Hydride transfer reactivity of tetrakis(trimethylphosphine) (hydrido)(nitrosyl)molybdenum(0)†

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Received 19th August 2005, Accepted 4th November 2005
First published as an Advance Article on the web 23rd November 2005
DOI: 10.1039/b511797f

The tetrakis(trimethylphosphine) molybdenum nitrosyl hydrido complex *trans*-$Mo(PMe_3)_4(H)(NO)$ (**2**) and the related deuteride complex *trans*-$Mo(PMe_3)_4(D)(NO)$ (**2a**) were prepared from *trans*-$Mo(PMe_3)_4(Cl)(NO)$ (**1**). From ^2H $T_{1\,min}$ measurements and solid-state ^2H NMR the bond ionicities of **2a** could be determined and were found to be 80.0% and 75.3%, respectively, indicating a very polar Mo–D bond. The enhanced hydridicity of **2** is reflected in its very high propensity to undergo hydride transfer reactions. **2** was thus reacted with acetone, acetophenone, and benzophenone to afford the corresponding alkoxide complexes *trans*-$Mo(NO)(PMe_3)_4(OCHR'R'')$ ($R' = R'' = Me$ (**3**); $R' = Me$, $R'' = Ph$ (**4**); $R' = R'' = Ph$ (**5**)). The reaction of **2** with CO_2 led to the formation of the formato-O-complex $Mo(NO)(OCHO)(PMe_3)_4$ (**6**). The reaction of **2** with $HOSO_2CF_3$ produced the anion coordinated complex $Mo(NO)(PMe_3)_4(OSO_2CF_3)$ (**7**), and the reaction with $[H(Et_2O)_2][BAr^F{}_4]$ with an excess of PMe_3 produced the pentakis(trimethylphosphine) coordinated compound $[Mo(NO)(PMe_3)_5][BAr^F{}_4]$ (**8**). Imine insertions into the Mo–H bond of **2** were also accomplished. PhCH=NPh (*N*-benzylideneaniline) and $C_{10}H_7CH$=NPh (*N*-1-naphthylideneaniline) afforded the amido compounds $Mo(NO)(PMe_3)_4[NR'(CH_2R'')]$ ($R' = R'' = Ph$ (**9**), $R' = Ph$, $R'' =$ naphthyl (**11**)). **9** could not be obtained in pure form, however, its structure was assigned by spectroscopic means. At room temperature **11** reacted further to lose one PMe_3 forming **12** ($Mo(NO)PMe_3)_3[N(Ph)CH_2C_{10}H_6)]$) with agostic stabilization. In a subsequent step oxidative addition of the agostic naphthyl C–H bond to the molybdenum centre occurred. Then hydrogen migration took place giving the chelate amine complex $Mo(NO)(PMe_3)_3[NH(Ph)(CH_2C_{10}H_6)]$ (**15**). The insertion reaction of **2** with $C_{10}H_7N$=CHPh led to formation of the agostic compound $Mo(NO)(PMe_3)_3[N(CH_2Ph)(C_{10}H_7)]$ (**10**). Based on the knowledge of facile formation of agostic compounds the catalytic hydrogenation of $C_{10}H_7N$=CHPh and PhN=$CHC_{10}H_7$ with **2** (5 mol%) was tested. The best conversion rates were obtained in the presence of an excess of PMe_3, which were 18.4% and 100% for $C_{10}H_7N$=CHPh and PhN=$CHC_{10}H_7$, respectively.

Introduction

The search for activated transition metal hydrides is of continuing interest in particular with regard to hydrogenations. Earlier, it has been shown that the strength of L_nM–H bonds depends on the electronegativity of the metal centre.[1a] Low electronegativities cause weaker bonds to hydrogen and in addition a hydridic polarization. On the basis of a ligand tuning nitrosyl substitution may be used to effect low orbital electronegativities[1b] at various metal centres thus simulating early transition metals.[2–10] It has also been demonstrated with *trans*-$W(CO)_2(H)(NO)(PR_3)_2$[2,11–13] and *mer*-$W(CO)(H)(NO)(PMe_3)_3$[14] that the hydridic character of the hydride is phosphine-dependent. Thus an increased number of phosphine ligands enhances the hydridic character of the hydride, which has also been observed in a $Re(CO)_n(H)(PR_3)_{5-n}$ ($n = 1$–3) series.[5,15] Based on the fact that molybdenum has generally weaker bonds to H than tungsten but similar electronegativity, it can be inferred that in a $Mo(NO)(CO)_{4-n}(H)(PR_3)_n$ ($n = 2$–4) series of complexes the Mo–H bond is expected to display higher reactivity than the analogous tungsten series.

The synthesis of *mer*-$Mo(CO)(PMe_3)_3(H)(NO)$ and the reactivity of this hydride was studied earlier in our group.[16] As a natural extension to this the $Mo(PMe_3)_4(H)(NO)$ complex was prepared and studied for reactivity.

Results and discussion

Synthesis and characterization of *trans*-$Mo(PMe_3)_4(H)(NO)$ (2)

Even though Liang *et al.*[16] and Hillhouse *et al.*[17] could prepare *mer*-$Mo(CO)(PMe_3)_3(H)(NO)$ and *mer*-$Mo(CO)(PMePh_2)_3(H)(NO)$ as complexes related to *trans*-$Mo(PMe_3)_4(H)(NO)$ (**2**) using *trans*-$Mo(AlCl_4)(CO)_4(NO)$ as a starting material, attempts to obtain **2** with a similar route failed. The substitution of the "fourth" CO ligand of *trans*-$Mo(AlCl_4)(CO)_4(NO)$ could not be accomplished. Carmona *et al.*[18] reported the preparation of *trans*-$Mo(PMe_3)_4(Cl)(NO)$ using 1% sodium amalgam reducing $MoCl_3(NO)(PMe_3)_3$ in the presence of PMe_3. $MoCl_3(NO)(PMe_3)_3$ was obtained from the reaction of $MoCl_3(PMe_3)_3$ with NO gas, a reaction difficult to control. This route was modified as shown

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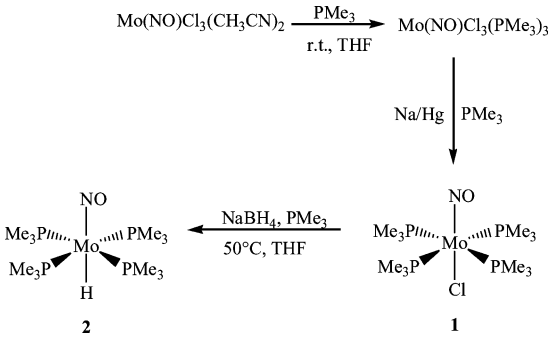
† Electronic supplementary information (ESI) available: 2D and 1D NMR spectra of **10** and **12** . See DOI: 10.1039/b511797f

in Scheme 1 using $Mo(NO)Cl_3(CH_3CN)_2$[19] and 5 equivalents of PMe_3. At room temperature the complex $Mo(NO)Cl_3(PMe_3)_3$ was formed, which was not isolated and immediately subjected to reduction with sodium amalgam. The purification of *trans*-$Mo(PMe_3)_4(Cl)(NO)$ was carried out as described in the literature.[18] Compound *trans*-$Mo(PMe_3)_4(Cl)(NO)$ (**1**) was obtained as yellow crystals in *ca.* 85% yield. The IR spectrum of **1** in solution shows a ν(NO) band in THF at 1544 cm^{-1} and at 1522 cm^{-1} in the solid state. In the ^1H NMR spectrum (benzene-d_6) at room temperature a broadened singlet resonance is found at 1.30 ppm for the Me groups. The broadening is interpreted in terms of an unresolved very small coupling to the H_{Me}, CH_2 protons. The ^{31}P NMR spectrum reveals a singlet at −2.3 ppm and in the ^{13}C NMR spectrum one signal of higher order is detected at 19.3 ppm in agreement with the high symmetry of **1**.



Scheme 1

2 was obtained by the treatment of *trans*-$Mo(PMe_3)_4(Cl)(NO)$ with 5 equivalents of $NaBH_4$ and 10 equivalents of PMe_3 in THF at 50 °C for 5 days (Scheme 1). After extraction with pentane, subsequent sublimation of the impurities at 60 °C *in vacuo*, and recrystallization from pentane **2** was isolated in 87% yield. Hydride **2** has been fully characterized by NMR, IR, Raman and MS spectroscopies and elemental analysis. The ^1H NMR spectrum of **2** in benzene-d_6 reveals a quintet at −2.51 ppm ($^2J_{HP}$ = 33.0 Hz), for the hydrido ligand coupled to the four chemically equivalent phosphorus nuclei of the PMe_3 ligands. The $^{31}P\{^1H\}$ NMR spectrum in toluene shows a singlet at 5.1 ppm.

The IR spectrum of **2** in the solid-state revealed a band at 1521 cm^{-1} assigned to overlapping ν(NO) and ν(Mo–H) vibrations. In hexane at room temperature the IR spectrum of **2** shows one ν(NO) band at 1562 cm^{-1} and at −25 °C a moderately strong additional band at 1521 cm^{-1}. The latter was attributed to the ν(Mo–H) vibration. To assure this assignment the IR spectrum of the corresponding deuteride *trans*-$Mo(PMe_3)_4(D)(NO)$ (**2a**) was studied in the solid state and in hexane. **2a** can be obtained by a procedure analogous to the preparation of hydride **2** using $NaBD_4$ instead of $NaBH_4$. In the solid state IR spectrum one finds the expected ν(NO) absorption of **2a** at 1498 cm^{-1}, which is shifted by 23 cm^{-1} to lower wavenumbers with respect to **2** indicating coupling of ν(NO) and ν(Mo–H) in **2**. The ν(Mo–D) vibration is observed at 1063 cm^{-1} in accord with the isotope shift. The isotopic ratio of ν(Mo–H)/ν(Mo–D) ratio is 1.43, which is close to the theoretical value of $\sqrt{2}$.[20] In the IR spectrum of **2a** in hexane one finds the ν(NO) vibration at 1548 cm^{-1}, which is shifted by −14 cm^{-1} with respect to **2**. The Raman spectrum of **2** exhibits in the solid-state a weak band at 1526 cm^{-1} which is attributed to the ν(NO) vibration. A ν(Mo–H) band expected at 1508 cm^{-1} could not be detected. The Raman spectrum of **2a** reveals a ν(Mo–D) band at 1066 cm^{-1} and a ν(NO) vibration at 1507 cm^{-1}; the latter is shifted to low wavenumbers by 19 cm^{-1} with respect to ν(NO) of **2** confirming again vibrational coupling.

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

Mo–N	1.827(3)	Mo–P(1)	2.4566(10)
Mo–H	2.06(4)	Mo–P(2)	2.4629(10)
N–O	1.218(4)	Mo–P(3)	2.4597(10)
Mo–P(4)	2.4375(10)		
N–Mo–H	175.7(11)	P(4)–Mo–P(2)	147.96(3)
O–N–Mo	176.2(3)	P(4)–Mo–P(1)	91.89(3)
P(1)–Mo–H	92.1(11)	P(4)–Mo–P(3)	91.01(3)
P(2)–Mo–H	70.8(11)	P(1)–Mo–P(3)	169.25(3)
P(3)–Mo–H	98.6(11)	N–Mo–P(1)	83.61(11)
P(4)–Mo–H	77.2(11)	N–Mo–P(2)	109.31(11)
P(1)–Mo–P(2)	91.38(3)	N–Mo–P(3)	85.66(11)
P(3)–Mo–P(2)	91.65(3)	N–Mo–P(4)	102.73(11)

Cooling a saturated pentane solution of **2** to −30 °C gave crystals suitable for an X-ray diffraction study. The X-ray data collection and processing parameters are compiled in Table 7. Selected bond distances and angles are given in Table 1. Fig. 1 shows the structure of **2**, which displays pseudo-octahedral coordination of the molybdenum centre.

