FULL PAPER

Molybdenum Nitrosyl Complexes and Their Application in Catalytic Imine Hydrogenation Reactions

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The reaction between [Mo(CO)$_4$(NO)(ClAlCl$_3$)] and the sterically hindered diphosphanes (P∩P) 1,3-bis(diisopropylphosphanyl)propane (dippp, **a**), 1,2-bis(diisopropylphosphanyl)ethane (dippe, **b**), 1,1′-bis(diisopropylphosphanyl)ferrocene (dippf, **c**) and 1,2-bis(dicyclohexylphosphanyl)ethane (dcype, **d**) produced the chlorides [Mo(P∩P)(CO)$_2$(NO)Cl] (**1a–1d**), which were transformed into the corresponding hydrides [Mo(P∩P)(CO)$_2$(NO)H] (**2a–2d**) by reaction with LiBH$_4$ in Et$_3$N at room temperature. The molybdenum–THF complex [Mo(dippp)(CO)$_2$(NO)(THF)][BAr$^F_4$] [**3a**; Ar^F = 3,5-(CF$_3$)$_2$-C$_6$H$_3$], obtained by the reaction of **2a** with [H(Et$_2$O)$_2$][BAr$^F_4$], was exemplarily tested in the hydrogenation of the imine PhCH=N(α-naphthyl). Replacement of the [BAr$^F_4$]$^-$ counterion by the more stable [B(C$_6$F$_5$)$_4$]$^-$ anion greatly increased the catalytic activity. The use of in situ mixtures of the hydrides **2a–2d** and [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] improved the hydrogenation activity. The hydride **2b** in combination with [H(Et$_2$O)$_2$]-[B(C$_6$F$_5$)$_4$] exhibited the highest TOF value of 123 h^{-1} in the reduction of PhCH=N(α-naphthyl). The hydrogenation of the imines PhCH=NPh, p-ClC$_6$H$_4$CH=NPh, p-ClC$_6$H$_4$CH=N-p-C$_6$H$_4$Cl, PhCH=NCH(Ph)$_2$ and PhCH=NMes showed TOF values of 34, 74, 41, 18 and 84 h^{-1} at room temperature and a H$_2$ pressure of 30 bar. A mechanism for the ionic hydrogenation with "proton-before-hydride transfer" is anticipated.

Introduction

Homogeneous hydrogenation reactions are crucial in the production of numerous fine chemicals. Wilkinson- or Osborn-type catalysts[1] are normally used in reactions involving the formal homolytic splitting of H$_2$.[2] These types of catalytic transformations are particularly suited to the hydrogenation of olefinic compounds. "Ionic hydrogenation", operating by the heterolytic cleavage of H$_2$, is largely a new approach.[3,4] It involves the transfer of a hydride (H$^-$) or proton (H$^+$) as a H$_2$ equivalent to the substrate.[5] Various catalytic systems enable the efficient hydrogenation of ketones[6–8] and imines[9–13] by Wilkinson/Osborn-type or ionic hydrogenation. However, most of these processes are presently based on precious metals, which require tedious catalyst recycling for economic and toxicity reasons. Therefore a global research approach has been initiated to develop non-precious metal catalysts.[14,15] Bullock and coworkers reported some molybdenum and tungsten complexes [Cp(CO)$_2$M(L)]$^+$[A]$^-$ {M = Mo, W; L = phosphane, carbene; A = BAr$^F_4$ [Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$], B(C$_6$F$_5$)$_4$} that showed catalytic activity in ketone hydrogenation,[16–20] but the TOF values achieved were still quite low. Mechan-

istic studies supported the "ionic hydrogenation" pathway with proton-before-hydride transfer.[4] Furthermore, in related systems, Kubas and co-workers demonstrated the crucial influence of phosphane substitution on hydrogen activation through their electron-donating capability.[21–24] For example, the complexes [Mo(CO)(iBu$_2$PCH$_2$CH$_2$PiBu$_2$)$_2$] bearing strong electron-donating ligands can split the H$_2$ molecule at ambient temperature to form a dihydride Mo(H)$_2$ species, whereas the structurally similar [Mo(CO)-(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] complex coordinates the hydrogen molecule with an elongated H–H bond. In isoelectronic cationic bis(diphosphane)nitrosylmolybdenum and -tungsten complexes the H$_2$ ligand adds oxidatively to form dihydride complexes.[25] H$_2$ complexes are normally more acidic than the corresponding dihydride complexes. Therefore the former species are preferably involved in heterolytic splitting by deprotonation and the latter foster catalyses of the Wilkinson type. The presence of nitrosyl ligands is expected to reduce the binding strength of H$_2$ ligands and enhance their acidity thus promoting the heterolytic splitting of H$_2$.[26,27] In addition we would expect for the deprotonated dihydrogen complexes the weakening of the resulting metal–hydride bonds to facilitate hydride transfers onto unsaturated compounds.[28,29]

Based on this we supposed that (diphosphane)nitrosyl complexes of the type [Mo(NO)(P∩P)(CO)$_2$L][A] (L = labile ligand) might render catalytic ionic hydrogenation systems, particularly for imine hydrogenations with proton-before-hydride transfer characteristics.

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Results and Discussion

Synthesis and Characterization

The addition of 1 equiv. of the ligand dippp [dippp = 1,3-bis(diisopropylphosphanyl)propane] to a THF solution of $[Mo(CO)_4(NO)ClAlCl_3]$ revealed the formation of the chloride compound $[Mo(dippp)(NO)(CO)_2(Cl)]$ (**1a**; Scheme 1), which was isolated in 75% yield. The $^{31}P\{^1H\}$ NMR spectrum of **1a** exhibits a single resonance at $\delta = 21.5$ ppm, which indicates the presence of two equivalent phosphorus atoms. The ^1H NMR spectrum of **1a** shows two multiplets at $\delta = 2.36$ and 2.27 ppm, attributed to the –CH protons of the isopropyl groups. In the $^{13}C\{^1H\}$ NMR spectrum the characteristic signal of the CO ligands appears as a doublet of doublets at $\delta = 215.9$ ppm ($^2J_{CP} = 22.9$ Hz). The IR spectrum reveals strong bands at 2019, 1950 [$\nu(CO)$] and 1610 cm^{-1} [$\nu(NO)$]. X-ray diffraction studies of **1a** confirmed the spectroscopically derived pseudo-octahedral structures. An ORTEP drawing of **1a** is presented in Figure 1.
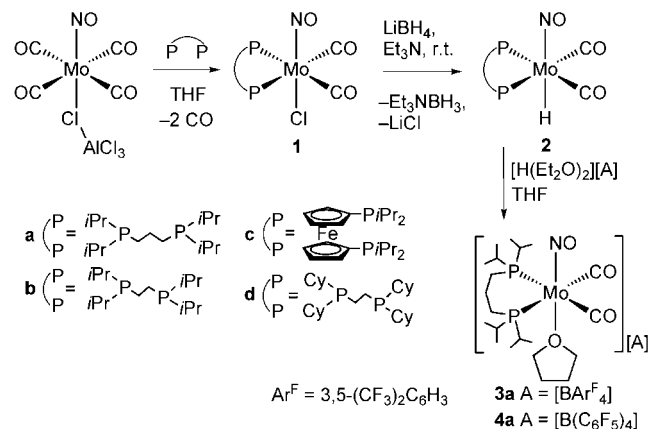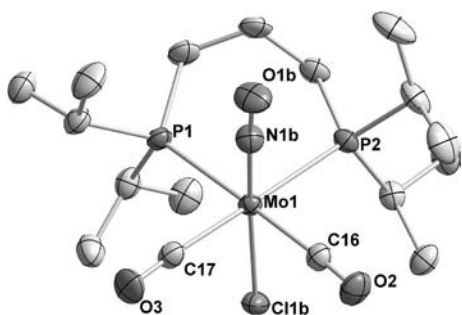

