₃₂-O₃.

It has to be noted that already a few years ago Haupt and co-workers reported the synthesis of [M(PNP-Ph)(CO₃)] (M = Mo, W) and [Mo(PNP)(CO)₃(CH₃CN)]⁺ and [Mo(PNP-iPr)(CO)₃(CH₃CN)]⁺. Haupt and co-workers noted that the pyridine nitrogen, respectively. The 31P{1H} NMR spectra comprise, in the 13C{1H} NMR spectrum, two low-intensity peaks with an excess of 10% sodium amalgam in THF gave the desired W(0) complexes [W(PNP-Ph)(CO)₃], [W(PNP-iPr)(CO)₃], and [W(PNP-tBu)(CO)₃] as yellow solids in 70−80% isolated yields (Scheme 3).

The method also yields the analogous Mo(0) complexes thus being an alternative method to that described previously. The use of Zn as reducing reagent turned out to be problematic, due to the formation of highly insoluble and, thus, difficult to remove bromozincate anions, e.g., [ZnBr₃-solvent]⁻ (solvent = acetone, THF) and ZnBr₂-solvent. Complexes 3a−c were fully characterized by a combination of 1H, 13C{1H}, and 31P{1H} NMR spectroscopy, IR spectroscopy, and elemental analysis. Characteristic features of 3a−c comprise, in the 13C{1H} NMR spectrum, two low-field triplet resonances (1/2 ratio) in the ranges of 206−221 and 196−210 ppm assignable to the carbonyl carbon atoms trans and cis to the pyridine nitrogen, respectively. The 31P{1H} NMR spectra exhibit singlet resonances at 85.2, 106.6, and 131.6 ppm with \( J_{WP} \) coupling constants of 315−329 Hz. The tungsten-phosphorus coupling was observed as a doublet satellite due to 153W, 14% abundance with \( I = \frac{1}{2} \) superimposed over the dominant singlet. The IR spectra show the typical three strong to medium absorption bands of a mer CO arrangement in the range of 1780−1760 cm⁻¹ assignable to one weaker symmetric and two strong asymmetric νCO stretching modes. The νCO frequencies, in particular the symmetric CO stretch, is indicative of the increasing electron donor strengths of the PNP ligands and follow the order PNP-Ph < PNP-iPr ≈ PNPMe-iPr < PNP-tBu (Table 1). The CO stretching frequencies are 1964 (2a, PNP-Ph), 1936 (2b, PNP-iPr), 1936 (2d, PNPMe-iPr), and 1922 cm⁻¹ (2c, PNP-tBu). The same order is found for the respective tungsten complexes. In all complexes the PNP ligand adopts the typical mer coordination mode with no evidence for any fac isomers.

In addition to the spectroscopic characterization, the solid-state structures of 2d and 5bc were determined by single-crystal X-ray diffraction. Structural views are depicted in Figures 3−5, respectively, with selected bond distances and angles given in the captions. The coordination geometry around the tungsten center of 5bc corresponds to a distorted octahedron with P1=W−P2 and trans-C₄₀=W−C₄₀ bond angles 154.43(4) and 165.7(2)° (5b), and 151.42(1) and 156.46(9)° (5c), respectively. For comparison, in the analogous
[Mo(PNP)(CO)₃] complexes 2a–d the P1–Mo–P2 angles are hardly affected by the size of the substituents of the phosphorus atoms, being 155.0(2), 155.62(1), 155.3(1), and 151.73(1)°, respectively. The carbonyl–Mo–carbonyl angles of the CO ligands trans to one another, on the other hand, vary strongly with the bulkiness of the PR₂ moiety (PNP-Ph₂ < PNP-iPr₂ < PNP-Me-iPr < PNP-tBu₂) and decrease from 171.1(8)° in [Mo(PNP-Ph)(CO)₃], to 166.03(5)° in [Mo(PNP-iPr)(CO)₃], to 162.93(7)° in [Mo(PNP-Me-iPr)(CO)₃], and finally to 156.53(4)° in [Mo(PNP-tBu)(CO)₃].