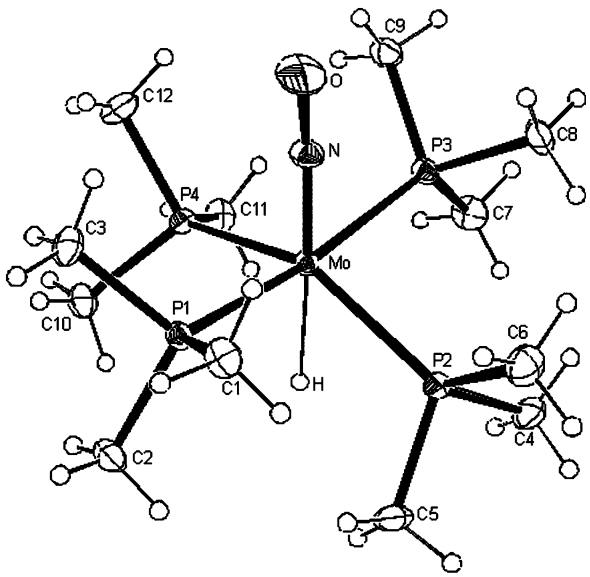


Fig. 1 ORTEP plot of the structure of **2**. Displacement ellipsoids are drawn with 30% probability.

The hydride is located *trans* to the nitrosyl ligand. Two *trans* phosphine ligands P(1) and P(3) were found pointing toward the hydride ligand, whilst the other two phosphine ligands P(2) and P(4) are bent up toward the nitrosyl group. The H atom was localized in the difference Fourier maps and could be refined with an isotropic displacement parameter of 0.021(10) $Å^2$. Thus, it is believed that the Mo bound H position can be taken with confidence. It is noteworthy that the Mo–H bond is quite long (2.06(4) Å) in comparison with that of *mer*-$Mo(H)(CO)(NO)(PMe_3)_3$ (1.84(3) Å).[16]

Ionicity of the Mo–H bond of *trans*-Mo(PMe$_3$)$_4$(H)(NO) (2)

L_nM–H bonds can be described as polar covalent linkages, in which a charge distribution is imposed on an essentially covalent bond between the transition metal and the hydrogen atom. Bond ionicities have been used to determine the hydridic character of M–H bonds.[21] The bond ionicity of the Mo–H bond of **2** was studied by deuterium quadrupole coupling constant (DQCC) measurements.[21] The direction of the polarization of such bonds can principally not be obtained by such experiments, however based on electronegativity it seems reasonable to assume that it is hydridic. It is also expected that the bond ionicities *i* remain the same in the case of an isotopic replacement.

In the ^{2}H NMR spectra (in toluene-h$_8$) the resonance for **2a** is observed at −2.60 ppm ($^2J_{PD} = 5$ Hz). The ^{31}P {^{1}H} NMR spectra (in toluene-h$_8$) shows a 1 : 1 : 1 triplet at 4.23 ppm and J_{DP} is 5 Hz.

The DQCC values were first attempted to be determined from ^{2}H NMR $T_{1\,min}$ measurements in toluene and then from a static solid-state ^{2}H NMR spectrum.[21,22] The plot of lnT_1 *vs.* $1/T$ is shown in Fig. 2, which allowed for the calculation of $T_{1\,min}$ = 55 ms at 188 K and subsequently a DQCC value of 45.5 kHz. The ionicity *i* of the Mo–D bond is 80.0%.

The bond ionicitiy *i* of **2a** could be determined from a static solid-state ^{2}H NMR spectrum. A Δ value of the "Pake Doublet" of 42 kHz was derived from a solid-state ^{2}H NMR spectrum, which allowed for the calculation of a DQCC value of 56 kHz, and a bond ionicity *i* of 75.3%. The deviating bond ionicities in solution and solid-state is presumably due to the non-zero asymmetry parameter in the solid state.[23]

The smallest experimental DQCC value was found for LiD (33 kHz), corresponding to a bond ionicity of 86%.[24] The large *i* value for **2a**, which is close to that of LiD, demonstrates a high ionicity of the Mo–D bond in **2a**. The *i* value is greater than that of its congener W(D)(NO)(PMe$_3$)$_4$ ($i = 77.6\%$),[25] which mirrors the fact that the electronegativity of Mo is smaller than that of W. Compared with the bond ionicity of *mer*-Mo(H)(CO)(NO)(PMe$_3$)$_3$ (78.5%),[26] the stronger bond polarity of **2** is expected to give rise to enhanced reactivity.

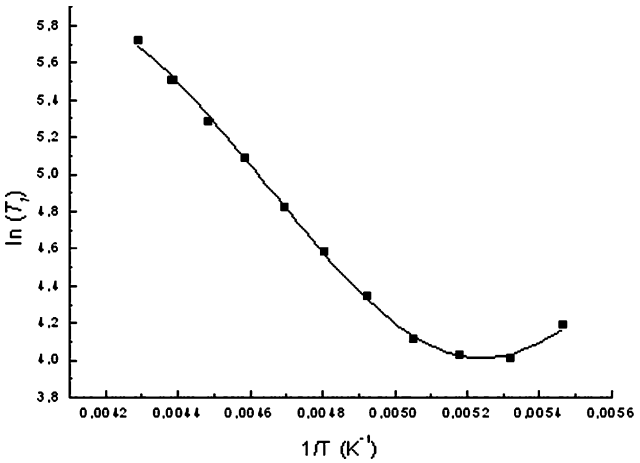
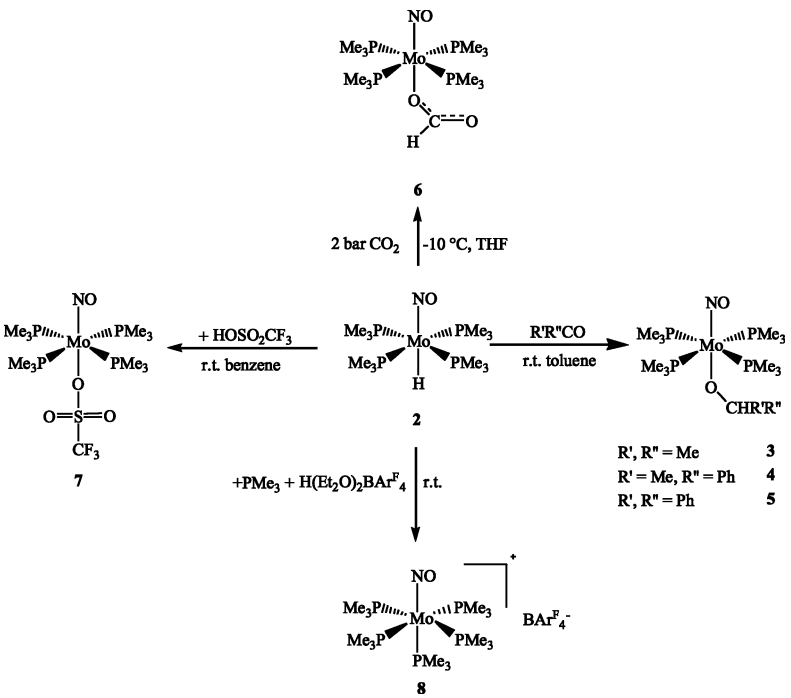


Fig. 2 Variable-temperature ^{2}H T_1 data (T_1 in ms) of **2a** in toluene-d$_8$.

Insertion reactions of *trans*-Mo(PMe$_3$)$_4$(H)(NO) (2) with ketones and CO$_2$

Insertion reactions of **2** were attempted with acetone, acetophenone and bezophenone at room temperature affording the corresponding alkoxide complexes **3**, **4** and **5** (Scheme 2).

Monitored by NMR spectroscopy in toluene-d$_8$ solution at room temperature, the reaction of **2** with 1 equivalent of acetone provided the isopropoxide **3** within 30 min. After a longer reaction time signals of an as yet unidentified product appeared. **3** was isolated as an analytically pure yellow solid in almost quantitative



Scheme 2

yield. Similarly the reaction of **2** with 1 equivalent of acetophenone or benzophenone in toluene took at room temperature about 4 or 10 hours for completion. The yellow alkoxides **4** and **5** were obtained in 85% and almost quantitative yield, respectively.

The IR specta of **3**, **4** and **5** revealed in the solid-state bands at 1500 cm^{-1}, 1508 cm^{-1} and 1502 cm^{-1}, corresponding to their ν(NO) bands. In the ^1H NMR spectra of **3**, **4** and **5** (benzene-d_6) the characteristic resonance of the newly formed CH moieties were observed at 3.70 ppm (sept., $^3J_{HH} = 6$ Hz), 4.51 ppm (quart., $^3J_{PH} = 6$ Hz) and 5.35 ppm (s, $^3J_{HH} = 6$ Hz), respectively. In the ^{13}C $\{^1H\}$ NMR spectra these CH carbon atoms gave rise to characteristic multiplets or a singlet at 68.9 ppm (**3**), 77.4 ppm (**4**) and 87.9 ppm (**5**). The ^{31}P $\{^1H\}$ NMR spectra of **3**, **4** and **5** showed singlets at −5.3 ppm, −5.3 ppm and −5.6 ppm, respectively. All complexes gave the correct elemental analyses.

Suitable crystals for an X-ray diffraction study were obtained from **5** by recrystallization from pentane at −30 °C. The structure was determined by X-ray diffraction and is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. The X-ray data collection and processing parameters are compiled in Table 7.

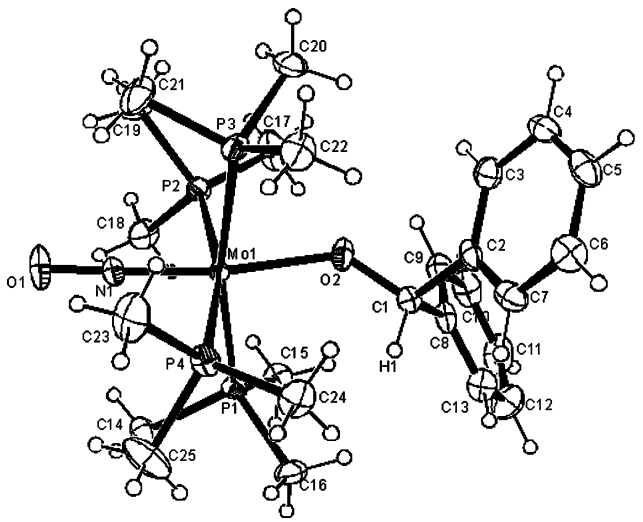


Fig. 3 ORTEP plot of the structure of **5**. Displacement ellipsoids are drawn with 30% probability.