Scheme 1.

Figure 1. ORTEP drawing of $[Mo(dippp)(NO)(CO)_2(Cl)]$ (**1a**). Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms and the positional disorder of NO and Cl have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **1a**: Mo1–P1 2.5576(4), Mo1–P2 2.5780(5), Mo1–C17 2.043(2), Mo1–C16 2.034(2), C17–O3 1.130(2), C16–O2 1.134(2), N1B–O1B 1.218(12), P1–Mo1–P2 90.13(1), C17–Mo1–C16 89.75(7).

The crystal structure of **1a** reveals a disorder between the Cl atom and the *trans*-nitrosyl group. The phosphorus atoms and the two carbon atoms of the carbonyl groups

are in-plane with the metal. The average Mo–P bond length is 2.5678(5) Å.

Treatment of the chloride **1a** with 5 equiv. of $LiBH_4$ in Et_3N at room temperature resulted in the formation of the hydride complex **2a** (Scheme 1).[25] The $^{31}P\{^1H\}$ NMR spectrum of **2a** exhibits a singlet at $\delta = 41.1$ ppm, which indicates the equivalence of the phosphane coordination. In addition to multiplets attributed to the resonance of the dippp protons, a characteristic triplet for the hydride ligand is observed in the ^1H NMR spectrum at –2.28 ppm ($^2J_{PH} = 24.0$ Hz). In the $^{13}C\{^1H\}$ NMR spectrum of **2a** the doublet of doublets at $\delta = 226.0$ ppm ($^2J_{CP} = 10.7$ Hz) has been attributed to the carbonyl ligands. The IR spectrum of **2a** reveals strong bands at 1983, 1910 [$\nu(CO)$], 1653 [$\nu(MoH)$] and 1570 [$\nu(NO)$] cm^{-1}.

An X-ray diffraction study was carried out on **2a** (Figure 2). Similar to the chloride compound **1a**, the hydride compound **2a** displays a pseudo-octahedral coordination geometry with the phosphorus atoms of the dippp ligand and the two carbonyl ligands in-plane with the metal centre and the hydride ligand located *trans* to the nitrosyl group. Structurally related bond lengths of **2a** are similar to those of the chloride **1a**.
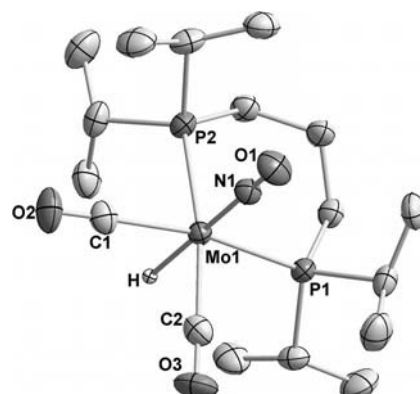

Figure 2. ORTEP drawing of $[Mo(dippp)(NO)(CO)_2(H)]$ (**2a**). Displacement ellipsoids are drawn at the 50% probability level. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **2a**: Mo1–N1 1.829(2), Mo1–P1 2.5569(6), Mo1–P2 2.5347(7), Mo1–C1 2.017(3), Mo1–C2 2.018(3), Mo1–H 1.66(3), C1–O2 1.136(4), C2–O3 1.136(4), N1–O1 1.190(3), P1–Mo1–P2 90.3(2), C1–Mo1–C2 88.1(1).

Treatment of **2a** with 1 equiv. of $[H(Et_2O)_2][BAr^F_4]$[30–32] [$Ar^F = 3,5-(CF_3)_2C_6H_3$] in THF afforded $[Mo(dippp)(NO)(CO)_2(THF)][BAr^F_4]$ (**3a**; Scheme 1), which was isolated in 69% yield. The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows a singlet at $\delta = 17.6$ ppm. In the ^1H NMR spectrum characteristic multiplet resonances of THF appear at $\delta = 3.62$ and 1.78 ppm with the integration value correlating to integrations of the dippp ligand signals. The $^{13}C\{^1H\}$ NMR spectrum reveals a carbonyl resonance at $\delta = 214.1$ ppm ($^2J_{CP} = 16.7$ Hz) and the IR spectrum of **3a** shows strong bands at 2044, 1978 [$\nu(CO)$] and 1682 [$\nu(NO)$] cm^{-1}.

The X-ray diffraction studies of **3a** (Figure 3) showed a structure with pseudo-octahedral coordination of the metal centre similar to the hydride and chloride complexes **1a** and

2a with the two phosphorus atoms of the dippp ligands and the carbonyl ligands in-plane with the metal centre. The average M–P bond length of 2.588(2) Å is slightly longer than the corresponding bond lengths in **2a**. The THF molecule is coordinated to the metal centre with a M–O bond length of 2.241(4) Å. In the related complex [(μ-H)W$_2$(CO)$_7$-(THF)$_2$(NO)][33] one THF molecule is also located *trans* to the nitrosyl ligand.
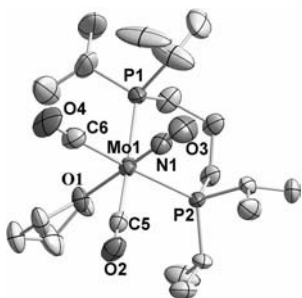
Figure 3. ORTEP drawing of [Mo(dippp)(NO)(CO)$_2$(THF)]-[BAr$^F_4$] (**3a**). Displacement ellipsoids are drawn at the 50% probability level. Only the main residues (without counterion and free solvent molecules) are shown. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **5a**: Mo1–N1 1.780(6), Mo1–P1 2.582(2), Mo1–P2 2.5840(15), Mo1–O1 2.241(4), Mo1–C6 2.053(8), Mo1–C5 2.060(7), C6–O4 1.12(1), C5–O2 1.12(1), N1–O3 1.188(7), P1–Mo1–P2 88.40(5), C1–Mo1–C2 87.6(3), O1–Mo1–N1 173.3(3).

