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Molybdenum Carbonyl Complexes Bearing PN Ligands Based on 2-Aminopyridine

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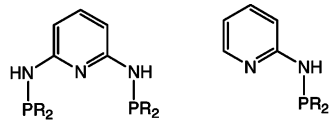
Dedicated to Prof. Peter Stanetty on the occasion of his 65th birthday

Keywords: Molybdenum / Carbonyl complexes / Phosphanes / Amines / Oxidative addition / Allyl ligands / Density functional calculations

Molybdenum complexes of the general formula $Mo(PN)(CO)_4$ containing both achiral and chiral phosphorus-nitrogen donor bidentate ligands based on 2-aminopyridine were prepared and characterized by their NMR and IR spectra. The oxidative addition of allyl bromide to $Mo(PN)(CO)_4$ was studied with PN = *N*-(diisopropylphosphanyl)-2-aminopyridine (PN-*i*Pr). X-ray structures of representative compounds were determined. The mechanism of the oxidative addition of allyl bromide to $Mo(PN\text{-}iPr)(CO)_4$ was analyzed by DFT/B3LYP calculations.

Introduction

Considering the comparative ease of phosphorus–nitrogen bond forming reactions compared to those in which phosphorus–carbon bonds are formed, relatively few examples of pyridylphosphanes in which the donor atoms are separated by amino groups are known. We have recently described the synthesis of a series of tridentate (pincer) PNP (**I**)[1] and bidentate PN ligands (**II**)[2] in which an amine acts as spacer between the aromatic ring and the phosphanes. In all these ligands, their electronic, steric, and stereochemical properties can be easily varied in a modular fashion by using different aryl and alkyl phosphanes as well as different P–O bond containing achiral and chiral phosphane units. With PNP ligands, we thus far studied their reactivity towards different transition metal fragments which has been resulting in the preparation of a range of new pincer complexes, including the first heptacoordinated molybdenum pincer complexes,[1a] various iron complexes acting as CO sensors,[1b,1d] and several pentacoordinate nickel complexes.[3] Surprisingly, as PN complexes with ligands of the type **II** are concerned, in the literature only few examples of transition metal complexes have been described.[4] In a preliminary study we have recently reported on the synthesis of a series of square planar Ni^{II} and Pd^{II} complexes featuring PN ligands.[2]



I (PNP) **II** (PN)

Here we extend our studies on PN complexes based on 2-aminopyridine and report on the synthesis of a series of molybdenum tetracarbonyl complexes of the general formula $Mo(PN)(CO)_4$. The oxidative addition of allyl bromide to $Mo(PN)(CO)_4$ is studied with PN = N-(diisopropylphosphanyl)-2-aminopyridine (PN-*i*Pr). Mechanistic aspects of this reaction will be supported by DFT/B3LYP calculations.

Results and Discussion

Synthesis

Similarly to the known ligands PN-Ph,[5] PN-*i*Pr, PN-BIPOL, and PN-TAR^{Me},[2] the new PN ligands PN-*t*Bu, PN-ETOL, and PN-$BIPOL^{2tBu}$ are prepared conveniently in 68–85% yield by treatment of 2-aminopyridine with 1 equiv. of the respective chlorophosphane or chlorophosphite in the presence of a base (NEt_3 and/or *n*BuLi) (Scheme 1). All reactions were carried out in toluene at temperatures between 25 to 90 °C for 15 h. The ligands were