Molybdenum(II) and Tungsten(II) Hydride Complexes. Addition of HBF₄ to a CH₂Cl₂ solution of [Mo(PNP)(CO)₃] (2a–d) and [W(PNP)(CO)₃] (5a–c) resulted in an immediate color change from yellow to pale yellow consistent with protonation at the tungsten and molybdenum centers to generate tungsten(II) and molybdenum(II) hydride complexes [Mo(PNP)(CO)₃H]BF₄ (7a–d) and [W(PNP)(CO)₃H]BF₄ (8a–c), respectively (Scheme 4). The protonation is fully reversible, and upon addition of NEt₃ as base the Mo(0) and W(0) complexes [M(PNP)(CO)₃] are re-formed.
quantitatively (Scheme 4). All hydride complexes are thermally robust pale yellow solids that are air stable in the solid state but slowly decompose in solution. Characterization was accomplished by elemental analysis and by $^1$H, $^{13}$C,$^1$H, and $^{31}$P,$^1$H NMR and IR spectroscopy (Table 1). The recording of a $^{13}$C,$^1$H NMR spectrum of 8c was precluded due to the poor solubility of this complex in most common solvents.

Seven-coordinate complexes are well-known for their fluxional behavior in solution,$^{23,24}$ since typically none of the idealized geometries such as capped prism, capped octahedron, and pentagonal bipyramid or any of the less symmetrical arrangements are typically characterized by a markedly lower total energy.$^{25}$ Hence, interconversions between these various structures are quite facile. The fluxional behavior of complexes 7a–d and 8a–c was evident in variable-temperature $^1$H and $^{31}$P,$^1$H NMR spectra. At room temperature, the $^1$H NMR spectrum of complexes 7 and 8 confirmed the presence of one hydride ligand, which appeared in the range of $–3.89$ to $–5.36$ ppm either as a well-resolved doublet of doublets (8b,c) or as triplets (7a–d, 8a).

At $–60^\circ$C, all hydride resonances appear as a well-resolved doublet of doublets with one large and one small coupling constant of about 21–36 and 47–53 Hz, respectively. As an example, the variable-temperature 300 MHz $^1$H NMR spectra of the hydride region of $[\text{Mo(PNP-Ph)(CO)}_3\text{H}]^+$ (7a) are shown in Figure 6. At low temperatures the hydride signal constitutes the X part of an AMX spin system, giving rise to a doublet of doublets which, at elevated temperatures in the fast exchange regime, becomes a simple A$_2$X spin system where the X part exhibits a triplet resonance.

In the $^{13}$C,$^1$H NMR spectrum of complexes 7a–d and 8a–d the most noticeable resonances are two low-field resonances of the carbonyl carbon atoms $\text{trans}$ and $\text{cis}$ to the pyridine nitrogen observed as two triplets in a 1:2 ratio. At room temperature, no $^{31}$P,$^1$H NMR signals could be detected for molybdenum complexes 7a–d and the tungsten complex 8a due to their fluxional behavior. At $–60^\circ$C, however, the $^{31}$P,$^1$H NMR spectra of all complexes 8 give rise to two doublets with a large geminal coupling constant of about 80 Hz, which is indicative of the phosphorus atoms being in mutually $\text{trans}$ positions. The IR spectra of 7 and 8 show three strong to

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Figure 3. Structural view of $[\text{Mo(PNP-iPr)(CO)}_3\text{H}]^+$ (2d) showing 50% thermal ellipsoids (H atoms are omitted for clarity; the complex is mirror symmetric; symmetry code i $x$, $1/2 – y$, $z$). Selected bond lengths (Å) and bond angles (deg): Mo–C(14) = 1.956(2), Mo–C(15) = 2.0153(13), Mo–N(1) = 2.2589(15), Mo–P(1) = 2.3977(5), Mo–P(2) = 2.4070(5); P(1)–Mo–P(2) = 154.43(4), N(1)–Mo–P(1) = 77.74(4), N(1)–Mo–C(15) = 98.52(4), C(15)–Mo–C(15’i) = 162.93(7).