The reaction of **2a** with [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] produced the cationic complex [Mo(dippp)(NO)(CO)$_2$(THF)]-[B(C$_6$F$_5$)$_4$] (**4a**). The ^{31}P{^{1}H} NMR spectrum exhibits a singlet resonance at δ = 16.5 ppm for the dippp ligand. The ^{13}C{^{1}H} NMR spectrum shows a doublet of doublets at δ = 214.0 ppm ($^2J_{CP}$ = 22.1 Hz) attributed to the carbonyl ligands. The IR spectrum of **4a** displays two strong ν(CO) bands at 2038 and 1970 cm^{-1} and a ν(NO) band at 1668 cm^{-1}. However, the elemental analysis did not match the expected values presumably due to the fact that **4a** is an oil and could not be isolated in crystalline form. We supposed that the substance contained an excess of THF, which could not be removed in vacuo and prevented **4a** from crystallization.

A study of the influence of phosphane ligands on the reactivity of the complexes was attempted by the preparation of a series of molybdenum hydrides with different phosphane ligands (Scheme 1). The chlorides **1b**–**1d** were prepared by the reaction of [Mo(CO)$_4$(NO)ClAlCl$_3$] with the diphosphane ligands 1,2-bis(diisopropylphosphanyl)-ethane (dippe, **b**), 1,1′-bis(diisopropylphosphanyl)ferrocene (dippf, **c**) and 1,2-bis(dicyclohexylphosphanyl)ethane (dcype, **d**) in THF at room temperature. Then the chlorides were treated with excess LiBH$_4$ in Et$_3$N to afford the hydride complexes **2b**–**2d**. The NMR and IR spectra reveal the close structural relationships between **1b**–**1d** and **1a** and between **2b**–**2d** and **2a**. The spectroscopic data for compounds **1** and **2** are summarized in Table 1.

Table 1. Selected spectroscopic data for **1a**–**d** and **2a**–**d**.

	δ(MoP) [ppm]	δ(MoH) [ppm]	δ(CO) [ppm]	IR vibration frequency [cm^{-1}]		
				ν(CO)	ν(MH)	ν(NO)
1a	21.5		215.9	2019	1950	1610
1b	61.1		217.1	2020	1949	1611
1c	29.8		216.5	2021	1950	1610
1d	53.5		217.4	2022	1948	1614
2a	41.1	–2.28	226.0	1983	1910	1653	1570
2b	84.5	–3.44	226.8	1983	1910	1653	1570
2c	48.3	–1.20	226.2	1981	1902	1637	1574
2d	53.5	–3.25	227.1	1986	1920	1647	1574

Complexes **1d** and **2b** were additionally characterized by X-ray diffraction analyses. The ORTEP drawings of **1d** and **2b** are shown in Figure 4. Similarly to **1a** the structure of **1d** displays a pseudo-octahedral coordination geometry with two phosphane atoms and two carbonyls in-plane with the molybdenum centre. The asymmetric unit of **1d** contains one half of the molecule as the metal centre lies on a crystallographic two-fold axis. Consequently, the *trans* Cl and NO ligands are positionally disordered with an occupancy ratio of 0.5. The Mo–P bond length is 2.5319(7) Å, which is slightly shorter than the corresponding mean value of **1a**, presumably due to the smaller bite angle of the dcype ligand in comparison with the dippp derivative.[34] A similar tendency can be observed on comparing the bond lengths of **2a** and **2b**. The mean Mo–P bond length in **2b** is 2.513 Å, whereas the mean Mo–P bond length in **2a** was found to be 2.546 Å. The Mo1–H bond is rather long [1.83(4) Å], which indicates the suitability of such a complex for hydride transfer processes.
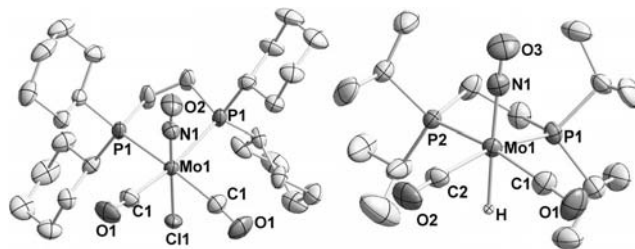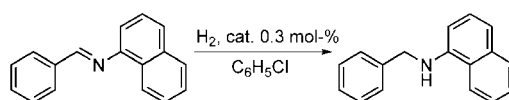
Figure 4. ORTEP drawings of [Mo(dcype)(NO)(CO)$_2$(Cl)] (**1d**) and [Mo(dippe)(NO)(CO)$_2$(H)] (**2b**). Displacement ellipsoids are drawn at the 50% probability level. Selected hydrogen atoms and the positional disorder of NO and Cl in **1d** have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **1d**: Mo1–N1 1.772(5), Mo1–P1 2.5319(7), Mo1–Cl1 2.517(3), Mo1–C1 2.043(2), C1–O1 1.135(4), N1–O2 1.195(6) Cl1B–Mo1–N1B 179.4(2), P1–Mo1–P1 81.23(2), C1–Mo1–C1 89.0(1). Selected bond lengths [Å] and angles [°] for **2b**: Mo1–N1 1.868(3), Mo1–P1 2.5054(8), Mo1–P2 2.5205(8), Mo1–H 1.83(4), Mo1–C1 2.007(3), Mo1–C2 2.023(3), C1–O1 1.148(7), C2–O2 1.137(4), N1–O3 1.152(4), P1–Mo1–P2 80.26(3), C1–Mo1–C2 90.1(1).

Imine Hydrogenation

Complex **3a** was first tested as a catalyst in the hydrogenation of the imine PhCH=N(α-naphthyl). The reaction was carried out at 10 bar H$_2$ and 80 °C in C$_6$H$_5$Cl.[35] However,

only 5% conversion of the imine was observed (Table 2). A kinetic analysis demonstrated that the reaction proceeded well during the initial 30 min after which the catalyst decomposed presumably due to the limited stability of the $[BAr^F_4]^-$ counterion.[36,37] We therefore looked for an alternative more stable counterion. The $[B(C_6F_5)_4]^-$ anion is known to display a lower coordination ability and higher stability towards fluorine abstraction than $[BAr^F_4]^-$.[38]

Table 2. Catalytic hydrogenation of PhCH=N(α-naphthyl).