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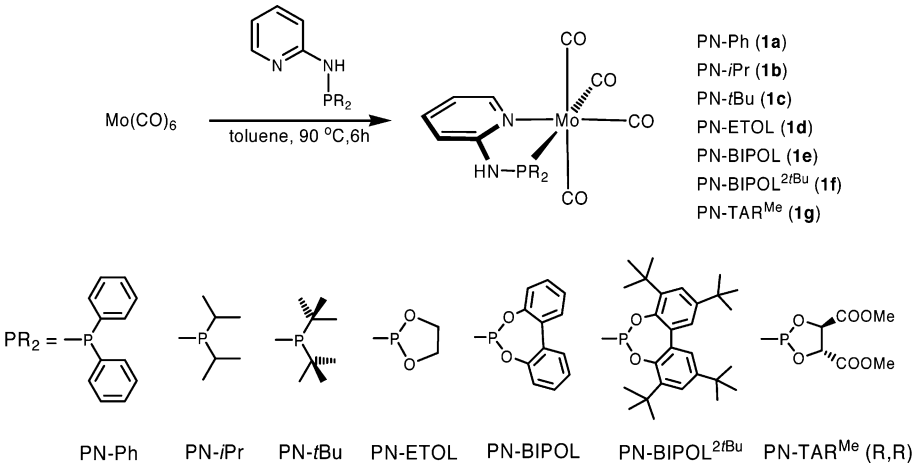


Scheme 1.

isolated as air stable solids or oils and were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Most diagnostic is the ^{31}P{^{1}H} NMR spectrum exhibiting a singlet at 71.3, 140.0, and 151.0 ppm for PN-*t*Bu, PN-ETOL, and PN-BIPOL$^{2t\mathrm{Bu}}$, respectively. In the ^{1}H NMR spectrum the NH proton gives rise to a slightly broadened singlet in the range of 5.90 to 6.60 ppm. All other resonances are unremarkable and are not discussed here. In addition, the solid-state structure of PN-*i*Pr was determined by X-ray crystallography. A structural view is shown in Figure 1 with selected bond lengths and angles given in the caption.

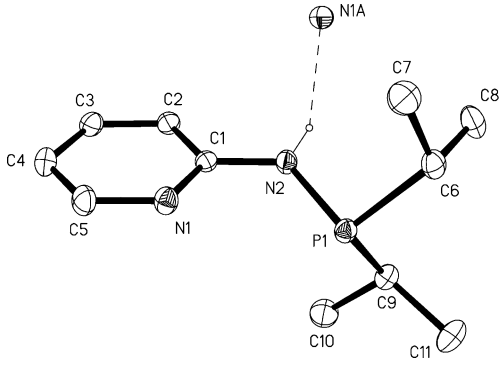


Figure 1. Molecular structure of PN-*i*Pr showing 50% displacement ellipsoids. Only N-bonded hydrogen is shown. Selected distances and angles (Å, deg): P1–N2 1.721(1), P1–C6 1.857(1), P1–C9 1.856(1), N1–C1 1.339(1), N1–C5 1.346(1), N2–C1 1.382(1), C1–C2 1.413(1), C2–C3 1.381(1), C3–C4 1.393(1), C4–C5 1.381(1); P1···N1 2.999(1); P1–N2–C1–N1–17.9(1); hydrogen bond N2-(H2n)···N1A 3.203(1).

Treatment of $Mo(CO)_6$ with 1 equiv. of the respective PN ligands in toluene at 90 °C for 6 h afforded the tetra carbonyl complexes $Mo(PN)(CO)_4$ (**1a**–**g**) in good isolated yields (74–91%) (Scheme 1). It has to be noted that the synthesis of **1a** was already reported elsewhere.[5] All complexes are thermally robust yellow solids that are air stable both in the solid state and in solution for several days. Their identity was unequivocally established by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR, IR spectroscopy, and elemental analysis.