Table 2 Selected bond lengths [Å] and bond angles [°] of **5**

Mo(1)–N(1)	1.7803(16)	N(1)–O(1)	1.227(2)
Mo(1)–O(2)	2.1025(14)	O(2)–C(1)	1.375(2)
Mo(1)–P(1)	2.5083(5)	C(1)–C(2)	1.536(3)
Mo(1)–P(2)	2.4979(5)	C(1)–C(8)	1.542(3)
Mo(1)–P(3)	2.4840(5)	C(1)–H(1)	0.9800
Mo(1)–P(4)	2.4872(6)		
N(1)–Mo(1)–O(2)	172.09(7)	O(1)–N(1)–Mo(1)	176.75(18)
N(1)–Mo(1)–P(3)	95.37(5)	C(1)–O(2)–Mo(1)	135.93(14)
O(2)–Mo(1)–P(3)	79.27(5)	O(2)–C(1)–C(2)	109.96(17)
N(1)–Mo(1)–P(4)	84.07(6)	O(2)–C(1)–C(8)	110.54(17)
O(2)–Mo(1)–P(4)	101.60(5)	C(2)–C(1)–C(8)	110.30(15)
P(3)–Mo(1)–P(4)	89.78(2)	O(2)–C(1)–H(1)	108.7
N(1)–Mo(1)–P(2)	82.20(6)	C(2)–C(1)–H(1)	108.7
O(2)–Mo(1)–P(2)	91.96(5)	C(8)–C(1)–H(1)	108.7
P(3)–Mo(1)–P(2)	90.37(2)	O(2)–Mo(1)–P(1)	89.25(5)
P(4)–Mo(1)–P(2)	166.229(19)	P(3)–Mo(1)–P(1)	168.288(18)
N(1)–Mo(1)–P(1)	96.28(5)	P(4)–Mo(1)–P(1)	90.22(2)
P(2)–Mo(1)–P(1)	92.396(19)		

CO_2 insertion into the metal–hydride bond to generate a metal formato-O-complex has been extensively studied, in particular with regard to the hydrogenation of CO_2 to formic acid.[27]

The reaction of **2** with 2 bar of CO_2 afforded at −10 °C the formato-O-complex Mo(η^1-OCHO)(PMe_3)$_4$(NO) (**6**) within 1 h (Scheme 2), which can be isolated as analytically pure brown crystals in 95% yield from diethyl ether at −30 °C. Full characterization was achieved by IR, NMR, elemental analysis and mass spectroscopy, which confirmed the η^1-formato structure. The IR spectrum of **6** revealed two characteristic bands: an intense ν(NO) band at 1533 cm^{-1} and a ν(OCO) band at 1626 cm^{-1}.[14,16] In the ^1H NMR spectrum in THF-d_8 the formato group of **6** displayed a singlet at 8.06 ppm and in the ^{13}C $\{^1H\}$ NMR spectrum the resonance of the respective carbon atom was observed as a singlet at 166.1 ppm.

Reactions of *trans*-Mo(PMe_3)$_4$(H)(NO) (2) with acids

Coordinatively unsaturated cationic species, as well as cationic complexes of weakly coordinating anions and solvent molecules are particularly useful in Lewis acidic catalysis and organometallic synthesis. The Mo–H bond of **2** was shown to possess a hydridic H atom, which may in turn point at the existence of a stabilized 16e$^-$ [Mo(PMe_3)$_4$(NO)]$^+$ cation. Removal of the hydride anion from hydride complexes is one of the routes generating such electrophilic cationic species with weakly coordinating or non-coordinating anions. Therefore the reactions of **2** with the strong acids $HOSO_2CF_3$ and [H(Et_2O)$_2$][BAr^F_4] were studied.

The reaction of **2** with 1 equivalent of $HOSO_2CF_3$ was monitored by NMR spectroscopy in benzene-d_6. It was completed immediately and H_2 was released. The triflate complex **7** was obtained in quantitative yield (Scheme 2). Complex **7** has been fully characterized by elemental analyses, IR, NMR spectroscopy and mass spectrometry, which revealed a pseudo-octahedral structure with a coordinated triflate anion. The IR spectrum in the solid state shows a band at 1551 cm^{-1} corresponding to the ν(NO) vibration. In the ^1H NMR spectrum of **7** (benzene-d_6) reveals a singlet resonance for the PMe_3 group at 1.24 ppm. The ^{31}P $\{^1H\}$ NMR spectrum displays a singlet at −3.2 ppm corresponding to the four chemically equivalent phosphorus atoms. The triflate ligand tends to be labile in coordination compounds, for that reason it was tested whether an intermediate 16e$^-$ species would exist, persistent enough to allow further reactions. **7** did however not react under hydrogenation conditions with H_2 and acetophenone, even under a pressure of 80 atm H_2. The $OSO_2CF_3^-$ anion seems to be too strongly coordinated to the Mo centre forming a relatively stable 18 electron compound.

The reaction of **2** with 1 equivalent of [H(Et_2O)$_2$][BAr^F_4] at room temperature was monitored by NMR spectroscopy in diethyl ether-d_{10}. The reaction was completed within 3 hours (Scheme 2). The ^1H NMR spectrum shows a singlet at 1.52 ppm and a doublet at 1.28 ppm in a 4 : 1 ratio. Accordingly, the ^{31}P $\{^1H\}$ NMR spectrum revealed a doublet at −11.6 ppm and a quintet at −35.9 ppm with a 4 : 1 ratio, which have the same coupling constant (26 Hz). This indicated the formation of an octahedral molecule with five PMe_3 ligands, four PMe_3 ligands are in one planar arrangement, while the other PMe_3 group is located *trans* to the nitrosyl ligand. Suitable crystals for X-ray diffraction analysis were obtained by pentane diffusion into the diethyl ether solution

Table 3 Selected bond lengths [Å] and bond angles [°] of **8**

Mo(1)–N(1)	1.778(6)	Mo(1)–P(3)	2.519(2)
N(1)–O(1)	1.187(8)	Mo(1)–P(5)	2.506(3)
Mo(1)–P(1)	2.543(2)	Mo(1)–P(4)	2.682(2)
Mo(1)–P(2)	2.499(3)		
N(1)–Mo(1)–P(1)	83.1(2)	P(1)–Mo(1)–P(5)	88.43(9)
N(1)–Mo(1)–P(2)	89.4(2)	P(2)–Mo(1)–P(3)	93.66(11)
N(1)–Mo(1)–P(3)	86.6(2)	P(2)–Mo(1)–P(4)	86.60(9)
N(1)–Mo(1)–P(4)	175.8(2)	P(2)–Mo(1)–P(5)	176.31(13)
N(1)–Mo(1)–P(5)	93.6(2)	P(3)–Mo(1)–P(4)	92.57(7)
P(1)–Mo(1)–P(2)	89.73(8)	P(3)–Mo(1)–P(5)	88.72(10)
P(1)–Mo(1)–P(3)	169.14(7)	P(4)–Mo(1)–P(5)	90.48(9)
P(1)–Mo(1)–P(4)	97.93(7)	O(1)–N(1)–Mo(1)	179.7(7)

of the reaction mixture. The isolated yield of **8** was approximately 30%. The X-ray data collection and processing parameters are compiled in Table 7. A structural model is displayed in Fig. 4. The Mo centre possesses a pseudo-octahedral geometry; the bond length of Mo–P_4 (*trans* to NO) is a little longer than the other Mo–P bonds (see Table 3). This is supposed to be due to the *trans* influence of the NO group.

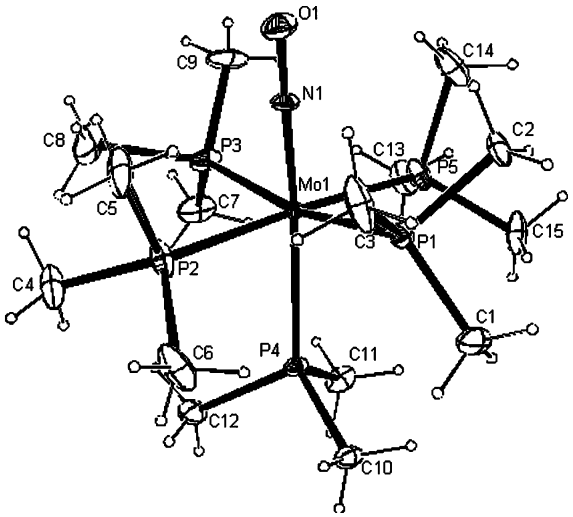


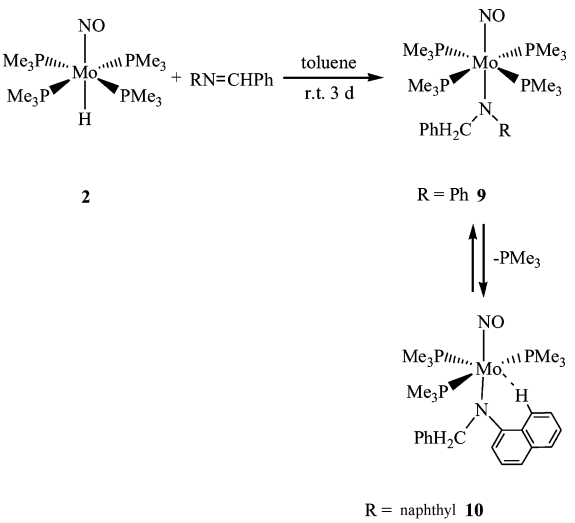
Fig. 4 ORTEP plot of the structure of **8**. Only the cation is shown. Displacement ellipsoids are drawn with 30% probability.

When the reaction was carried out in the presence of 5 equivalents of PMe_3, **8** was obtained almost quantitatively and the reaction was complete within 10 minutes at room temperature. During this period of time **8** partly precipitated from solution. By this route **8** was obtained as orange crystals by diffusion of pentane into the reaction mixture. The solid state IR spectrum of **8** showed a band at 1593 cm^{-1} corresponding to the ν(NO) vibration. The elemental analysis is consistent with the composition of the complex.

Insertion reactions of *trans*-Mo(PMe_3)$_4$(H)(NO) (2) with imines

The insertion of imines into transition metal–hydride bonds is assumed to be the crucial step in various catalytic hydrogenations of imines generating amines,[28–34] but it is difficult to isolate this step.[16] Recently insertion reactions of the hydride *trans*-Mo(dmpe)$_2$(H)(NO) with imines were reported. Disubstitued aromatic imines were shown to insert into its Mo–H bond.[35] Therefore, the insertion capability of **2** was studied with several imines Ph(Me)C=NPh, Ph_2C=NH, PhCH=NPh, PhCH=$NC_{10}H_7$ and $C_{10}H_7$CH=NPh. The C-disubstituted imines showed no reaction at room temperature and even at 60 °C. The other imines inserted into the Mo–H bond to form amido complexes, but in most cases these were not stable and underwent further transformations.

Treatment of **2** with an equimolar amount of *N*-benzylideneaniline in toluene-d_8 at room temperature afforded after 3 days the amido complex **9** (Scheme 3). In the ^{1}H NMR spectrum a characteristic singlet at 4.42 ppm was observed for the newly formed NCH_2 group. In the ^{31}P {^{1}H} NMR spectrum of **9** a very broad signal at −9.0 ppm was found at room temperature, which became sharp and shifted to −7.1 ppm when the sample was cooled to −50 °C. This presumably indicates reversible PMe_3 dissociation at room temperature.