Entry	Cat.	Pressure [bar]	Temp. [°C]	Initial TOF [h^{-1}]	Conv. [%]	Reaction time [h]
1	**3a**	10	80	–	5	0.5
2	**2a**[a]	30	r.t.	106	>99	13
3	**4a**	30	r.t.	95	>99	14
4	**2b**[a]	30	r.t.	123	>99	11
5	**2c**[a]	30	r.t.	68	>99	16
6	**2d**[a]	30	r.t.	50	>99	19

[a] A mixture of the corresponding hydride and $[H(Et_2O)_2][B(C_6F_5)_4]$ was used as a catalyst.

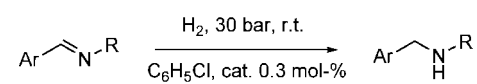The use of **4a** as the catalyst in the imine hydrogenation of PhCH=N(α-naphthyl) revealed 100% conversion of the substrate and a TOF value of 95 h^{-1} in the first hour at room temperature under a H$_2$ pressure of 30 bar (Table 2). An increase in temperature led to significantly lower conversions, presumably due to the decomposition of the catalyst during catalysis. Note that no hydrogenation was observed when the reaction was conducted in THF as solvent. Moreover, more quantitative experiments, in which THF was initially added to the reaction mixture in various amounts, demonstrated an inverse dependence of the rate of hydrogenation on the amount of added THF. We supposed that THF acts as a ligand and thereby blocks catalytically crucial vacant sites of various intermediates and consequently reduces the catalytic turnover. Hydrogenation reactions without the involvement of THF were also realized by the direct use of the pure hydride **2a** and $[H(Et_2O)_2]$-$[B(C_6F_5)_4]$ as a co-catalyst. Solutions of the substrate in C_6H_5Cl were added to this mixture and pressurized with 30 bar of H$_2$. This approach revealed a slightly higher rate of hydrogenation (TOF = 105 h^{-1}) than with pure **4a**.

To study the influence of the bite angle of the diphosphane ligands[39] on the reactivity the hydrides **2b**–**2d** were also tested in the hydrogenation of PhCH=N(α-naphthyl) (Table 2). The lowest rate of hydrogenation was found for **2d** (initial TOF = 50 h^{-1}), presumably due to the high steric congestion of the cyclohexyl substituent of the dcype ligand, which prevents a facile approach of the PhCH=N(α-naphthyl) substrate to the metal centre. Complexes **2a**–**2c** showed a strong dependence of the diphosphane bite angle[40] on the rate of hydrogenation. Complex **2c** with the largest bite angle in this series demonstrated the lowest activity (initial TOF = 68 h^{-1}), whereas the hydrides **2a** and **2b**

exhibited significantly higher rates of hydrogenation (initial TOF values: 106 h^{-1} for **2a**, 123 h^{-1} for **2b**). Most likely, the shorter bridge "pulls" the sterically demanding isopropyl group to one side opening up another side of the molecule to allow the substrate enter.

The hydride **2b** showed the best catalytic performance of all the experiments with PhCH=N(α-naphthyl) and was therefore used in the hydrogenation of other imines. The results of these catalytic experiments are presented in Table 3.

Table 3. Catalytic hydrogenation of imines with **2b** as catalyst.


cat. = **2b** + $[H(Et_2O)_2][B(C_6F_5)_4]$

Entry	Substrate	TOF [h^{-1}]	Conv. [%]	Reaction time [h]
1	PhCH=N(α-naphthyl)	123	>99	11
2	PhCH=NPh	34	80	24
3	p-ClC$_6$H$_4$CH=NPh	74	96	16
4	p-ClC$_6$H$_4$CH=N-p-C$_6$H$_4$Cl	41	66	17
5	PhCH=NCHPh$_2$	18	45	35
6	PhCH=NMes	84	>99	20
7	PhCH=N*i*Bu	–	≈0.3	–

A mechanism for the hydrogenation of imines with the Mo catalysts is presented in Scheme 2. The initial protonation of the hydride results in a short-lived dihydrogen complex,[41] which is the key species that drives the catalytic cycle. An iminium salt might then be formed by proton transfer from the acidic dihydrogen complex.[4,13] To validate the iminium as a key intermediate in the hydrogenation, a reduction was carried out in which a catalytic amount of separately obtained iminium salt and **2b** were used. This experiment did not reveal any significant difference in the rate of hydrogenation and conversion compared with the result described above (Table 2, entry 1). Both the imine and amine product are expected to be involved in a protolytic equilibrium, which would require that the electrophilic iminium as a reactant is present in sufficient concentration that subsequent hydride transfer could become kinetically feasible. The deprotonation of the dihydrogen ligand comprises the heterolytic splitting of H$_2$ and this presumably is the rate-limiting step. The highest rates of hydrogenation were observed with more bulky substrates (entries 1 and 6, Table 3), which apparently facilitate the amine dissociation from the molybdenum centre required for re-entry of H$_2$ into the cycle. Amine, imine and H$_2$ coordination have to be considered competitive.

Crucial to the course of the hydrogenation reaction is the formation of the iminium cation, which competes with the formation of the ammonium salt produced from the protonation of the amine products. All imine/amine pairs with aryl substituents generally showed low basicities, but the imine is the stronger base. Conversely, the basicities of alkyl-substituted imine/amine are generally higher with the
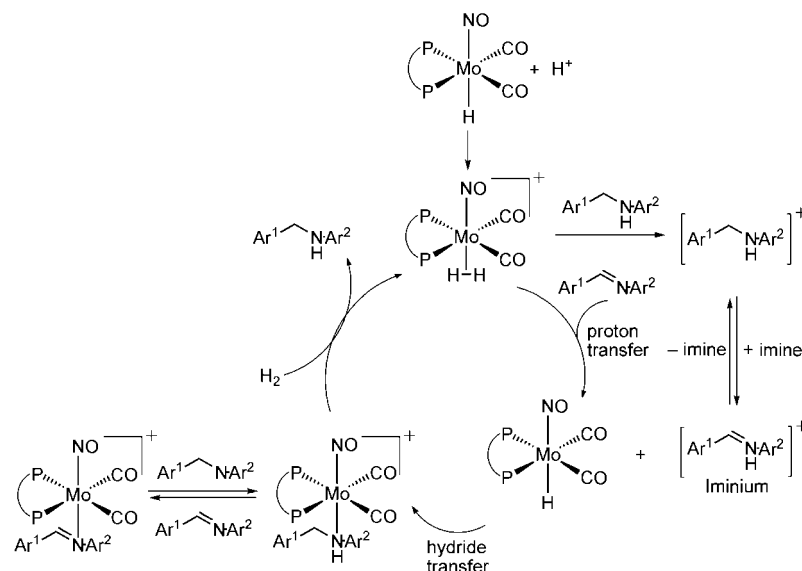
Scheme 2. Mechanism of imine hydrogenation following a proton-before-hydride transfer scheme.