In the ^{31}P{^{1}H} NMR spectra, **1a**–**f** exhibit singlets which show the expected low-field shifts relative to the free uncoordinated ligands [**1a**: 95.9 ppm ($\Delta\delta$ = 58.4 ppm), **1b**: 124.1 ppm ($\Delta\delta$ = 64.0 ppm), **1c**: 138.2 ppm ($\Delta\delta$ = 66.9 ppm), **1d**: 190.6 ppm ($\Delta\delta$ = 50.6 ppm), **1e**: 196.5 ppm ($\Delta\delta$ = 39.1 ppm), **1f**: 194.2 ppm ($\Delta\delta$ = 43.2 ppm), **1f**: 202.9 ppm ($\Delta\delta$ = 52.8 ppm)]. In the ^{13}C{^{1}H} NMR spectra of **1a**–**f** the carbon atoms of the four CO ligands give rise to three characteristic low-field doublets. For instance, **1a** exhibits signals at 220.7 (J_{PC} = 7.0 Hz), 216.1 (J_{PC} = 34.9 Hz), and 209.1 (J_{PC} = 9.5 Hz) ppm. The two smaller coupling constants are diagnostic for the phosphorus atom in *cis* position with respect to the CO ligand.

The IR spectra of **1a**–**f** show the typical pattern for *cis*-$[Mo(CO)_4(L)(L')]$ complexes [with local C_{2v} symmetry, i.e., when only the symmetry of the $Mo(CO)_4$ moiety of the complexes is considered] in the carbonyl region. However, in these and also related complexes[6] usually only three of the four expected absorptions are observed. For instance, while **1c** exhibits four strong ν(C=O) absorptions at 2010, 1903, 1880, and 1812 cm^{-1}, **1b** gives rise to three absorptions at 2019, 1879, and 1818 cm^{-1}.

The solid-state structures of **1a**–**1d** were determined by X-ray crystallography. Structural views of **1b**, **1c**, and **1d** are shown in Figures 2, 3 and 4 with selected bond lengths and angles given in Table 2. The coordination geometry around the molybdenum center of the four complexes corresponds to a modestly distorted octahedron with Mo–N 2.273 to 2.296 Å, Mo–P 2.409 (for **1d**) to 2.560 Å (for **1c**), and Mo–C 1.963 to 2.064 Å. There is a clear trend that the Mo–C bonds *trans* to the pyridine N atom are short, *trans* to phosphorus are intermediate, and that the remaining are long. The bite angle N–Mo–P is near 76°. All other *cis*-bond angles about Mo are closer to 90°, varying between 82 and 100°. All complexes deviate significantly from a possible mirror symmetry for which Mo, P, pyridylamine, and

two CO groups would lie on a mirror plane. The r.m.s. aplanarity of this moiety is in fact between 0.034 Å for **1d** (here the complex is closest to mirror symmetry) and 0.103 Å for **1c**. It can be noted that the PN ligands cause a systematic outward bending of the CO ligands off from the PN ligand. This effect is due to the bulkiness of the PR_2 moiety ($PtBu_2 > PiPr_2 > ETOL \approx PPh_2$) and is largest for the *t*Bu bearing complex **1c**, which shows the longest Mo–P bond length of 2.560 Å and the smallest C–Mo–C *trans*-bond angle of 166.5° (all other corresponding angles lie between 172.5 and 174.4°). A typical feature of all four complexes is the acidity of the NH group, which leads to intermolecular hydrogen bonding with the carbonyl oxygen atom of a neighboring complex at N···O distances of 3.00–3.17 Å. In case of **1d** this is a almost symmetrically branched bifurcated hydrogen bond to O2 (N···O 3.10 Å) and O3 (N···O 3.17 Å).

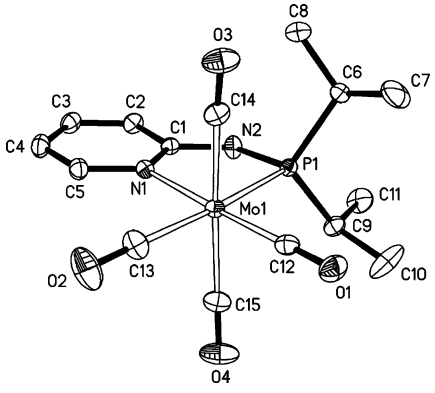


Figure 2. Molecular structure of **1b** showing 50% displacement ellipsoids. H atoms omitted for clarity.