Scheme 3

The reaction of **2** with *N*-benzylidene-1-naphthylamine was monitored by ^{1}H NMR spectroscopy in toluene-d_8 at room temperature. After 3 days the reaction is almost complete. The C–H agostic tris(trimethylphosphine) complex **10** was isolated in 59% yield (Scheme 3). The structure of **10** was assigned based on NMR spectroscopy. The ^{31}P {^{1}H} NMR spectrum of **10** at room temperature displays a triplet at 16.7 ppm ($^2J_{PP}$ = 20 Hz) and a broadened signal at −5.4 ppm, indicating the meridional disposition of the three phosphine ligands. When the ^{31}P {^{1}H} NMR spectrum is recorded at −70 °C, the broadened signal splits into two doublet of doublet patterns at 1.2 and −8.4 ppm with $^2J_{PP\text{-}cis}$ = 20 Hz, $^2J_{PP\text{-}trans}$ = 190 Hz couplings, respectively. In the ^{1}H NMR spectrum there is a singlet at 4.43 ppm corresponding to the resonance of the newly formed NCH_2 group and a broadened signal appearing at 2.97 ppm. From the ^{13}C–^{1}H correlation spectrum (Fig. S.1, ESI†) it was derived that this signal possesses correlation with a ^{13}C resonance having a chemical shift of 117.0 ppm in the aromatic range. The drastic upfield shift of this proton resonance supports its agostic nature.[36] Further evidence for the agostic interaction comes from ^{1}H {^{31}P} NMR spectroscopy. In this spectrum the resonance at 2.97 ppm is sharp and split into a doublet due to coupling with the neighboringing aromatic proton ($^2J_{HH}$ = 5 Hz). The broadening is interpreted in terms of an additional coupling to phosphorus nuclei through the agostic bond.

From the gated ^{13}C NMR spectrum of **10** (Fig. S.2, ESI†), the $^{1}J_{CH}$ of the agostic proton is determined to be 125 Hz, significantly lower than usual aromatic $^{1}J_{CH}$ couplings (155–165 Hz). The coupling constant is reduced by about 30–35 Hz, which is a typical value for an agostic interaction. The *v*(CH) bond of the agostic C–H bond could not be detected by IR or Raman spectroscopy. The *v*(NO) absorption appears at 1557 cm^{-1} in the solid state IR spectrum, and at 1558 cm^{-1} in the solid state Raman spectrum.

The reaction of **2** with *N*-1-naphthylideneaniline, an isomer of *N*-benzylidene-1-naphthylamine, has been monitored by NMR spectroscopy in toluene-d_8 at room temperature. After 4 days the reaction was almost complete and showed the amido complex **11** as the only product. Beside signals for the aromatic protons of the amido moiety appearing in the range 6.10–9.12 ppm and a singlet for the methyl protons of the PMe_3 ligands at 1.12 ppm, the ^{1}H NMR spectrum of the reaction mixture in toluene-d_8 revealed the characteristic resonance of the NCH_2 group as a singlet at 4.89 ppm. In the ^{31}P $\{^{1}H\}$ NMR spectrum a very broad signal at −9.0 ppm was observed at room temperature. The signal appeared at −7.6 ppm and became sharp at −30 °C suggesting that there is ligand dissociation as in **9**. **11** however could not be isolated, because upon crystallization it lost a PMe_3 ligand to form the agostic complex **12** (Scheme 4). **12** was obtained as red crystals in 45% yield by diffusion of pentane into a saturated toluene solution. Similar to **10**, the agostic *v*(CH) band of **12** could not be observed in the IR or Raman spectra. In the solid-state IR spectrum a band at 1578 cm^{-1} is assigned to the *v*(NO) vibration.

The ^{31}P $\{^{1}H\}$ NMR spectrum of **12** (toluene-d_8) displayed at room temperature very broadened signals, which became sharp at low temperature. In the ^{31}P $\{^{1}H\}$ NMR spectrum at −60 °C a doublet and a triplet resonance appeared at −8.0 and 33.1 ppm ($^{2}J_{PP}$ = 17 Hz) typical for a meridonal phosphine substitution pattern. In the ^{1}H NMR spectrum the agostic proton appeared at 3.29 ppm and was also identified in a ^{13}C–^{1}H correlation spectrum (Fig. S.3, ESI†). The corresponding "agostic" ^{1}H NMR signal shows correlation with a ^{13}C NMR resonance in the aromatic region (91.5 ppm). A $^{1}J_{CH}$ of 131 Hz is determined for the agostic proton. The agostic interaction causes the coupling constant to be reduced by about 25–30 Hz.

The molecular structure of **12** was determined by an X-ray diffraction analysis. Suitable crystals were obtained by diffusion of pentane into a concentrated toluene solution of **12**. The ORTEP plot is shown in Fig. 5. Selected bond lengths and bond angles are listed in Table 4. The X-ray data collection and processing parameters are compiled in Table 7. The Mo centre possesses a pseudo-octahedral geometry: the amido group is located *trans* to the nitrosyl ligand and the 5-phenyl proton (H15) in involved in the agostic interaction with the molybdenum centre. The agostic H is *trans* to a phosphorus atom, forming an angle of 166° (P2–Mo–H15). The distance between H15 and the Mo centre is 2.11 Å, and of C15 and Mo is 2.68 Å, the angle of the agostic hydrogen C15–H15–Mo is 117°. All these structural data are typical for agostic C–H bonding.[37]

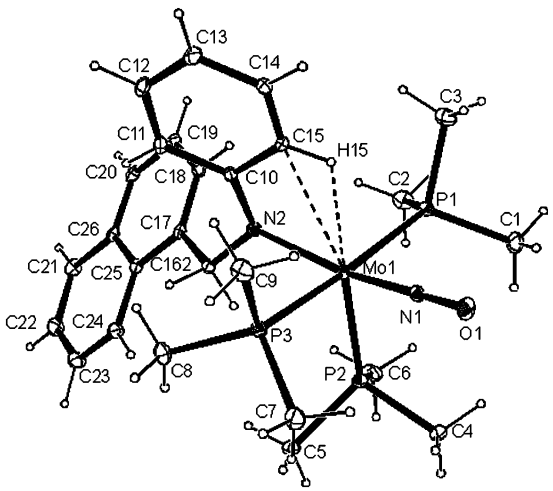
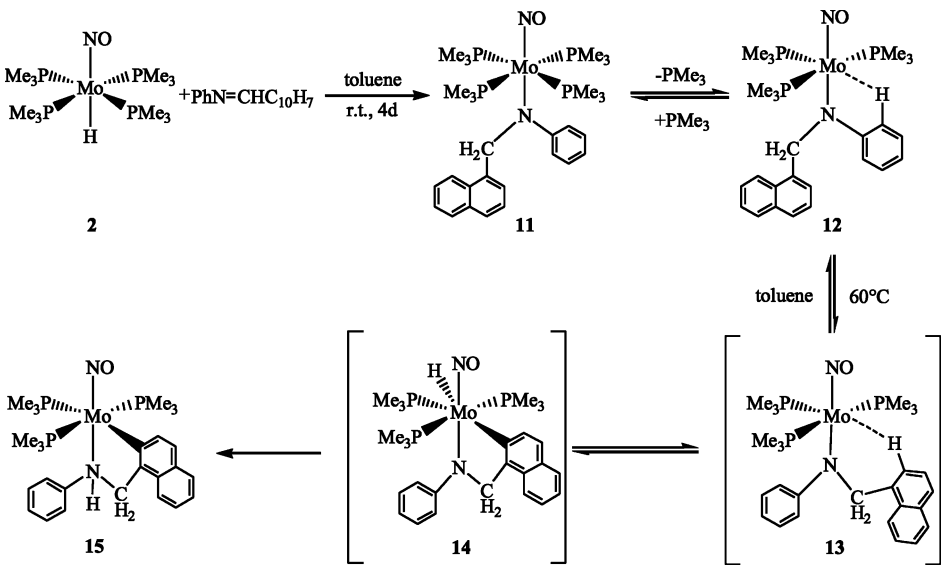


Fig. 5 ORTEP plot of the structure of **12**. Displacement ellipsoids are drawn with 10% probability.



Scheme 4

Table 4 Selected bond lengths [Å] and bond angles [°] of **12**

Mo(1)–N(1)	1.783(3)	N(2)–C(10)	1.386(5)
Mo(1)–N(2)	2.193(3)	N(2)–C(161)	1.448(14)
Mo(1)–P(1)	2.5044(11)	N(2)–C(162)	1.456(9)
Mo(1)–P(2)	2.4134(10)	C(161)–C(17)	1.585(19)
Mo(1)–P(3)	2.5036(11)	C(162)–C(17)	1.487(11)
N(1)–O(1)	1.232(4)		
N(1)–Mo(1)–N(2)	166.98(12)	P(2)–Mo(1)–P(3)	93.89(4)
N(1)–Mo(1)–P(1)	91.95(10)	C(10)–N(2)–Mo(1)	100.9(2)
N(1)–Mo(1)–P(2)	92.33(10)	C(161)–N(2)–Mo(1)	130.9(7)
N(1)–Mo(1)–P(3)	84.45(10)	C(162)–N(2)–Mo(1)	127.6(4)
N(2)–Mo(1)–P(1)	90.60(8)	C(10)–N(2)–C(161)	110.6(14)
N(2)–Mo(1)–P(2)	100.31(8)	C(10)–N(2)–C(162)	121.9(7)
N(2)–Mo(1)–P(3)	91.51(8)	N(2)–C(161)–C(17)	113.9(13)
P(1)–Mo(1)–P(2)	92.64(4)	N(2)–C(162)–C(17)	119.6(6)
P(1)–Mo(1)–P(3)	172.67(4)		

When the reaction of **2** was carried out at 60 °C with 1 equivalent of *N*-1-naphthylideneaniline the amino complex **15** was obtained within 2 weeks. The ^{31}P $\{^1H\}$ NMR spectrum of **15** displayed a doublet and a triplet at −10.1 ppm and −19.5 ppm ($^2J_{PP} = 23$ Hz), corresponding to a meridional arrangement of the three phosphine ligands. The ^1H NMR spectrum of **15** (benzene-d_6) showed besides resonances for the aromatic protons in the range 9.03 to 6.42 ppm and those for the PMe_3 ligand in the range 1.02 to 0.98 ppm, a characteristic doublet at 4.32 ppm ($^2J_{HH} = 5$ Hz) attributed to the NCH_2 group. In the ^{13}C $\{^1H\}$ NMR spectrum the resonance of the respective carbon atom appears as a singlet at 46.3 ppm. The ^1H NMR spectrum of **15** displays another broadened signal at 3.3 ppm, which can be assigned to the NH group. This assignment was further supported by a NOE experiment. When the signal at 3.3 ppm was irradiated, apparently positive NOE signals were detected at 6.42 ppm and 4.32 ppm, which were attributed to the resonance for the *o*-Ph and the NCH_2 protons.

Complex **15** could only be isolated with some impurities, thus preventing its full spectroscopic characterization. However a single crystal was picked out, which allowed its structure to be established by X-ray diffraction analysis. The ORTEP plot is shown in Fig. 6. Selected bond lengths and bond angles are listed in Table 5. The X-ray data collection and processing parameters are compiled in Table 7.

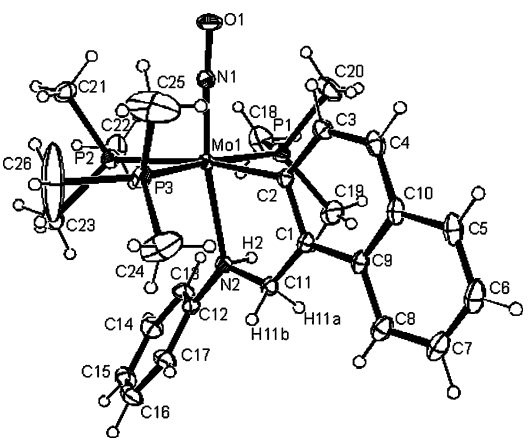


Fig. 6 ORTEP plot of the structure of **15**. Displacement ellipsoids are drawn with 30% probability.