Figure 4. Structural view of $[\text{W(PNP-iPr)(CO)}_3\text{H}]$–THF ($^5$b·THF) showing 30% thermal ellipsoids (H atoms, solvent molecules, and alternative orientation of iPr group C(16a)–C(17a)–C(17a) omitted for clarity). Selected bond lengths (Å) and bond angles (deg): W–C(18) = 2.014(5), W–C(19) = 2.015(5), W–C(20) = 1.934(4), W–N(1) = 2.257(2), W–P(1) = 2.4080(12), W–P(2) = 2.4013(12); P(1)–W–P(2) = 154.43(4), N(1)–W–P(1) = 77.74(4), N(1)–W–P(2) = 77.51(4), N(1)–W–C(15) = 98.52(4), C(15)–W–C(15’) = 162.93(7).

Figure 5. Structural view of $[\text{W(PNP-iBu)}_2\text{(CO)}_3\text{H}]$·THF ($^5$c·THF) showing 50% thermal ellipsoids (H atoms and solvent molecule omitted for clarity). Selected bond lengths (Å) and bond angles (deg): W–C(22) = 1.941(3), W–C(23) = 1.997(2), W–C(24) = 2.001(2), W–N(1) = 2.277(2), W–P(1) = 2.4583(5), W–P(2) = 2.4656(5); P(1)–W–P(2) = 151.42(2), N(1)–W–P(1) = 76.52(4), N(1)–W–C(22) = 76.00(4), N(1)–W–C(23) = 113.16(8), N(1)–W–C(24) = 90.27(7), C(23)–W–C(24) = 156.46(9).

Scheme 4
medium absorption $\nu_{\text{CO}}$ bands of the one symmetric and the two asymmetric vibration modes (Table 1), which again are typical for a mer CO arrangement.

In addition to the spectroscopic characterization, the solid-state structures of 7a, d and 8a were determined by single-crystal X-ray diffraction. Structural diagrams are depicted in Figures 7–9, respectively, with selected bond distances given in the captions. The coordination geometry around the molybdenum center corresponds to a distorted capped octahedron, in which a hydride ligand occupies the capping position of an octahedral face. The crystal structure showed the tridentate PNP ligand to be bound meridionally with three carbonyl ligands filling the remaining three sites. The carbonyl trans to nitrogen was pushed toward one of the phosphine ligands to accommodate the hydride ligand. The metal–hydride bond length in the three complexes averages 1.65 Å (1.64–1.70 Å), the mean bond angle $\mathrm{H}–\mathrm{M}–\mathrm{P}$ to the nearest P atom is 67° (65–69°), and the mean bond angle $\mathrm{H}–\mathrm{M}–\mathrm{C}$ between hydride and the equatorial carbonyl group is 53° (50–55°). The hydride to carbonyl C atom distance (1.62 Å in 7d) and the almost linear attachment of the equatorial carbonyl group (Mo1–C22–O3 = 179° in 7d) do not indicate a significant bonding interaction between hydride and the adjacent carbonyl C atom in the three structurally characterized hydrido carbonyl complexes.