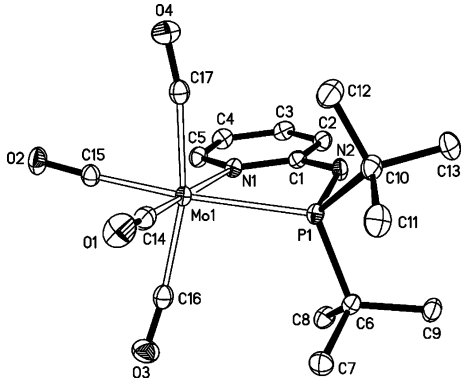


Figure 3. Molecular structure of **1c** (50% displacement ellipsoids, H atoms omitted for clarity). The Figure emphasizes the steric effect of the bulky *t*Bu groups on the two carbonyl groups C16–O3 und C17–O4. P1 deviates by –0.315(2) Å from the least-squares plane of the pyridine ring, Mo1 by 0.152(2) Å. P1–N2–C1–N1 15.8(1)°.

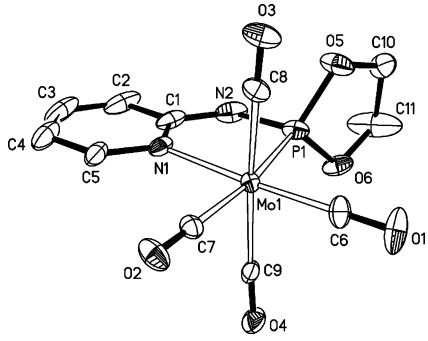
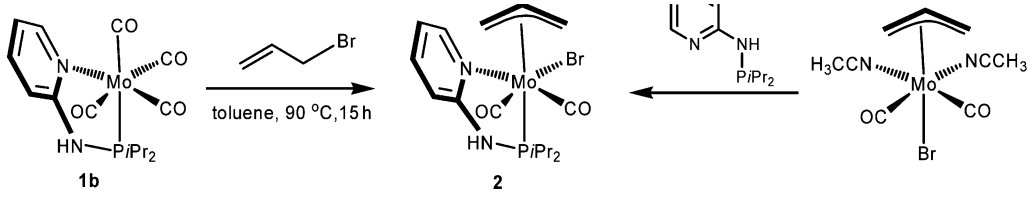


Figure 4. Molecular structure of **1d**. This complex approaches a non-crystallographic C_s symmetry.

As part of our interest in the chemistry of molybdenum PN complexes, we have begun to investigate the reactivity of complexes **1** towards allyl bromide with the intention to obtain η^3-allyl complexes of the type $Mo(PN)(\eta^3\text{-}CH_2CHCH_2)(CO)_2Br$. In the present study we have chosen **1b** as model complex. Accordingly, the reaction of **1b** with 1 equiv. of allyl bromide in toluene at 90 °C afforded, upon workup, the seven coordinate η^3-allyl complex Mo(PN-*i*Pr)(η^3-CH_2CHCH_2)$(CO)_2Br$ (**2**) as air-stable orange solid in 82% yield (Scheme 2). Alternatively, however, **2** can be also obtained under mild conditions (room temperature) in 84% yield by treatment of $Mo(\eta^3\text{-}CH_2CHCH_2)(CO)_2(CH_3CN)_2Br$ with 1 equiv. of PN-*i*Pr in CH_2Cl_2. The identity of **2** was established by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, IR spectroscopy, and elemental analysis.