amine more basic than the corresponding imine derivatives. Thus, we anticipated that the hydrogenation of aniline derivatives could be readily accomplished because their imines are stronger bases than the amines and the iminium cation should therefore be available in kinetically relevant concentrations. In the case of alkylimine derivatives (entries 5 and 7, Table 3) we could not achieve satisfactory conversions probably due to the fact that the amine is the stronger base and would consume a significant proportion of the protons thus blocking their involvement in the catalytic cycle. The alkylamines would also be stronger ligands and could block the metal centre if not enough protons can be supplied to scavenge the amine as an ammonium salt. In the case of N-alkyl-substituted PhCH=NCHPh₂, the basicities of the amine and the imine are presumably comparable and the reaction was found to stop when a certain amount of amine is produced, which would be in accord with the given rationalization of the protolytic equilibrium.

The difference in pK_b of the PhCH=N*i*Bu/PhCH₂NH*i*Bu pair seems to be so high that only the amine is expected to be present in the protonated form. Indeed, the rate of hydrogenation of this compound was zero. Presumably the low yield of the reaction of entry 4 of Table 3 with a chlorine-containing substrate can be related to a blocking of the molybdenum centre with chloride released during catalysis.[42]

Conclusions

A series of hydride complexes of the type [Mo(P∩P)-(CO)₂(NO)H] bearing bulky diphosphane ligands have been prepared by the reaction of [Mo(P∩P)(CO)₂(NO)Cl] with LiBH₄ in Et₃N at room temperature. In combination with [H(Et₂O)₂][B(C₆F₅)₄] the hydrides showed valuable catalytic activity in the hydrogenation of the imine PhCH=N(α-naphthyl). The widely used [BАrF₄]⁻ counterion apparently

is too unstable under the conditions employed in the imine hydrogenations. In contrast, in the presence of the [B(C₆F₅)₄]⁻ anion the reactive 16e⁻ molybdenum centre possesses enough stability and flexibility to promote the proper exchanges of weak ligands. The complex [Mo(dippe)-(CO)₂(NO)H] (**2b**) displayed the best activity with an initial TOF of 123 h⁻¹ in the hydrogenation of PhCH=N(α-naphthyl). This hydride was also tested as a catalyst to hydrogenate various other aryl imines. The hydrogenation of alkyl imines was found to be inferior to aryl imines. All these observations can be explained on the basis of an "ionic hydrogenation" pathway occurring with heterolytic cleavage of H₂ and "proton-before-hydride" transfer.

Experimental Section

General: Reagent-grade benzene, toluene, pentane, diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl prior to use. Acetone and CH₂Cl₂ were dried with CaH₂ and then distilled. Literature procedures were used to prepare the following compounds: 1,3-bis(diisopropylphosphanyl)propane (dippp),[43] 1,2-bis(diisopropylphosphanyl)ethane (dippe), 1,2-bis(dicyclohexylphosphanyl)ethane (dcype),[44] 1,1′-bis(diphenylphosphanyl)ferrocene (dippf),[45] [H(Et₂O)₂][BArF₄],[46] [H(Et₂O)₂]-[B(C₆F₅)₄][38] and [Mo(CO)₄(NO)(ClAlCl₃)].[47] Other reagents were purchased and used without further purification. All the manipulations were carried out under nitrogen using Schlenk techniques or in a dry glovebox. IR spectra were obtained with a Bio-Rad FTS-45 instrument. NMR spectra were recorded with Varian Mercury 200 (200.1 MHz for ¹H, 81.0 MHz for ³¹P{¹H}), Bruker DRX 500 (500.2 MHz for ¹H, 202.5 MHz for ³¹P{¹H}, 125.8 MHz for ¹³C{¹H}) and Bruker DRX 400 spectrometers (400.1 MHz for ¹H, 162.0 MHz for ³¹P{¹H}, 100.6 MHz for ¹³C{¹H}). Chemical shifts in ¹H and ¹³C{¹H} NMR spectra are given in ppm relative to TMS (SiMe₄), the resonances in the ³¹P{¹H} NMR spectra are referenced to 98% external H₃PO₄. Elemental analyses were performed with a Leco CHN(S)-932 instrument. The hydrogen pressure in the catalytic reactions was monitored with "WIKA" Transmitter CPT

2500 instrument. The GC–MS spectra were recorded with a Varian Saturn 2000 spectrometer equipped with a Varian 450-GC chromatograph. Gas flow: 1.0 mL/min. Temperature regime: 70 °C, 0.5 min hold, then 20 °C/min. The following column was used: VF-5ms 30.0 m×0.25 mm, ID = 0.25 mm.

General Procedure for the Synthesis of the Diphosphane-Substituted Complexes [Mo(P∩P)(CO)$_2$(NO)Cl] (1a–1d): A solution of the diphosphane ligand (1.0 mmol) in THF (10 mL) was added to a solution of [Mo(CO)$_4$(NO)ClAlCl$_3$] (1.0 mmol) in THF (15 mL). The reaction mixture was stirred for 10 h at room temperature. Then the solvent was removed in vacuo. The residue was extracted with Et$_2$O until the extracted solution became colourless. The combined Et$_2$O fractions were concentrated to the half of their original volume and cooled to –30 °C. The precipitate formed was filtered off and dried in vacuo.

[Mo(dippp)(CO)$_2$(NO)Cl] (1a): Yield 75%, 372.2 mg. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$, 25 °C): δ = 2.36 [m, 2 H, PCH(CH$_3$)$_2$], 2.27 [m, 2 H, PCH(CH$_3$)$_2$], 2.12 (m, 4 H, PCH$_2$CH_2CH$_2$P), 1.90 (m, 8 H, PCH_2CH$_2$CH_2P), set of multiplets from 1.33 to 1.25 (24 H, CH_3) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 25 °C): δ = 21.5 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 25 °C): δ = 215.9 (dd, $^2J_{CP}$ = 38.2, $^2J_{CP}$ = 22.7 Hz, CO), 27.4 [m, PCH(CH$_3$)$_2$], 26.6 [m, PCH(CH$_3$)$_2$], 21.9 (m, PCH$_2$CH_2CH$_2$P), 20.0 (m, PCH$_2$CH_2CH$_2$P), 19.9 (s, CH_3), 19.7 (s, CH_3), 19.1 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 2019, 1950 (CO) 1610 (NO) cm^{-1}. C$_{17}$H$_{34}$ClMoNO$_3$P$_2$ (493.8): calcd. C 41.35, H 6.94, N 2.84; found C 41.08, H 7.04, N 2.69.