The mechanism of the dynamic process of the hydrido carbonyl complexes was investigated by means of DFT calculations.
corresponding OC–M–CO angle and bending away from the CO ligands have to create enough space to allow the CO and hydride ligands in the complexes \([\text{M}(\text{PNP})(\text{CO})_3\text{H}]^+ (\text{M} = \text{W}, \text{Mo})\). These intermediates were obtained from the known dinuclear carbonyl and halo carbonyl \(\text{Mo(II)}\) and \(\text{W(II)}\) complexes of the type \([\text{M}(\text{PNP})(\text{CO})_3\text{Br}]^+\) and \([\text{M}(\text{PNP})(\text{CO})_3\text{H}]^+\) featuring PNP pincer ligands based on 2,6-diaminopyridine were prepared and fully characterized. The synthesis of the \(\text{Mo(0)}\) complexes \([\text{Mo}(\text{PNP})(\text{CO})_3]_{\text{n}}\) was accomplished by treatment of \([\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})]_3\) with the respective PNP ligands. The analogous \(\text{W(0)}\) complexes were prepared by reduction of the bromo carbonyl complexes \([\text{W}(\text{PNP})(\text{CO})_3\text{Br}]^+\) with \(\text{NaHg}\). These intermediates were obtained from the known dinuclear complex \([\text{W}(\text{CO})_3(\mu-\text{Br})\text{Br}]_2\), prepared in situ from \(\text{W}(\text{CO})_6\) and stoichiometric amounts of \(\text{Br}_2\). Addition of HBF_4 to \([\text{M}(\text{PNP})(\text{CO})_3]_{\text{n}}\) resulted in protonation at the tungsten and corresponding transition states \(\text{TS}\) are shown in Figures 11 and 12. In the fluxional process, the CO and the hydride ligands in the PNP plane exchange positions in a single-step path. During that process the rest of the molecule has to change in order to accommodate the overall transformations associated with the pseudorotation. The main geometry change that happens along the path is the hydride ligand moving from the PNP plane to the perpendicular plane, i.e., the plane of the three CO ligands, in the transition state (\(\text{TS}\)) and then back to the PNP plane again but on the other side of the CO ligand. Thus, in \(\text{TS}\), the two \(\text{trans CO}\) ligands have to create enough space to allow the presence of an extra ligand in the NCCC plane, opening the corresponding OC–M–CO angle and bending away from the hydride ligand. Accordingly, in the case of the molybdenum and tungsten PNP complexes bearing the less bulky \(\text{Ph}\) and \(\text{iPr}\) substituents (\(7a, b, 8a, b\)), the C30–W1–C31 angle changes from about 177° in the ground-state structure to 166° in \(\text{TS}\), where both \(\text{trans CO}\) ligands are bent toward the PNP ligand (Figure 11). On the other hand, in the case of the molybdenum and tungsten PNP complexes bearing the bulky \(\text{tBu}\) substituents (\(7c, 8c\)) the situation is somewhat different. The C30–W1–C31 angle increases from 169° in the minima to 178° in \(\text{TS}\), while one of the two \(\text{trans CO}\) ligands is severely bent away from the PNP ligand and the other one is bent toward the PNP ligand (Figure 12). In the course of all these transformations also the H1–W1–C32 angles change from about 55° in \(7a, c, 8a, c\) to roughly 43° in \(\text{TS}\), respectively. Bond distances are hardly affected by the interconversion. It is interesting to note that, in agreement with the X-ray structures of \(7a, 7d, 8a\) (Figures 6–8), the distance between H1 and C32 is rather short, being in the range of 1.80–1.66 Å. A Wiberg index of 0.20, in \(8c\), seems to indicate an attractive interaction between the hydride and the neighboring CCO atom (C32). Most importantly, the free energy barriers \(\Delta G^f\) are 18.6 and 21.3 kcal/mol for \(7c\) and \(8c\), respectively, containing the bulky \(\text{tBu}\) substituents. In the case of all other complexes the free energy barrier is lower, being in the range of 12.5–16.1 kcal/mol, as shown in Figure 9. These results corroborate a process that can be stopped in the temperature range employed in the NMR studies and a more facile process in the case of the \(\text{Mo}\) species, as observed.