Table 5 Selected bond lengths [Å] and bond angles [°] of **15**

Mo(1)–N(1)	1.7819(18)	N(1)–O(1)	1.224(2)
Mo(1)–C(2)	2.112(2)	N(2)–C(11)	1.315(3)
Mo(1)–N(2)	2.2551(17)	N(2)–C(12)	1.420(3)
Mo(1)–P(1)	2.4835(6)	N(2)–H(2)	0.9300
Mo(1)–P(2)	2.5674(6)	C(1)–C(11)	1.416(3)
Mo(1)–P(3)	2.4945(6)	C(1)–C(2)	1.427(3)
N(1)–Mo(1)–C(2)	95.02(8)	N(2)–C(11)–C(1)	118.5(2)
N(1)–Mo(1)–N(2)	168.82(7)	C(11)–N(2)–C(12)	118.46(19)
N(1)–Mo(1)–P(1)	90.13(6)	C(11)–N(2)–Mo(1)	115.16(14)
N(1)–Mo(1)–P(2)	92.09(6)	C(12)–N(2)–Mo(1)	126.32(14)
N(1)–Mo(1)–P(3)	91.11(6)	C(11)–N(2)–H(2)	90.8
N(2)–Mo(1)–P(1)	87.40(5)	C(12)–N(2)–H(2)	90.8
N(2)–Mo(1)–P(2)	99.07(5)	Mo(1)–N(2)–H(2)	90.8
N(2)–Mo(1)–P(3)	89.37(5)	C(11)–C(1)–C(2)	113.99(19)
P(1)–Mo(1)–P(2)	99.52(2)	C(11)–C(1)–C(9)	123.1(2)
P(1)–Mo(1)–P(3)	169.48(2)	C(2)–C(1)–C(9)	122.9(2)
C(2)–Mo(1)–N(2)	73.94(7)	C(1)–C(2)–C(3)	115.40(19)
C(2)–Mo(1)–P(1)	85.67(6)	C(1)–C(2)–Mo(1)	118.18(15)
C(2)–Mo(1)–P(2)	171.20(6)	C(3)–C(2)–Mo(1)	126.33(16)
C(2)–Mo(1)–P(3)	83.81(6)	C(13)–C(12)–N(2)	119.1(2)
P(3)–Mo(1)–P(2)	90.88(2)	C(17)–C(12)–N(2)	121.8(2)
O(1)–N(1)–Mo(1)	176.07(17)		

Scheme 4 presents a plausible pathway for the formation of **15**. The first step is imine insertion into the Mo–H bond to form the amido complex **11**, which subsequently loses one PMe_3 ligand and establishes an equilibrium with the agostic complex **12**. When the system was heated to 60 °C, other equilibria are assumed to come into play leading to the agostic species **13**. Oxidative addition of the agostic C–H bond produces **14** and H transfer to the amide ligand eventually gives **15**. The intermediates **13** and **14** were not observed. However, an analogous seven-coordinate hydride species has been isolated from the reaction of a related tungsten hydride $W(NO)(H)(PMe_3)_4$ with *N*-benzylidene-1-naphthylamine.[28] This might point to the fact that in the molybdenum hydride case, the related seven-coordinated hydride complex is less stable and is immediately transformed to **15**.

Investigations on the homogeneous hydrogenation of imines

The transition-metal catalyzed hydrogenation of imines is more difficult to achieve than that of olefins and ketones.[37] There are only a few imine hydrogenation systems, based on Rh(I),[38–46] Ir(I),[45,47–56] Ru(II)[57–65] and titanocene catalysts,[27,28,66,67] since the catalytic generation of amines is quite often circumvented by the hydrogenation of enamines. H_2 activation by transition metal complexes is well understood, but relatively little is known about the activation of imines and the required H-atom transfer steps. Several factors effect the hydrogenation of imines.[33] First, there is a smaller thermodynamic gain from the reduction of C=N bonds (approx. −60 kJ mol^{-1}) relative to C=C bonds (approx. −130 kJ mol^{-1}). Secondly, the typical end-on η^1 binding mode of the azomethine groups contrasts with the side-on η^2 binding of olefins, which results in less effective orbital overlaps with the metal centre. Thirdly there is competitive coordination with the products of the hydrogenation (amines) causing 'catalyst self poisoning'.[68,69]

The reactions of complexes **10** and **12** with H_2 have been investigated applying various conditions. **10** and **12** can be viewed as a 16 electron species stabilized by an agostic interaction. The relative stability of these coordinatively unsaturated species

challenged us to investigate their potential for the catalytic hydrogenation of respective imines.

Stoichiometric hydrogenation of *N*-benzylidene-1-naphthylamine and *N*-1-naphthylideneaniline

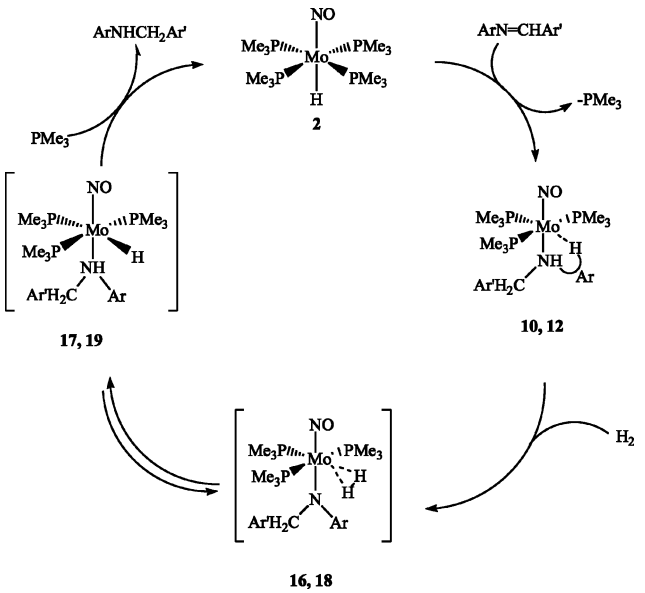
The reaction of **10** with H_2 (1.5 bar), has been monitored by NMR spectroscopy in toluene-d_8 at room temperature and also at −30 °C with the same results for both experiments. After one day, the ^{1}H NMR spectrum of the reaction mixture revealed a doublet at 4.08 ppm ($^3J_{HH} = 5$ Hz) and a broadened signal at 4.52 ppm, which corresponded to NCH_2 and NH resonances of the formed *N*-[(1-naphthyl)methyl]aniline ($C_{10}H_7NHCH_2Ph$). The presence of amine was also proven by MS. The ^{31}P $\{^1H\}$ NMR spectrum of the reaction mixture showed besides the resonance of **10** also singlets at 32.2 and −61.3 ppm, which indicated that under these conditions **10** partly decomposed to release PMe_3 and unidentifiable products. After 2 days, the resonances of **10** disappeared in the ^{1}H and ^{31}P $\{^1H\}$ NMR spectra. Only the resonances of a decomposed species (32.2 ppm) and of free PMe_3 (−61.3 ppm) remained in the ^{31}P $\{^1H\}$ NMR spectrum.

The insertion reaction of **2** with *N*-benzylidene-1-naphthylamine to yield **10** and 1 equivalent of PMe_3 took 3 days. This reaction mixture was treated with 1.5 bar H_2, which is related to the reaction of **10** with H_2 in the presence of 1 equivalent of PMe_3 and was then monitored by NMR spectroscopy in toluene-d_8 at room temperature. After one day, the ^{1}H NMR spectrum showed the resonances of the amine $C_{10}H_7NHCH_2Ph$ and a characteristic quintet of the hydride **2** at −2.50 ppm ($^3J_{PH} = 33$ Hz). The ^{31}P $\{^1H\}$ NMR spectrum of the reaction mixture displayed besides the resonances of **2** and **10** also resonances of decomposition products and PMe_3. After still longer reaction time (>4 day), the resonances of **2** increased and those of **10** disappeared in the ^{1}H and ^{31}P $\{^1H\}$ NMR spectra.

The latter reaction has also been monitored by NMR spectroscopy at −30 °C. The result was different from the reaction at room temperature. In the ^{1}H and ^{31}P $\{^1H\}$ NMR spectra only resonances of the amine product ($C_{10}H_7NHCH_2Ph$) and of the decomposition species were observed.

Based on the fact that only the reaction of **10** with H_2 in the presence of additional PMe_3 at room temperature afforded the amine and **2**, a possible reaction pathway could be established. According to Scheme 5 the agostic complex **10** reacts with H_2 to form either the dihydride or the dihydrogen intermediate **16**. Heterolysis with H^+ transfer[37] leads to the amine species **17** from which the amine is supposed to be replaced by PMe_3 giving **2**. **16** and **17** could not be detected in the NMR spectra. In particular **17** is suspected to be so short-lived that it rapidly decomposes to the mentioned unidentifiable species, when PMe_3 is not present for its stabilization.

The reactions of **12** with H_2 (1.5 bar) in the presence of and without additional PMe_3 have also been studied by NMR spectroscopy in toluene-d_8 at room temperature. They showed the same results. After one day the reaction mixtures revealed in their ^{1}H NMR spectrum a doublet at 4.25 ($^3J_{HH} = 5$ Hz) besides a characteristic quintet of hydride **2** at −2.50 ppm ($^3J_{PH} = 33$ Hz) and a broadened signal at 3.33 ppm corresponding to the resonance of the NCH_2 and NH protons of the benzylnaphth-1-ylamine ($PhNHCH_2C_{10}H_7$). Its presence was additionally proven



Scheme 5

by GC-MS. In the ^{31}P $\{^1H\}$ NMR spectrum the resonance of **2** was observed at 5.0 ppm.

Similar to **10** the reaction of the agostic species **12** with H_2 was supposed to proceed *via* the H_2 complex **18** and the amine species **19** (Scheme 5). The substitution of the amine ligand of **19** for PMe_3 is supposed to be more facile than in **17** revealing **2** as the main NMR detectable product.

Catalytic hydrogenation of *N*-benzylidene-1-naphthylamine and *N*-1-naphthylideneaniline

Based on the fact that the reactions of **10** or **12** with H_2 produced the corresponding amine and the hydride complex **2**, the optimization of these hydrogenations of *N*-benzylidene-1-naphthylamine and of *N*-1-naphthylideneaniline in terms of catalysis were of great interest. These reactions have therefore been tested under various conditions. Table 6 shows results of the hydrogenation pursued by GC.

From Table 6 one can derive that the catalytic hydrogenation reactions of both $PhCH{=}NC_{10}H_7$ and $C_{10}H_7CH{=}NPh$ are slow at room temperature. Highest conversion rates are 15.5% for $C_{10}H_7N{=}CHPh$ and 18.3% for $PhN{=}CHC_{10}H_7$. At 60 °C the catalyses showed higher conversions.

In the proposed catalytic cycle of Scheme 5, PMe_3 was believed to stabilize the intermediates **16**, **17**, **18** and **19**. Therefore if additional PMe_3 is added into the reaction system, higher catalyst stabilities were found. Therefore experiments were carried out in the presence of excess of PMe_3, which produced satisfactory results. 5 equivalents of PMe_3 H_2 (pressure of 120 bar and a temperature of 60 °C) brought about conversions of 18.6% and 85.6% for $C_{10}H_7N{=}CHPh$ and $PhN{=}CHC_{10}H_7$, respectively. With 20 equivalents of PMe_3, 120 bar H_2 pressure and 60 °C even 100% conversion of $PhN{=}CHC_{10}H_7$ was reached.