[Mo(dippe)(CO)$_2$(NO)Cl] (1b): Yield 43%, 205.9 mg. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$, 25 °C): δ = 2.41 [m, 2 H, PCH(CH$_3$)$_2$], 2.30 [m, 2 H, PCH(CH$_3$)$_2$], 1.94 (m, 4 H, PCH_2CH_2P), set of multiplets from 1.37 to 1.23 (24 H, CH_3) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 25 °C): δ = 61.1 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 25 °C): δ = 217.0 (dd, $^2J_{CP}$ = 51.3, $^2J_{CP}$ = 10.7 Hz, CO), 25.6 [m, PCH(CH$_3$)], 24.0 [m, PCH(CH$_3$)$_2$], 22.9 (dd, $^1J_{CP}$ = 17.9, $^1J_{CP}$ = 14.3 Hz, PCH_2CH_2P), 20.5 (s, CH_3), 20.3 (s, CH_3), 20.2 (s, CH_3), 18.6 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 2020, 1949 (CO), 1611 (NO) cm^{-1}. C$_{16}$H$_{32}$ClMoNO$_3$P$_2$ (479.8): calcd. C 40.05, H 6.72, N 2.92; found C 40.21, H 6.63, N 2.81.

[Mo(dippf)(CO)$_2$Cl] (1c): Yield 64%, 406.8 mg. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$, 25 °C): δ = 4.56 (s, 2 H, Cp), 4.45 (s, 2 H, Cp), 4.44 (s, 2 H, Cp), 4.41 (s, 2 H, Cp), 2.55 [m, 4 H, PCH-(CH$_3$)$_2$], set of multiplets from 1.55 to 1.23 (24 H, CH_3) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 25 °C): δ = 29.8 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 25 °C): δ = 216.5 (dd, $^2J_{CP}$ = 61.2, $^2J_{CP}$ = 18.1 Hz, CO), 76.4 [m, PC(CH)$_2$(CH)$_2$], 75.6 [t, $^2J_{CP}$ = 5.0 Hz, PC(CH)$_2$(CH)$_2$] 75.3 [t, $^2J_{CP}$ = 4.0 Hz, PC(CH)$_2$(CH)$_2$], 71.7 [t, $^2J_{CP}$ = 2.0 Hz, PC(CH)$_2$(CH)$_2$], 71.4 [t, $^2J_{CP}$ = 2.0 Hz, PC(CH)$_2$(CH)$_2$], 29.2 [t, $^1J_{CP}$ = 8.03 Hz, PCH(CH$_3$)$_2$], 28.7 [t, $^1J_{CP}$ = 9.0 Hz, PCH(CH$_3$)$_2$], 20.9 (s, CH_3), 20.5 (s, CH_3), 19.8 (s, CH_3), 18.8 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 2021, 1950 (CO) 1610 (NO) cm^{-1}. C$_{24}$H$_{36}$ClFeMoNO$_3$P$_2$ (635.7): calcd. C 45.34, H 5.71, N 2.20; found C 45.23, H 5.80, N 2.15.

[Mo(dcype)(CO)$_2$(NO)Cl] (1d): Yield 83%, 265.6 mg. ^{1}H NMR (500.2 MHz, CD$_2$Cl$_2$, 25 °C): set of multiplets from 2.2 to 1.1. ^{31}P{^{1}H} NMR (202.5 MHz, CD$_2$Cl$_2$, 25 °C): δ = 53.5 (s) ppm. ^{13}C{^{1}H} NMR (160.5 MHz, CD$_2$Cl$_2$, 25 °C): δ = 217.4 (dd, $^2J_{CP}$ = 51.3, $^2J_{CP}$ = 10.7 Hz, CO), 35.9 (m, PCH), 34.0 (m, PCH), 30.7 (s, Cy), 30.6 (s, Cy), 30.3 (s, Cy), 29.1 (s, Cy), 28.1 (m, Cy), 27.8 (m, Cy), 27.7 (m, Cy), 26.7 (s, Cy), 26.6 (s, Cy), 21.0 (dd, $^1J_{CP}$ = 17.9, $^1J_{CP}$ = 14.3 Hz, PCH_2CH_2P) ppm. IR (ATR): $\tilde{v}$ = 2022, 1948 (CO), 1614 (NO) cm^{-1}. C$_{28}$H$_{48}$ClMoNO$_3$P$_2$ (640.0): calcd. C 52.54, H 7.56, N 2.19; found C 52.38, H 7.47, N 2.15.

General Procedure for the Synthesis of the Diphosphane-Substituted Hydrides [Mo(P∩P)(CO)$_2$(NO)H] (2a–2d): Et$_3$N (10 mL) was added to a mixture of [Mo(P∩P)(CO)$_2$(NO)Cl] (0.25 mmol) and LiBH$_4$ (27.5 mg, 1.25 mmol). The reaction mixture was stirred at room temperature until no trace of the starting material [monitoring with ^{31}P(^{1}H) NMR] was observed (≈10 h). The Et$_3$N was removed in vacuo. The residue was extracted with benzene until the extracted solution became colourless. After removal of the benzene the residue was extracted again with hexane until the extracted solution became colourless. Then the combined hexane fractions were concentrated to half of their original volume and cooled to –30 °C. The precipitate formed was filtered off and dried in vacuo.

[Mo(dippp)(CO)$_2$(NO)H] (2a). Yield 67%, 76.8 mg. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 25 °C): set of multiplets from 1.82 to 1.62 [4 H, PCH(CH$_3$)$_2$], set of multiplets from 1.62 to 1.28 (6 H, PCH_2CH_2CH_2P), set of multiplets from 1.15 to 0.79 (24 H, CH_3), –2.28 (t, $^2J_{PH}$ = 24.0 Hz, 1 H, Mo-H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$, 25 °C): δ = 41.1 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 226.0 (t, $^2J_{CP}$ = 10.7 Hz, CO), 29.2 [t, $^1J_{CP}$ = 10.7 Hz, PCH(CH$_3$)$_2$], 27.6 [t, $^1J_{CP}$ = 13.1 Hz, PCH-(CH$_3$)$_2$], 22.7 (t, $^2J_{CP}$ = 4.8 Hz, PCH$_2$CH_2CH$_2$P), 20.0 (t, $^1J_{CP}$ = 9.5 Hz, PCH_2CH$_2$CH_2P), 19.6 (s, CH_3), 18.8 (s, CH_3), 18.8 (s, CH_3), 17.5 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 1983, 1910 (CO), 1653 (MoH), 1570 (NO) cm^{-1}. C$_{17}$H$_{35}$MoNO$_3$P$_2$ (459.4): calcd. C 44.45, H 7.68, N 3.05; found C 44.27, H 7.99, N 3.10.