**CONCLUSION**

In the present study the \(\text{Mo(0)}\) and \(\text{W(0)}\) complexes \([\text{M}(\text{PNP})(\text{CO})_3]_{\text{n}}\) as well as seven-coordinate cationic hydrido carbonyl and halo carbonyl \(\text{Mo(II)}\) and \(\text{W(II)}\) complexes of the type \([\text{M}(\text{PNP})(\text{CO})_3\text{Br}]^+\) and \([\text{M}(\text{PNP})(\text{CO})_3\text{H}]^+\) featuring PNP pincer ligands based on 2,6-diaminopyridine were prepared and fully characterized. The synthesis of the \(\text{Mo(0)}\) complexes \([\text{Mo}(\text{PNP})(\text{CO})_3]_{\text{n}}\) was accomplished by treatment of \([\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})]_3\) with the respective PNP ligands. The analogous \(\text{W(0)}\) complexes were prepared by reduction of the bromo carbonyl complexes \([\text{W}(\text{PNP})(\text{CO})_3\text{Br}]^+\) with \(\text{NaHg}\). These intermediates were obtained from the known dinuclear complex \([\text{W}(\text{CO})_3(\mu-\text{Br})\text{Br}]_2\), prepared in situ from \(\text{W}(\text{CO})_6\) and stoichiometric amounts of \(\text{Br}_2\). Addition of HBF_4 to \([\text{M}(\text{PNP})(\text{CO})_3]_{\text{n}}\) resulted in protonation at the tungsten and...
molybdenum centers to formally generate the Mo(II) and W(II) hydride complexes [M(PNP)(CO)H]²⁻. The protonation is fully reversible, and upon addition of NE₃ as base the Mo(0) and W(0) complexes [M(PNP)(CO)]⁻ are re-formed quantitatively. All seven-coordinate complexes exhibit fluxional behavior in solution, since none of the idealized geometries (capped prism, capped octahedron, and pentagonal bipyramid) or any of the less symmetrical arrangements are typically characterized by a markedly lower total energy. The mechanism of the dynamic process of the hydrido carboxyl complexes was investigated by means of DFT calculations, revealing that it occurs in a single step. Thereby the CO and the hydride ligands which are situated in the PNP plane are interconverted.

The structures of representative complexes were determined by X-ray single-crystal analyses.

**EXPERIMENTAL SECTION**

**General Considerations.** All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures. The ligands and complexes N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (PNP-PHₐ), N,N'-bis(diisopropylphosphino)-2,6-diaminopyridine (PNP-PHₐ), N,N'-bis(di-tert-butylphosphino)-2,6-diaminopyridine (PNP-Buₐ), [Mo(PNP-PHₐ)]²⁻ (2a), [Mo(PNP-PHₐ)]²⁻ (2b), and [Mo(PNP-Buₐ)]²⁻ (2c) were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ¹H, ¹³C, and ³¹P{¹H} NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-300 DPX spectrometers and were referenced to SiMe₃ and H₂PO₄ (85%), respectively.

**N,N'-Bis(diisopropylphosphino-borane)-2,6-diaminopyridine (PNP-PHₐ·(1H·BH₃), BF₃·THF (43.1 mL, 1.0 M, 43.06 mmol) was added slowly to a solution of 1b (7.00 g, 20.50 mmol) in 100 mL of dry THF. After the mixture was stirred for 30 min at room temperature, the solvent was evaporated under reduced pressure. The white solid was further dried under vacuum for 2 h to give the product in quantitative yield. Anal. Calcd for C₂₅H₄₃P₂N₃: C, 55.32; H, 10.65; N, 11.39. Found: C, 55.28; H, 10.70; N, 11.43. ¹H NMR (δ, CDCλ, 20 °C): 7.32 (t, J = 7.9 Hz, 1H, py), 6.06 (d, J = 7.9, 2H, py), 4.58 (δ, J = 8.4 Hz, 2H, NH), 2.62 (sept, J = 6.9 Hz, J = 13.7 Hz, 4H, CH(CH₃)₂), 1.16 (m, 2CH₂, CH(C₃H₆)), 0.60 to 0.15 (bs, 6H, BH₃). ¹³C{¹H} NMR (δ, CDCλ, 20 °C): 154.4 (s, py), 140.1 (s, py), 103.1 (s, py), 24.5 (δ, J = 36.3 Hz, CH(C₃H₇)), 17.2 (δ, J = 4.3 Hz, CH(CH₃₂)), 17.0 (s, CH(CH₃₂)), 88.5 (br, m).