Conclusions

The tetrakis(phosphine)-substituted molybdenum hydride **2** displays a Mo–H bond with a high bond ionicity value of 80.0%.

Table 6 Catalytic hydrogenation of amines with **2** in toluene. If not stated otherwise the duration was 2 days

Substrate	Catalyst	Pressure/bar	Temperature/°C	Conversion (%)
$C_{10}H_7N{=}CHPh$	**2**[a]	60	r.t.	7.1
	10[a]	60	60	6.4
	2[a]	60	60	13.8
	10 + PMe_3[b]	60	60	7.2
	2[a]	120	r.t.	5.3
	2[a]	120	60	15.5
	2 + PMe_3[c]	120	60	18.4
$PhN{=}CHC_{10}H_7$	**2**[d]	60	r.t	5.1
	12[d]	60	60	5.1
	2[d]	60	60	16.2
	12 + PMe_3[e]	60	60	14.4
	2[d]	120	r.t.	4.2
	2[d]	120	60	18.3
	2 + PMe_3[f]	120	60	85.6
	2 + PMe_3[g]	120	60	100

[a] 5 mol%. [b] Mix 5 mol% of **2** and $C_{10}H_7N{=}CHPh$ at r.t. for 3 days. [c] 5 mol% of **2** and 25 mol% of PMe_3. [d] 5 mol%. [e] Mix 5 mol% of **2** and $PhN{=}CHC_{10}H_7$ at r.t. for 3 days. [f] 5 mol% of **2** and 25 mol% of PMe_3. [g] 5 mol% of **2** and 100 mol% of PMe_3.

Presumably based on this, **2** shows a very high propensity for hydride transfer to ketones, CO_2 and imines. Due to facile loss of PMe_3 catalysis of imine hydrogenation could become reality. The catalytic hydrogenation of *N*-benzylidene-1-naphthylamine ($C_{10}H_7N{=}CHPh$) and *N*-1-naphthylideneaniline ($PhN{=}CHC_{10}H_7$) with **2** (5 mol%) have thus been investigated under various conditions. 100% conversion was observed for $PhN{=}CHC_{10}H_7$ in the presence of an excess of PMe_3.

Experimental

General procedures

All reactions and manipulations with air-sensitive compounds were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques or a glovebox. Solvents were dried by standard methods and freshly distilled under nitrogen before use (*e.g.*, pentane, hexane, diethyl ether, benzene, toluene, THF were purified by reflux over sodium/benzophenone, dichloromethane and acetonitrile were refluxed over P_2O_5). The deuterated solvents were also dried over appropriate drying agents and vacuum transferred before use. NMR spectra were recorded on the following spectrometers. Varian Gemini-300 instrument; ^1H at 300.1 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121.5 MHz, ^{19}F at 282.2 MHz. Varian Gemini-200 instrument: ^1H at 200.0 MHz, ^{13}C at 50.3 MHz, ^{31}P at 80.9 MHz, ^{19}F at 188.2 MHz. Bruker DRX-500 instrument: ^1H at 500.2 MHz, ^2H at 76.7 MHz, ^{13}C at 125.8 MHz, ^{31}P at 202.5 MHz, ^{11}B at 160.5 MHz. $\delta(^1H)$, $\delta(^{13}C)$ relative to $SiMe_4$, $\delta(^{31}P)$ relative to 85% H_3PO_4, $\delta(^{19}F)$ relative to trifluorotoluene and $\delta(^{11}B)$ rel to $BF_3{\cdot}OEt_2$. IR spectra: Biorad FTS-45 and FTS-3500 instrument. Raman spectra: Renishaw Labram Raman microscope. Mass spectra: Finnigan-MAT-8400 spectrometer. Elemental analyses: Leco CHN(S)-932 instrument. GC-MS: Varian CP-3800 instrument; MS: Saturn 2000. The compounds $Mo(NO)Cl_3(CH_3CN)_2$,[19,70] *N*-1-naphthylideneaniline,[71] *N*-benzenylidene-1-naphthylamine,[71] $[H(Et_2O)][BAr^F{}_4]$,[72] *trans*-$Mo(CO)_4(NO)(ClAlCl_3)$[73] were prepared according to literature procedures. Other reagents were obtained from commercial supplies.

Syntheses

Preparation of *trans*-$Mo(PMe_3)_4(NO)Cl$ (1). 1.96 g (6.2 mmol) of $Mo(NO)Cl_3(CH_3CN)_2$ was dissolved in *ca.* 20 ml THF in a Young-Schlenk tube and 3.5 ml (33.8 mmol) of PMe_3 was introduced *via* a syringe. The mixture was covered by a Teflon cap and stirred at room temperature for 20 hours. During the reaction some dark orange precipitate formed. The suspension was transferred into another Young–Schlenk tube, in which a 1% sodium amalgam (0.80 g (34.8 mmol) sodium in 80.0 g mercury) was prepared. The mixture was stirred overnight then filtered. The residue was extracted with THF until the extracts were colorless. The filtrate and the extracts were combined and dried *in vacuo*. The residue was washed with hexane (3 × 20 ml) and extracted with THF (25 ml). Cooling to −30 °C overnight afforded **1** as yellow crystals. Yield: 2.5 g (84%). IR (cm^{-1}, THF): 1544 (s) (NO). IR (cm^{-1}, ATR): 1522 (s) (NO). ^1H NMR (benzene-d_6, 300 MHz, 20 °C): δ 1.30 (s). ^{13}C $\{^1H\}$ NMR (benzene-d_6, 50.3 MHz, 20 °C): δ 19.3 (m). ^{31}P $\{^1H\}$ NMR (benzene-d_6, 121.5 MHz, 20 °C): δ − 2.3 (s). EI-MS: 464 (18, $[M^+]$), 428 (7, $[M^+ - Cl]$), 388 (19, $[M^+ - PMe_3]$), 314 (21, $[M^+ - 2PMe_3]$), 298 (5, $[M^+ - 2PMe_3 - O]$), 238 (10, $[M^+ - 3PMe_3]$), 76 (100, PMe_3). Anal. Calcd for $C_{12}H_{36}ClMoNOP_4$: C 30.95, H 7.79, N 3.01. found: C 30.95, H 8.17, N 3.20%.

Preparation of *trans*-$Mo(PMe_3)_4(H)(NO)$ (2). A mixture of 0.73 g (1.6 mmol) of **1** and 0.32 g (8.5 mmol) of $NaBH_4$ was dissolved in *ca.* 20 ml THF in a Young–Schlenk tube and 2.0 ml (18.4 mmol) of PMe_3 was introduced *via* a syringe. The mixture was covered by a Teflon cap, and then heated to 50 °C. After 5 days the solution was removed *in vacuo* and the Young–Schlenk tube was transferred into a glovebox. The remaining residue was extracted with pentane. Removal of pentane at room temperature was followed by sublimation of the $PMe_3{\cdot}BH_3$ adduct at 60 °C for 24 hour *in vacuo*. Redissolution of the product in pentane, concentration and chilling of the solution to −30 °C gave orange crystals of **2**. Yield: 0.59 g (87%). IR (cm^{-1} ATR): 1522 (s) (NO). IR (cm^{-1}, THF): 1558 (s) (NO). IR (cm^{-1}, hexane, 25 °C): 1562 (s) (NO). IR (cm^{-1}, hexane, −25 °C): 1562 (m) (NO), 1521 (m) (Mo–H). Raman (cm^{-1}): 1526 (NO). ^1H NMR (toluene-d_8, 300 MHz,

20 °C): δ 1.25 (s, 36H, PMe_3), −2.51 (quint, $^3J_{PH}$ = 33 Hz, 1H, Mo–H). ^{13}C {^1H} NMR (toluene-d_8, 75.4 MHz, 20 °C): δ 23.2 (m, PMe_3). ^{31}P {^1H} NMR (toluene-d_8, 121.5 MHz, 20 °C): δ 5.1 (s). EI-MS: 432 (5, M^+), 247 (8, [M^+ − $4PMe_3$]), 128 (90, [M^+ − $4PMe_3$]). Anal. Calcd for $C_{12}H_{37}MoNOP_4$: C 33.42, H 8.65, N 3.25. found: C 33.58, H 8.70, N 3.22%.

Preparation of *trans*-Mo(PMe_3)$_4$(D)(NO) (2a). **2a** was prepared by a procedure analogous to that for **2** except that $NaBD_4$ was used in the conversion of the chloride Mo(NO)(PMe_3)$_4$Cl. IR (cm^{-1} ATR): 1498 (s) (NO), 1063 (m) (Mo–D). IR (cm^{-1}, hexane, 25 °C): 1548 (s) (NO). Raman (cm^{-1}): 1507 (NO), 1066 (Mo–D). ^2H NMR (benzene-h_6, 300.1 MHz, 20 °C): δ − 2.35 (quint, $^2J_{PD}$ = 5 Hz). ^{31}P {^1H} NMR (benzene-h_6, 121.5 MHz, 20 °C): δ 4.2 (t, $^2J_{PD}$ = 5 Hz).

Preparation of *trans*-Mo(PMe_3)$_4$[OCH(CH_3)$_2$](NO) (3). A 0.0217 g (0.050 mmol) sample of **2** was dissolved in *ca.* 0.7 ml benzene and 3.7 µl (0.050 mmol) acetone was added. After 30 min (NMR monitoring) the solvent was removed *in vacuo*. The residue was extracted with pentane and the combined solutions were dried *in vacuo* to afford the yellow compound **3**. Yield: 0.024 g (98%). IR (cm^{-1} ATR): 1500 (s) (NO). ^1H NMR (benzene-d_6, 300 MHz, 20 °C): δ 3.70 (septet, $^3J_{HH}$ = 6 Hz, 1H, OCH), 1.29 (s, 36H, PMe_3), 1.05 (d, 6H, $^3J_{HH}$ = 6 Hz, -CH_3). ^{13}C {^1H} NMR (benzene-d_6, 50.3 MHz, 20 °C): δ 68.9 (m, OCH), 29.8 (s, CH_3), 20.0 (m, PMe_3). ^{31}P {^1H} NMR (benzene-d_6, 121.5 MHz, 20 °C): δ − 5.3 (s). Anal. Calcd for $C_{15}H_{43}MoNO_2P_4$: C 36.82, H 8.86, N 2.86. found: C 37.11, H 8.75, N 2.92%.

Preparation of *trans*-Mo(PMe_3)$_4$[OCH(CH_3)(Ph)](NO) (4). A 0.0222 g (0.051 mmol) sample of **2** was dissolved in *ca.* 0.7 ml benzene and 6.0 µl (0.051 mmol) acetophenone was added. After 4 hours (NMR monitoring) the solvent was removed *in vacuo*. The residue was extracted with pentane and the combined solutions were dried *in vacuo* to afford yellow compound **4**. Yield: 0.024 g (85%). IR (cm^{-1} ATR): 1508 (s) (NO). ^1H NMR (benzene-d_6, 300 MHz, 20 °C): δ 7.36–7.22 (m, 4H, Ph), 7.13–6.99 (m, 1H, Ph), 4.51 (quart, $^3J_{HH}$ = 6 Hz, 1H, OCH), 1.25 (s, 36H, PMe_3), 0.87 (d, $^3J_{HH}$ = 6 Hz, 3H, -CH_3). ^{13}C {^1H} NMR (benzene-d_6, 75.4 MHz, 20 °C): δ 155.2, 132.7, 126.3, 125.6 (4s, Ph), 77.4 (m, OCH), 31.6 (s, CH_3), 19.9 (m, PMe_3). ^{31}P {^1H} NMR (benzene-d_6, 121.5 MHz, 20 °C): δ − 5.3 (s). Anal. Calcd for $C_{20}H_{45}MoNO_2P_4$: C 43.56, H 8.23, N 2.54. found: C 43.67, H 8.11, N 2.46%.