[Mo(dippe)(CO)$_2$(NO)H] (2b): Yield 53%, 59.4 mg. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 25 °C): δ = 1.78 [m, 2 H, PCH(CH$_3$)$_2$], 1.67 [m, 2 H, PCH(CH$_3$)$_2$], 1.18 (m, 4 H, PCH_2CH_2P), set of multiplets from 1.09 to 0.81 (24 H, CH_3), 3.43 (t, $^2J_{PH}$ = 26.3 Hz, 1 H, Mo-H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$, 25 °C): δ = 84.5 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 226.8 (dd, $^2J_{CP}$ = 33.4, $^2J_{CP}$ = 10.7 Hz, CO), 28.3 [m, PCH(CH$_3$)$_2$], 26.7 [m, PCH(CH$_3$)$_2$], 22.5 (t, $^1J_{CP}$ = 15.5 Hz, PCH_2CH_2P), 19.7 (s, CH_3), 19.5 (s, CH_3), 19.3 (s, CH_3), 18.8 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 1983, 1910 (CO), 1653 (MoH), 1570 (NO) cm^{-1}. C$_{16}$H$_{33}$MoNO$_3$P$_2$ (445.3): calcd. C 43.15, H 7.47, N 3.15; found C 42.71, H 7.79, N 3.18.

[Mo(dippf)(CO)$_2$(NO)H] (2c): Yield 49%, 74.6 mg. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 25 °C): δ = 4.17 (s, 2 H, Cp), 4.03 (s, 2 H, Cp), 4.01 (s, 2 H, Cp), 3.98 (s, 2 H, Cp), 2.12 [m, 4 H, PCH(CH$_3$)$_2$], set of multiplets from 1.27 to 0.96 (24 H, CH_3), –1.20 (t, $^2J_{PH}$ = 23.6 Hz, 1 H, Mo-H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$, 25 °C): δ = 48.2 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 226.2 (dd, $^2J_{CP}$ = 38.1, $^2J_{CP}$ = 11.0 Hz, CO), 76.9 [m, PC(CH)$_2$(CH)$_2$], 75.3 [t, $^2J_{CP}$ = 4.0 Hz, PC(CH)$_2$(CH)$_2$], 74.9 [t, $^2J_{CP}$ = 4.0 Hz, PC(CH)$_2$(CH)$_2$], 71.0 [t, $^2J_{CP}$ = 2.0 Hz, PC(CH)$_2$-(CH)$_2$], 70.9 [t, $^2J_{CP}$ = 2.0 Hz, PC(CH)$_2$(CH)$_2$], 29.2 [dd, $^1J_{CP}$ = 11.0, $^1J_{CP}$ = 9.0 Hz, PCH(CH$_3$)$_2$], 26.5 [dd, $^1J_{CP}$ = 12.1, $^1J_{CP}$ = 10.0 Hz, PCH(CH$_3$)$_2$], 20.0 (s, CH_3), 19.8 (s, CH_3), 19.1 (s, CH_3), 19.1 (s, CH_3) ppm. IR (ATR): $\tilde{v}$ = 1983, 1902 (CO), 1637 (MoH), 1574 (NO) cm^{-1}. C$_{24}$H$_{37}$FeMoNO$_3$P$_2$ (601.3): calcd. C 47.94, H 6.20, N 2.33; found C 47.80, H 6.11, N 2.27.

[Mo(dcype)(CO)$_2$(NO)H] (2d): Yield 63%, 95.6 mg. ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 25 °C): set of multiplets from 2.2 to 1.1, –3.25 (t, $^2J_{PH}$ = 26.3 Hz, 1 H, Mo-H) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, C$_6$D$_6$, 25 °C): δ = 53.5 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, 25 °C): δ = 227.1 (dd, $^2J_{CP}$ = 32.2, $^2J_{CP}$ = 10.7 Hz, CO), 38.0 (m, PCH), 37.0 (m, PCH), 29.9 (s, Cy), 29.8 (s, Cy), 29.2 (s, Cy), 28.9 (s, Cy), 27.8 (m, Cy), 26.8 (s, Cy), 26.6 (s, Cy), 22.6 (dd, $^1J_{CP}$ = 17.6, $^1J_{CP}$ = 15.5 Hz, PCH_2CH_2P) ppm. IR (ATR): $\tilde{v}$ = 1986, 1920 (CO), 1647 (MoH), 1574 (NO) cm^{-1}. C$_{28}$H$_{49}$MoNO$_3$P$_2$ (605.6): calcd. C 55.53, H 8.16, N 2.31; found C 55.17, H 8.34, N 2.26.

Synthesis of [Mo(dippp)(CO)$_2$(NO)(THF)][BArF$_4$] (3a): A solution of [H(Et$_2$O)$_2$][BArF$_4$] (43.8 mg, 0.043 mmol) in THF (2 mL) was slowly added to a solution of [Mo(dippp)(CO)$_2$(NO)H] (20.0 mg, 0.043 mmol) in THF (2 mL) at room temperature. The reaction mixture was stirred for 2 h. Then the solvent was evaporated in vacuo. Hexane (2 mL) was added to the residue and then the Et$_2$O was added dropwise to the suspension until the solid was completely dissolved. The solution was cooled to –30 °C to afford a precipitate of **3a** that was filtered and dried in vacuo. Yield 69%, 41.4 mg. ^{1}H NMR (400.1 MHz, [D$_8$]THF, 25 °C): δ = 7.79 (s, 8 H, *o*-Ph), 7.57 (s, 4 H, *p*-Ph), 3.62 (m, 4 H, THF), 2.48 [m, 4 H, PC*H*(CH$_3$)$_2$], 2.23 (m, 4 H, PC*H*$_2$CH$_2$C*H*$_2$P), 1.91 (m, 2 H, PCH$_2$C*H*$_2$CH$_2$P), 1.77 (m, 4 H, THF), set of multiplets from 1.39 to 1.28 (24 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, [D$_8$]THF, 25 °C): δ = 17.7 (s) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, 25 °C): δ = 214.1 (dd, $^2J_{CP}$ = 32.2, $^2J_{CP}$ = 16.7 Hz, CO), 163.0 (q, $^1J_{BC}$ = 50.0 Hz, *i*-BArF$_4$), 135.8 (s, *o*-BArF$_4$), 130.1 (m, *m*-BArF$_4$), 125.5 (q, $^1J_{CF}$ = 273.4 Hz, CF$_3$), 118.4 (s, *p*-BArF$_4$), 68.2 (s, THF), 27.9 [m, PC*H*(CH$_3$)$_2$], 26.4 (s, THF), 22.5 (t, $^2J_{CP}$ = 8.3 Hz, PC*H*$_2$CH$_2$C*H*$_2$P), 20.4 (s, C*H*$_3$), 20.1 (s, PCH$_2$C*H*$_2$CH$_2$P), 19.4 (s, C*H*$_3$), 19.1 (s, C*H*$_3$), 18.7 (s, C*H*$_3$) ppm. IR (ATR): $\tilde{v}$ = 2044, 1978 (CO), 1682 (NO) cm^{-1}. C$_{53}$H$_{54}$BF$_{24}$MoNO$_4$P$_2$ (1393.7): calcd. C 45.68, H 3.91, N 1.01; found C 45.61, H 3.78, N 1.00.