**N,N'-Bis(diisopropylphosphino-borane)-N,N'-methyl-2,6-diaminopyridine (PNP-PHₐ·1H·BH₃).** To a solution of 1b·BH₃ (7.45 g, 20.19 mmol) in THF (50 mL) at −20 °C was slowly added n-BuLi (17.0 mL, 2.5 M, 41.39 mmol). The reaction mixture was allowed to reach room temperature and was stirred for 2 h. Methyl iodide (3.15 mL, 50.46 mmol) was then added slowly via syringe. After the mixture was stirred for 12 h at room temperature, the reaction was quenched with a saturated NH₄Cl solution (100 mL) and 5 mL of concentrated NH₄OH. The aqueous phase was extracted twice with CH₃Cl and the combined organic phases were washed with 25 mL of brine and dried over Na₂SO₄. The solvent was removed under reduced pressure to afford 1b·BH₃ as a yellow oil. The crude product was purified via flash chromatography using silica gel and THF to give the product as a white solid. Anal. Calcd for C₂₅H₄₅N₃P₂: C, 57.56; H, 10.91; N, 10.58. Found: C, 57.62; H, 10.89; N, 10.61. Yield: 5.05 g (63%). ¹H NMR (δ, CDCλ, 20 °C): 7.48 (t, J = 8.0 Hz, 1H, py), 6.49 (δ, J = 8.0, 2H, py), 3.17 (δ, J = 7.9Hz, 6H, NCH₃), 2.80 (sept, J = 7.0 Hz, J = 21.2 Hz, 4H, CH(CH₃₂)), 1.22 (dd, J = 6.9 Hz, J = 16.5 Hz, 1H, CH(CH₃₂)), 1.03 (dd, J = 7.0 Hz, J = 15.1 Hz, 12H, CH(CH₃₂)), 0.70 to −0.30 (bs, 6H, BH₃). ¹³C{¹H} NMR (δ, CDCλ, 20 °C): 156.9 (s, py), 139.1 (s, py), 105.8 (s, py), 37.6 (s, NCH₃), 25.6 (δ, J = 36.2 Hz, CH(CH₃₂)), 17.8 (s, CH(CH₃₂)), 17.2 (s, CH(CH₃₂)). ³¹P{¹H} NMR (δ, CDCλ, 20 °C): 105.9 (br, m).
This complex was prepared analogously to 5a with 4b (88 mg, 0.13 mmol) and NaH (9 mg, 0.39 mmol) as starting materials. Yield: 61 mg (90%). All spectral data for 2a are identical with those of the authentic sample reported previously.

This complex was prepared analogously to 7a with 2b (200 mg, 0.38 mmol) and HBF$_4$ (78 µL, 0.51 mmol) as starting materials. Yield: 270 mg (87%). All spectral data for 7b are identical with those of the authentic sample reported previously.

This complex was prepared analogously to 7a with 2c (24 mg, 0.42 mmol) and HBF$_4$ (85 µL, 0.62 mmol) as starting materials. Yield: 243 mg (87%). All spectral data for 7c are identical with those of the authentic sample reported previously.
Table 2. Details for the Crystal Structure Determinations of Compounds 3a·CH$_3$OH, 4b, 2d, 5b·THF,$^1$/$_2$C$_6$H$_{14}$, 5c·THF, 7a, 7d·CH$_2$Cl$_2$, and 8a