Preparation of *trans*-Mo(PMe_3)$_4$[OCH(Ph)$_2$](NO) (5). A 0.0205 g (0.046 mmol) sample of **2** was dissolved in *ca.* 0.7 ml benzene and 0.0088 g (0.048 mmol) benzophenone was added. After 10 hours (NMR monitoring) the solvent was removed *in vacuo*. The residue was extracted with pentane and the combined solutions were concentrated and cooled to −30 °C to afford yellow crystals of **5**. Yield: 0.027 g (96%). IR (cm^{-1} ATR): 1502 (s) (NO). ^1H NMR (benzene-d_6, 300 MHz, 20 °C): δ 7.72–6.92 (m, 10H, Ph), 5.35 (s, 1H, OCH), 1.21 (s, 36H, PMe_3). ^{13}C {^1H} NMR (benzene-d_6, 75.4 MHz, 20 °C): δ 155.9, 129.9, 129.1, 127.9 (4s, Ph), 87.9 (m, OCH), 21.9 (m, PMe_3). ^{31}P {^1H} NMR (benzene-d_6 121.5 MHz, 20 °C): δ − 5.6 (s). Anal. Calcd for $C_{25}H_{47}MoNO_2P_4$: C 48.94, H 7.72, N 2.28. found: C 48.55, H 7.51, N 2.35%.

Preparation of *trans*-Mo(PMe_3)$_4$(OCHO)(NO) (6). 0.062 g (0.14 mmol) of **2** was dissolved in about 0.7 ml THF in an NMR tube. The solution was frozen, and the NMR tube was evacuated and then filled with CO_2 (2 bar). The tube was sealed and kept at −10 °C for 30 min. The resulting mixture was allowed to warm to room temperature and the solvent and excess CO_2 was evaporated *in vacuo* and the residue was extracted with pentane. Removal of the solvent *in vacuo* afforded the brown compound **6**. Yield: 0.065 g (95%). IR (cm^{-1} ATR): 1626 (OCO) (s), 1529 (s) (NO). ^1H NMR (THF-d_8, 300 MHz, 20 °C): δ 8.13 (s, 1H, OCHO), 1.43 (s, 36H, PMe_3). ^{13}C {^1H} NMR (THF-d_8, 50.3 MHz, 20 °C): δ 166.6 (s, OCHO), 19.9 (m, PMe_3). ^{31}P {^1H} NMR (THF-d_8, 121.5 MHz, 20 °C): δ − 1.8 (s). EI-MS: 398 (62, [M^+ − PMe_3]), 323 (75, [M^+ − $2PMe_3$]), 277 (72, [M^+ − $2PMe_3$ − OCHO]). Anal. Calcd for $C_{13}H_{37}MoNO_3P_4$: C 32.85, H 7.85, N 2.95. found: C 32.87, H 7.91, N 3.01%.

Preparation of *trans*-Mo(PMe_3)$_4$(NO)(OSO_2CF_3) (7). 0.010 g (0.023 mmol) of **2** was dissolved in *ca.* 0.7 ml benzene-d_6 in an NMR tube and 2.5 µl (0.029 mmol) of $HOSO_2CF_3$ was added. Bubbles evolved and the reaction was immediately complete (^1H NMR monitoring). The solvent was removed *in vacuo* to obtain **7** as a yellow powder. Yield: 0.012 g (89%). IR (cm^{-1} ATR):1551 (s) (NO). ^1H NMR (THF-d_8, 300 MHz, 20 °C): δ 1.50 (m, PMe_3). ^{13}C {^1H} NMR (THF-d_8, 75.4 MHz, 20 °C): δ 120.4 (quart, $^1J_{CF}$ = 319 Hz, CF_3), 19.4 (m, PMe_3). ^{31}P {^1H} NMR (THF-d_8, 121.5 MHz, 20 °C): δ − 2.6 (s). ^{19}F {^1H} NMR (THF-d_8, 282.2 MHz, 20 °C): δ − 79.8 (s). Anal. Calcd for $C_{13}H_{36}F_3MoNO_4P_4S$: C 26.95, H 6.26, N 2.42. found: C 27.34, H 6.02, N 2.46%.

Preparation of [Mo(PMe_3)$_5$(NO)][BAr^F_4] (8). A 0.020 g (0.046 mmol) sample of **2** was dissolved in an NMR tube in *ca.* 1 ml diethyl ether and 0.051 g (0.054 mmol) of [H(Et_2O)][BAr^F_4] was added in a glovebox. The NMR tube was sealed with a Teflon cap and immediately transferred out of the glovebox and frozen in liquid nitrogen. 25 µl of PMe_3 (0.242 mmol) was added *via* syringe then the liquid nitrogen was removed and the reaction mixture was allowed to warm to room temperature. Within 10 minutes the reaction was complete (^{31}P NMR monitoring), and some **8** precipitated from the solution. Pentane was laid over this solution and after 24 hours orange crystals of **8** were collected and dried. Yield: 0.047 g (72%). IR (cm^{-1} ATR): 1593 (NO). ^1H NMR (THF-d_8, 300 MHz, 20 °C): δ 7.79 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 1.52 (s, 36H, PMe_3 *trans* each other), 1.28 (m, 9H, PMe_3 *trans* to NO). ^{13}C {^1H} NMR (THF-d_8, 75.4 MHz, 20 °C): δ 165.0 (quart, br, $^1J_{BC}$ = 50 Hz, *i*-BAr^F_4), 137.6 (s, *o*-BAr^F_4), 130.2 (m, *m*-BAr^F_4), 127.5 (quart, $^1J_{CF}$ = 272 Hz, CF_3), 120.1 (m, *p*-BAr^F_4), 23.9 (m, PMe_3 *trans* each other), 22.0 (m, PMe_3 *trans* to NO). ^{31}P {^1H} NMR (THF-d_8, 121.5 MHz, 20 °C): δ − 9.8 (d, $^2J_{PP}$ = 26 Hz, 4P, PMe_3 *trans* each other), −34.2 (quint, $^2J_{PP}$ = 26 Hz, 1P, PMe_3 *trans* to NO). ^{19}F {^1H} NMR (THF-d_8, 282.2 MHz, 20 °C): δ − 63.2 (s). EI-MS: 403 (82, [M^+ − PMe_3 − NO]), 354 (10, [M^+ − $2PMe_3$]), 337 (20, [M^+ − $2PMe_3$ − O]), 173 (5, [M^+ − $3PMe_3$ − NO]), 76 (100, PMe_3). Anal. Calcd for $C_{47}H_{57}BF_{24}MoNOP_5$: C 41.22, H 4.20, N 1.02. found: C 41.46, H 3.98, N 1.21%.

Reaction of [Mo(PMe_3)$_4$(H)(NO)] (2) with *N*-benzylideneaniline. A mixture of 0.020 g (0.046 mmol) of **2** and 0.008 g (0.044 mmol) of *N*-benzylideneaniline was dissolved in *ca.* 0.7 ml of toluene-d_8 in an NMR tube. The reaction was monitored by NMR. After 3 days at room temperature the reaction was complete and

9 was obtained (^{1}H and ^{31}P NMR monitoring). Analytically pure product could not be obtained. NMR data of **9**: ^{1}H NMR (toluene-d_8, 500.2 MHz, 20 °C): δ 7.72–6.47 (m, 10H, Ph), 4.42 (s, 2H, NCH_2), 1.12 (s, 36H, PMe_3). ^{1}H NMR (toluene-d_8, 500.2 MHz, −50 °C): δ 7.78–6.45 (m, 10H, Ph), 4.48 (s, 2H, NCH_2), 1.11 (s, 36H, PMe_3). ^{13}C {^{1}H} NMR (toluene-d_8, 125.8 MHz, −50 °C): δ 160.9, 144.4, 129.4, 128.9, 128.1, 127.5, 121.5, 111.2 (8s, Ph), 60.4 (m, NCH_2), 22.8 (PMe_3). ^{31}P {^{1}H} NMR (toluene-d_8, 202.5 MHz, 20 °C): δ − 9.0 (br). ^{31}P {^{1}H} NMR (toluene-d_8, 202.5 MHz, −50 °C): δ − 7.1 (s).

Preparation of Mo[N(CH$_2$Ph)(C$_{10}$H$_7$)](PMe$_3$)$_3$(NO) (10). A mixture of 0.031 g (0.072 mmol) of **2** and 0.016 g (0.069 mmol) of *N*-benzylidene-1-naphthylamine was dissolved in *ca.* 0.7 ml of toluene-d_8 in an NMR tube. The reaction was monitored by NMR. After 3 days at room temperature the reaction was complete (^{1}H and ^{31}P NMR monitoring). The solvent was removed *in vacuo*, the residue was extracted with pentane, the combined solutions were concentrated and cooled to −30 °C to give a red powder of **10**. Yield: 0.024 g (59%). IR (cm^{-1} ATR): 1557 (s) (NO). Raman (cm^{-1}): 1558 (NO). ^{1}H NMR (toluene-d_8, 500.2 MHz, 20 °C): δ 7.50 (d, $^2J_{HH}$ = 8 Hz, 1H, 5-naphthyl), 7.47 (t, $^2J_{HH}$ = 7 Hz, 1H, 7-naphthyl), 7.11 (t, $^2J_{HH}$ = 8 Hz, 1H, 6-naphthyl), 7.07 (d, $^2J_{HH}$ = 7 Hz, 2H, *o*-Ph), 7.02 (t, $^2J_{HH}$ = 6 Hz, 1H, 3-naphthyl), 7.01 (t, $^2J_{HH}$ = 8 Hz, 2H, *m*-Ph), 6.94 (t, $^2J_{HH}$ = 8 Hz, 1H, *p*-Ph), 6.63 (d, $^2J_{HH}$ = 8 Hz, 1H, 4-naphthyl), 5.92 (d, $^2J_{HH}$ = 7 Hz, 1H, 2-naphthyl), 4.43 (s, 2H, NCH_2), 2.97 (br, 1H, 8-naphthyl), 1.10 (m, 9H, PMe_3 *trans*-agostic), 0.78 (s, 18H, PMe_3 *cis*-agostic). ^{13}C {^{1}H} NMR (toluene-d_8, 125.8 MHz, 20 °C): δ 160.1 (s, 1-naphthyl), 142.2 (s, *i*-Ph), 136.7 (s, 9-naphthyl), 135.1 (s, 10-naphthyl), 131.7 (s, 7-naphthyl), 129.0 (s, 5-naphthyl), 128.7 (s, 3-naphthyl), 128.3 (s, *m*-Ph), 127.3 (s, *o*-Ph), 126.1 (s, 6-naphthyl), 125.8 (s, *p*-Ph), 117.0 (d, $^3J_{CP}$ = 9 Hz, 8-naphthyl), 108.9 (s, 4-naphthyl), 105.6 (s, 2-naphthyl), 56.8 (d, $^3J_{CP}$ = 6 Hz, NCH_2), 21.3 (m, PMe_3 *trans*-agostic), 18.2 (m, PMe_3 *cis*-agostic). ^{31}P {^{1}H} NMR (toluene-d_8, 202.5 MHz, 20 °C): δ 16.7 (t, $^2J_{PP}$ = 19 Hz, *trans*-agostic), −5.5 (br, PMe_3 *cis*-agostic). Anal. Calcd for $C_{26}H_{41}MoN_2OP_3$: C 53.25, H 7.05, N 4.78. found: C 53.49, H 6.96, N 4.72%.