Synthesis of [Mo(dippp)(CO)$_2$(NO)(THF)][B(C$_6$F$_5$)$_4$] (4a): A solution of [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] (37.1 mg, 0.043 mmol) in THF (2 mL) was slowly added to a solution of [Mo(NO)(dippp)(CO)$_2$H] (20.0 mg, 0.043 mmol) in THF (2 mL) at room temperature. The reaction mixture was stirred for 2 h. Then the solvent was evaporated in vacuo to afford an oil that was used without further purification. ^{1}H NMR (400.1 MHz, [D$_8$]THF, 25 °C): δ = 3.37 (m, 4 H, THF), 2.59 [m, 4 H, PC*H*(CH$_3$)$_2$], 2.23 (m, 4 H, PC*H*$_2$CH$_2$C*H*$_2$P), 1.91 (m, 2 H, PCH$_2$C*H*$_2$CH$_2$P), 1.77 (m, 4 H, THF), set of multiplets from 1.38 to 1.28 (24 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, [D$_8$]THF, 25 °C): δ = 16.5 (s) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF, 25 °C): δ = 214.0 (dd, $^2J_{CP}$ = 32.1, $^2J_{CP}$ = 22.1 Hz, CO), 149.0 (br. d, $^1J_{CF}$ = 235.9 Hz, *o*-C$_6$F$_5$), 139.1 (dm, $^1J_{CF}$ = 242.1 Hz, *p*-C$_6$F$_5$), 137.0 (dm, $^1J_{CF}$ = 244.1 Hz, *m*-C$_6$F$_5$), 125.7 (br. m, *i*-C$_6$F$_5$), 68.10 (s, THF), 28.0 [m, PC*H*(CH$_3$)], 26.0 (s, THF), 22.6 (t, $^2J_{CP}$ = 8.0 Hz, PC*H*$_2$CH$_2$C*H*$_2$P), 20.5 (s, C*H*$_3$), 20.2 (s, PCH$_2$C*H*$_2$CH$_2$P), 19.5 (s, C*H*$_3$), 19.2 (s, C*H*$_3$), 18.8 (s, C*H*$_3$) ppm. IR (ATR): $\tilde{v}$ = 2038, 1970 (CO), 1668 (NO) cm^{-1}. The elemental analysis did not match the theoretical values due to presence of THF in a non-stoichiometric ratio.

General Procedure for the Catalytic Experiments: A solution of the substrate (2.0 mmol) in C$_6$H$_5$Cl (5 mL) was added to a mixture of the [Mo(P∩P)(CO)$_2$(NO)H] catalyst (0.006 mmol, 0.3 mol-%) and [H(Et$_2$O)$_2$][B(C$_6$F$_5$)$_4$] (5.0 mg, 0.006 mmol). The mixture was placed in an autoclave and pressurized with 30 bar H$_2$. The H$_2$ pressure was monitored by a precision pressure probe. When the pressure changes were approaching zero, the reaction mixture was removed from the autoclave and filtered through silica gel. Without any further purification, a GC–MS spectrum was recorded to determine the conversion of the hydrogenation reaction and identify the products. PhCH=N(α-naphthyl): t_R = 10.532 min, *m/z* = 231; PhCH$_2$NH(α-naphthyl): t_R = 10.607 min, *m/z* = 233; PhCH=NPh: t_R = 7.460 min, *m/z* = 181; PhCH$_2$NHPh: t_R = 7.695 min, *m/z* = 183; *p*-ClC$_6$H$_4$CH=NPh: t_R = 8.636 min, *m/z* = 215; *p*-ClC$_6$H$_4$CH$_2$NHPh: t_R = 8.989 min, *m/z* = 217; *p*-ClC$_6$H$_4$CH=N-*p*-C$_6$H$_4$Cl: t_R = 9.639 min, *m/z* = 249; *p*-ClC$_6$H$_4$CH$_2$NH-*p*-C$_6$H$_4$Cl: t_R = 10.114 min, *m/z* = 251; PhCH=NCHPh$_2$: t_R = 10.589 min, *m/z* = 271; PhCH$_2$NHCHPh$_2$: t_R = 10.386 min, *m/z* = 273; PhCH=NMes: t_R = 8.301 min, *m/z* = 223; PhCH$_2$NHMes: t_R =

8.491 min, *m/z* = 225; PhCH=N*i*Bu: t_R = 4.876 min, *m/z* = 161; PhCH$_2$NH*i*Bu: t_R = 5.756 min, *m/z* = 163.

X-ray Diffraction Studies of 1a, 1d, 2a, 2b and 3a: Relevant details regarding the structural refinements are given in Tables S1 and S2 of the Supporting Information and selected geometrical parameters are included in the captions of the corresponding figures Intensity data were collected at 183(2) K with an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with Mo-K_α radiation, λ = 0.71073 Å).[48] Suitable selected single crystals were mounted using polybutene oil on the top of a glass fibre fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and absorption corrections were performed with CrysAlisPro.[48] The crystal structures were solved with SHELXS-97[49] using direct methods. The structure refinements were performed by full-matrix least-squares methods on $F2$ with SHELXL-97.[49] PLATON[50] was used to check the results of the X-ray analyses. All programs used during the crystal structure determination process are included in the WINGX software.[51] The hydride atoms were located in difference Fourier maps and all other hydrogen atoms were placed at ideal positions and refined with fixed isotropic displacement parameters using a riding model.

CCDC-791648 (for **1a**), -791649 (for **1d**), -791650 (for **2a**), -791651 (for **2b**) and -791652 (for **3a**) 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): X-ray crystallographic data for all determined molecular structures.

Acknowledgments

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