| Compound | 3a·CH$_3$OH | 4b | 2d | 5b·THF,$^1$/$_2$C$_6$H$_{14}$ |
|----------|-------------|---|---|-------------------------------|
| Formula  | C$_{33}$H$_{29}$Br$_2$N$_3$O$_4$P$_2$W | C$_{22}$H$_7$MoN$_2$O$_4$P$_2$ | C$_{20}$H$_{33}$Br$_2$MoN$_3$O$_3$P$_2$ | C$_{27}$H$_{48}$N$_3$O$_4$P$_2$W |
| Fw      | 937.20      | 549.43 | 681.19 | 724.47 |
| Cryst size, mm | 0.16 × 0.06 × 0.05 | 0.24 × 0.14 × 0.10 | 0.50 × 0.40 × 0.20 | 0.50 × 0.40 × 0.20 |
| Color, shape | orange prism | yellow prism | yellow plate | yellow plate |
| Cryst syst | triclinic | orthorhombic | monoclinic | monoclinic |
| Space group | P1 (No. 2) | C2/c (No. 15) | Pnma (No. 62) | P2$_1$/c (No. 14) |
| a, Å    | 10.1741(6) | 29.6913(15) | 18.6552(5) | 10.1399(10) |
| b, Å    | 13.1580(7) | 10.7919(5) | 12.1772(5) | 15.5053(18) |
| c, Å    | 14.1040(8) | 16.7764(8) | 10.9035(2) | 20.036(2) |
| α, deg | 99.456(3) | 90 | 90 | 90 |
| β, deg | 95.412(3) | 90 | 90 | 90 |
| γ, deg | 104.306(3) | 90 | 90 | 90 |
| θ range, deg | 1.96–30.00 | 2.30–30.00 | 2.18–30.07 | 1.66–30.00 |
| No. of reflns measd | 46633 | 36362 | 20758 | 77629 |
| Rint | 0.060 | 0.022 | 0.033 | 0.042 |
| No. of unique reflns | 10399 | 7732 | 3770 | 9124 |
| No. of reflns with I > 2σ(I) | 7880 | 6562 | 3328 | 6686 |
| No. of params/restraints | 393/6 | 294/96 | 167/0 | 335/75 |
| R1 (I > 2σ(I)) | 0.0385 | 0.0273 | 0.0217 | 0.0398 |
| R1 (all data) | 0.0625 | 0.0507 | 0.042 | 0.075 |
| wR2 (I > 2σ(I)) | 0.0822 | 0.0534 | 0.0907 | 0.0805 |
| wR2 (all data) | 0.0884 | 0.0534 | 0.0907 | 0.0805 |
| Min/max diff Fourier peaks, e Å$^{-3}$ | −1.39/1.56 | −1.01/0.97 | −0.32/0.43 | −1.80/1.85 |

| Compound | 5c·THF | 7a | 7d·CH$_2$Cl$_2$ | 8a |
|----------|--------|---|---|---|
| Formula  | C$_{28}$H$_{49}$N$_3$O$_4$P$_2$W | C$_{32}$H$_{36}$BF$_4$MoN$_3$O$_3$P$_2$ | C$_{23}$H$_{40}$BCl$_2$F$_4$MoN$_3$O$_3$P$_2$ | C$_{32}$H$_{26}$BF$_4$N$_3$O$_3$P$_2$W |
| Fw      | 737.48 | 745.25 | 722.17 | 833.16 |
| Cryst size, mm | 0.30 × 0.17 × 0.15 | 0.42 × 0.35 × 0.28 | 0.32 × 0.30 × 0.14 | 0.24 × 0.08 × 0.06 |
| Color, shape | yellow block | yellow block | yellow plate | yellow column |
| Cryst syst | monoclinic | orthorhombic | monoclinic | orthorhombic |
| Space group | P2$_1$/n (No. 14) | Pnca (No. 61) | Pnca (No. 61) | Pnca (No. 61) |
| a, Å    | 8.9480(2) | 17.4696(5) | 17.4696(5) | 17.5150(4) |
| b, Å    | 16.2069(4) | 23.4895(7) | 15.5022(3) | 23.3387(5) |
| c, Å    | 21.6874(5) | 23.3940(6) | 16.2384(5) | 23.3387(5) |
| α, deg | 90 | 90 | 90 | 90 |
| β, deg | 95.412(3) | 90 | 90 | 90 |
| γ, deg | 104.306(3) | 90 | 90 | 90 |
| θ range, deg | 1.89–30.00 | 1.96–30.00 | 2.17–30.00 | 1.96–30.00 |
| No. of reflns measd | 59364 | 147535 | 103531 | 63369.2 |
| Rint | 0.0625 | 0.0507 | 0.042 | 0.075 |
| No. of unique reflns | 91399 | 7732 | 3770 | 9124 |
| No. of reflns with I > 2σ(I) | 8540 | 8380 | 8280 | 8120 |
| No. of params/restraints | 355/0 | 440/0 | 366/0 | 440/0 |
| R1 (I > 2σ(I)) | 0.0202 | 0.0576 | 0.0751 | 3.809 |
| R1 (all data) | 0.0226 | 0.0253 | 0.0253 | 0.0260 |
| wR2 (I > 2σ(I)) | 0.0470 | 0.0595 | 0.0504 | 0.0385 |