Reaction of [Mo(PMe$_3$)$_4$(H)(NO)] (2) with *N*-1-naphthylideneaniline.

At room temperature. A mixture of 0.032 g (0.074 mmol) of **2** and 0.016 g (0.069 mmol) of *N*-1-naphthylideneaniline was dissolved in *ca*. 0.7 ml of toluene-d_8 in an NMR tube. The reaction was monitored by NMR at room temperature. After 4 days the reaction was complete (^{1}H and ^{31}P NMR monitoring). The solvent was removed *in vacuo*, the residue was dissolved in *ca*. 0.1 ml toluene and diffusion of pentane into the toluene solution afforded **12** as red crystals. Yield: 0.013 g (45%). IR (cm^{-1}, ATR): 1578 (s) (NO). Raman (cm^{-1}): 1582 (NO). ^{1}H NMR (toluene-d_8, 500.2 MHz, −60 °C): δ 8.11 (d, $^2J_{HH}$ = 8 Hz, 1H, 8-naphthyl), 7.61 (d, $^2J_{HH}$ = 8 Hz, 1H, 5-naphthyl), 7.53 (d, $^2J_{HH}$ = 8 Hz, 1H, 2-naphthyl), 7.47 (d, $^2J_{HH}$ = 8 Hz, 1H, 4-naphthyl), 7.39 (t, $^2J_{HH}$ = 8 Hz, 1H, 7-naphthyl), 7.29 (t, $^2J_{HH}$ = 8 Hz, 1H, 6-naphthyl), 7.23 (d, $^2J_{HH}$ = 8 Hz, 1H, 3-Ph), 7.21 (t, $^2J_{HH}$ = 8 Hz, 1H, 3-naphthyl), 7.00 (m, 1H, 5-Ph), 6.58 (t, $^2J_{HH}$ = 8 Hz, 1H, 4-Ph), 5.87 (d, $^2J_{HH}$ = 8 Hz, 1H, 6-Ph), 4.74 (s, 2H, NCH_2), 3.29 (br, 1H, 2-Ph), 0.98 (s, 18H, PMe_3 *cis*-agostic), 0.94 (m, 9H, PMe_3 *trans*-agostic). ^{13}C {^{1}H} NMR (toluene-d_8, 125.8 MHz, −60 °C): δ 157.8 (s, *i*-Ph), 136.0 (s, 1-naphthyl), 135.6 (s, 3-Ph), 134.1 (s, 9-naphthyl), 131.7 (s, 10-naphthyl), 131.1 (s, 5-Ph), 129.4 (s, 5-naphthyl), 126.4 (s, 4-naphthyl), 125.7 (s, 3-naphthyl), 125.3 (s, 7-naphthyl), 125.2 (s, 6-naphthyl), 124.2 (s, 2-naphthyl), 122.4 (s, 8-naphthyl), 113.4 (s, 4-Ph), 108.9 (s, 6-Ph), 91.5 (s, br, 2-Ph), 51.4 (s, NCH_2), 20.9 (m, PMe_3 *trans*-agostic), 17.6 (m, PMe_3 *cis*-agostic). ^{31}P {^{1}H} NMR (toluene-d_8, 202.5 MHz, −60 °C): δ 33.1 (t, $^2J_{PP}$ = 17 Hz, *trans*-agostic), −8.0 (d, $^2J_{PP}$ = 17 Hz, PMe_3 *cis*-agostic). Anal. Calcd for $C_{26}H_{41}MoN_2OP_3$: C 53.25, H 7.05, N 4.78. found: C 53.63, H 7.14, N 4.87%.

At 60 °C. A 0.014 g (0.032 mmol) sample of **2** was dissolved in *ca*. 0.7 ml of toluene-d_8 in an NMR tube then 0.008 g (0.034 mmol) of *N*-1-naphthylideneaniline was added. The resulting solution was heated to 60 °C. After 2 days the reaction was complete (^{1}H and ^{31}P NMR monitoring). The solvent was removed *in vacuo* and the remaining residue was extracted with pentane. The combined solutions were concentrated and cooled to −30 °C overnight, which gave a mixture of a brown solid and green-brown crystals. Single crystals suitable for a X-ray diffraction study could be picked out from the mixture, which was demonstrated to be **15**. An analytically pure product could not be obtained.

Catalytic hydrogenations of imines with 2 under H$_2$ pressure

These reactions were carried out as follows: a mixture of the catalyst **2** and PhCH=NC$_{10}$H$_7$ or C$_{10}$H$_7$CH=NPh was dissolved according to Table 6 in *ca.* 2 ml of toluene in a steel autoclave. The reaction vessel was then pressurized with 60 or 120 bar H_2. The contents were stirred and heated for given temperature and periods of times. The mixtures were filtered over silica gel. The conversions were determined by GC.

X-Ray crystal structure analyses of 2, 5, 8, 12 and 15

All crystals were grown and prepared under a nitrogen atmosphere in a glove box in order to avoid deterioration of these compounds by air and moisture. Before the crystals were sent out for selection, they were embedded in polybutene oil in the glove box. Good quality single crystals for the X-ray diffraction studies have been chosen under polarized light using a polarizing microscope. The selected single crystal was mounted on top of a glass fibre and fixed on a goniometer head, then it was transferred immediately to the Stoe IPDS diffractometer where the crystal was cooled to 183(2) K, using an Oxford Cryogenic System. Centreing of the crystal was performed with the support of a video camera, which is incorporated in the Stoe IPDS diffractometer and controlled by the computer terminal.

X-Ray diffraction data were collected at 183(2) K using an imaging plate detector system (Stoe IPDS) with graphite monochromated Mo-Kα radiation. A total of 200, 218, 200, 200 and 300 images were exposed at constant times of 7.00, 1.00, 2.00, 2.20 and 1.50 min per image for **2**, **5**, **8**, **12**, **15** respectively. The crystal-to-image distances were set to 50.0 mm (60.0 mm for **8** and **15**) (θ_{max} = 30.29°, 30.34°, and 30.41° for **2**, **5**, and **12**; θ_{max} = 28.09° and 28.09° for **8** and **15**). ϕ-oscillation (**2**) or rotation scan modes (**5**, **8**, **12**, **15**) were selected for the ϕ increments of 1.3°, 1.1°, 1.2°, 1.4° and 0.7° per exposure for **2**, **5**, **8**, **12**, **15** respectively. Total exposure times for the five compounds were 37, 19, 21, 17 and 28 hours in the order of the complexes as given above. The intensities were integrated after using a dynamic

Table 7 Summary of X-ray diffraction studies for **2**, **5**, **8**, **12** and **15**

	2	**5**	**8**	**12**	**15**
Empirical formula	$C_{12}H_{37}MoNOP_4$	$C_{23}H_{47}MoNO_2P_4$	$C_{47}H_{57}BF_{24}MoNOP_5$	$C_{26}H_{41}MoN_2OP_3$	$C_{26}H_{41}MoN_2OP_3$
Formula weight/g mol^{-1}	431.25	613.46	1369.54	586.46	586.46
T/K	183(2)	183(2) K	183(2)	183(2)	183(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*Cc*	$P2_1/c$	*Pn*	$P2_1$	*Pbca*
a/Å	9.5261(7)	10.0261(9)	13.1223(18)	10.1601(7)	13.4047(9)
b/Å	15.6484(15)	16.7255(10)	13.2643(12)	13.9020(9)	14.3370(13)
c/Å	14.6607(11)	18.7690(18).	18.473(2)	10.9422(8)	30.111(2)
α/°	90	90	90	90	90
β/°	98.876(9)	94.046(11)	108.728(15)	107.548(8)	90
γ/°	90	90	90	90	90
V/Å^3	2159.3(3)	3139.6(5)	3045.2(6)	1473.62(18)	5786.9(8)
Z, d_{calcd}/Mg m^{-3}	4, 1.327	4, 1.298	2, 1.494	2, 1.322	8, 1.346
μ/mm^{-1})	0.899	0.642	0.455	0.628	0.640
F(000)	904	1288	1384	612	2448
Reflections collected/unique	16665/6197 [R(int) = 0.0593]	44839/9353 [R(int) = 0.0443]	33425/14600 [R(int) = 0.0628]	23862/8795 [R(int) = 0.0744]	44150/6985 [R(int) = 0.0505]
Goodness-of-fit on F^2	0.882	1.000	0.869	0.671	0.876
Final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0337$, $wR2 = 0.0709$	$R1 = 0.0305$, $wR2 = 0.0787$	$R1 = 0.0611$, $wR2 = 0.1474$	$R1 = 0.0348$, $wR2 = 0.0687$	$R1 = 0.0300$, $wR2 = 0.0759$
R indices (all data)	$R1 = 0.0469$, $wR2 = 0.0737$	$R1 = 0.0408$, $wR2 = 0.0809$	$R1 = 0.1017$, $wR2 = 0.1637$	$R1 = 0.0622$, $wR2 = 0.0712$	$R1 = 0.0410$, $wR2 = 0.0780$
Absolute struct. param.	0.01(4)		−0.01(4)	0.03(3)	

[a] $R1 = \sum(F_o - F_c)/\sum F_o$; $I > 2\sigma(I)$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

peak profile analysis and estimated mosaic spread (EMS) check[73] was performed to prevent overlapping intensities. 8000 reflections (7998 for **8**) were selected out of the whole limiting sphere for the cell parameter refinements. A total of 16665, 44839, 33425, 23862 and 44150 reflections were collected, of which 6197, 9353, 14600, 8795 and 6985 reflections were unique (R_{int} = 5.93%, 4.43%, 6.28%, 7.44% and 5.05%); data reduction and numerical absorption correction used 7, 14, 9, 7 and 16 indexed crystal faces.[74] All five structures were solved by the Patterson method using an improved version of SHELXS-97[75] and refined with SHELXL-97.[76] Compound **2** crystallizes in the non-centrosymetric achiral[77] space group *Cc* (no. 9). Many structures published wrongly in space group *Cc* were detected by Baur *et al.*[78] and Marsh.[79,80] Compound **8** crystallizes in the non-centrosymmentric achiral space group *Pn* (no. 7, cell choice 2 of space group *Pc*), which is also a candidate for overlooked higher symmetry (*e.g.* space groups $P2/n$ or $P2_1/n$). The program PLATON[81] was used to find centrosymmetric symmetry for structure **2** (*e.g.* space group $C2/c$, no. 14) and structure **8** (*e.g.* $P2/n$, or $P2_1/n$, no. 13 or no. 14), however, no higher symmetry was found for both structures. The absolute structures of **2** and **8** and the chiral structure of **12** (space group $P2_1$) were determined by using Flack's X-parameter refinement.[82,83] The absolute structure parameters X for compounds **2**, **8** and **12** are given in Table 7. No twinning by merohedry was noted for these non-centrosymmetric structures.

CCDC reference numbers 281546–281550.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511797f

Acknowledgements

Financial support from the Swiss National Science Foundation (SNSF) and University of Zürich are gratefully acknowledged.

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