Organometallics

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127.9 (d, 13.0 Hz, Ph), 129.5 (d, inversion; the solid is therefore py), 159.3 (d, room temperature using CH2Cl2/diethyl ether (Cpy), 141.6 (s, py), 100.4 (d, °0.49 mmol) as starting materials. Yield: 207 mg (90%). Anal. Calcd for 8.15 (s, 8H, Ph), 8.25 (t, JHP = 83.6 Hz), 126.8 (d, 2H, py), 198.0 (t, J = 4.2 Hz, CH(CO)), 31P{1H} NMR (δ = 8.4 Hz, 1H, py), 8.15 (m, 8H, Ph), 7.94 (t, J = 9.4 Hz, 2H, py), 4.83 (dd, J = 23.3 Hz, JHP = 54.7 Hz, 1H, WH). 13C{1H} NMR (δ = 7.7 Hz, 2H, py), 1.59 (s, 18H, 1.30 (m, 4H, CH(CH3)2), 1.30 (m, 8H, CH(CH3)2), 1.03/1.40 e Å. The contribution of 3a-CH6 and CO). 1910 ( ν CO), 1906 ( ν CO). 1906 ( ν CO).

IR (ATR, cm−1): 2027 (vC=O), 1910 (vC=O), 1990 (vC=O).

[X(NP-rip)(CO)H]BF4 (8c). This complex was prepared analogously to 8a with 5c (200 mg, 0.30 mmol) and HBF4 (20 μL, 0.49 mmol) as starting materials. Yield: 207 mg (90%). Anal. Calcld for C54H89BF4N6O6P8W: C, 34.46; H, 4.92; N, 6.03. Found: C, 34.55; H, 5.02; N, 6.10. 1H NMR (δ, CDCl3, 20 °C): 8.47 (bs, 2H, NH), 7.50 (t, J = 8.5 Hz, 1H, py), 6.67 (d, J = 7.7 Hz, 2H, py), 2.41 (m, 4H, CH(CH3)2), 1.53 (s, 18H, CH(CH3)2)), 1.04 (d, J = 6.4 Hz, py), 1.19 (s, J = 12.5 Hz, Ph), 127.9 (d, J = 4.6 Hz, Ph), 102.0 (d, J = 9.4 Hz, py). 31P{1H} NMR (δacetonite-d6 − 60 °C): 95.5 (d, Jpp = 85.9 Hz), 84.8 (d, Jpp = 85.9 Hz). IR (ATR, cm−1): 2038 (vC=O), 1963 (νC=O), 1918 (νC=O).

Supporting Information. Variants are as follows. The solid-state structure of 7a is 0.540(3)/0.460(3) and in the tungsten complex 8a is 0.586(4)/0.414(4) (for C32, O3, H1, C32′, O3′, H1′; cf. Figures 7 and 9, which depict only the dominant nonprimed part). In contrast, the analogous molybdenum hydridocarbonyl complex 7d·CH3Cl1 was perfectly ordered and gave on refinement with high-quality diffraction data a hydride position in very good agreement with complexes 7a and 8a, fully supporting the split atom refinements of these two crystal structures.

Computational Details. All calculations were performed using the GAUSSIAN 09 software package33 on the Phoenix Linux Cluster of the Vienna University of Technology and the B3LYP functional33 without symmetry constraints. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SD) basis set34 to describe the electrons of the tungsten and molybdenum atoms. For all other atoms a standard 6-31g** basis set was employed.35 All geometries were optimized without symmetry constraints. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. All energies reported are Gibbs free energies and thus contain zero-point, thermal, and entropy effects at 298 K and 1 atm pressure. A natural population analysis (NPA)36 and the resulting Wiberg indices27 were used to study the electronic structure and bonding of the optimized species. The NPA analysis was performed with the NBO 5.0 program.37

ASSOCIATED CONTENT

Supporting Information
CIF files giving complete crystallographic data and technical details for complexes 3a, 4b, 4d, 5c, 7a-d, and 8a. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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