The ^1H NMR spectrum shows the expected resonances for the allyl moiety giving rise to five signals. The central allylic hydrogen atom exhibits a multiplet at δ = 4.30 ppm, while the signals of the terminal allylic protons appear as doublets or broad singlets at 4.10, 3.58, 1.81, and 1.70 ppm (the latter being superimposed with the CH_3 protons of the *i*Pr substituent). In the $^{13}C\{^1H\}$ NMR spectrum the allylic carbon atoms appear at 120.6, 77.2, and 62.0 ppm. The characteristic resonance of the magnetically inequivalent *cis* carbonyl ligands give rise to resonances at δ = 226.3 and 223.1 ppm with coupling constants J_{CP} of 13.2 and 8.0 Hz, respectively, indicating that the CO ligands are both coordinated *cis* with respect to the iPr_2 moiety. The IR spectrum displays the two expected peaks for a *cis* dicarbonyl structure at 1925 and 1835 cm^{-1}.



Scheme 2.

The molecular structure of **2** was unequivocally determined by X-ray crystallography. A structural view is shown in Figure 5 with selected bond lengths and angles given in the caption. This molecule can be described as pseudo octahedral with the assumption that the η^3-allyl moiety occupies one coordination site. An equatorial plane can be defined to include the two carbonyls [C(15)–O(1) and C(16)–O(2)], the halogen [Br(1)], and the nitrogen atom [N(1)] of the PN-*i*Pr ligand. The η^3-allyl ligand and the phosphorus atom of PN-*i*Pr lie *trans* to one another in apical positions above and below the equatorial plane. This is in contrast to $Mo(\eta^3\text{-}CH_2CHCH_2)(CO)_2(CH_3CN)_2Br$ where the bromide ligand is coordinated *trans* to the η^3-allyl moiety. Thus, the substitution of the CH_3CN ligands by PN-*i*Pr is obviously accompanied by an isomerization step. The Mo–N, Mo–P, and Mo–C_{CO} bond lengths are close to those observed for complexes **1a** through **1d** (Table 2). The allyl group adopts an orientation, which is fixed by intramolecular contacts between the allyl group and the pyridine ring, with the C5 group of the pyridine ring intercalated between the allyl CH group C13 and the allyl CH_2 group C14. Different from complexes **1a** through **1d**, the N–H group forms an intermolecular hydrogen bond to Br rather than to O, N2···Br1 3.465(2) Å.

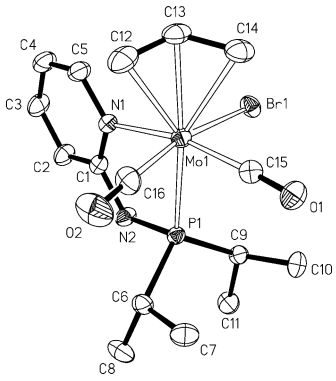


Figure 5. Molecular structure of **2** (50% displacement ellipsoids, H atoms omitted for clarity). Selected bond lengths and angles (Å, deg): Mo1–C16 1.935(2), Mo1–C15 1.957(2), Mo1–C13–2.223(2), Mo1–C12–2.328(2), Mo1–N1 2.329(2), Mo1–C14 2.351(2), Mo1–P1–2.5215(5), Mo1–Br1–2.6863(3) Å; N1–Mo1–P1 75.20(4), P1–Mo1–C13 163.46(5).

Mechanistic Aspects of the Oxidative Addition of Allyl Bromide

In the absence of detectable intermediates on the way from **1b** (**A** in the calculations) to the η^3-allyl complex **2** (**G1** in the calculations) we performed DFT (B3LYP) calculations using Gaussian03. Along these lines several pathways and key intermediates can be proposed and these are depicted in Figures 6, 7, and 8 (free energies in kcal/mol). The reliability of the computational method (Details in Experimental Section) is supported by the excellent agreement between the calculated geometries of **1b** and **2** and their X-ray structures.

The reaction is most likely initiated by CO loss from **A** creating a vacant coordination site for an incoming substrate. For comparison, it has to be mentioned that in related complexes such as $Mo(CO)_5$(pyridine) and $Mo(CO)_5$-(piperidine) first bond dissociation energies have been experimentally determined to be 29.7 and 43.7 kcal/mol, respectively.[7] For $Mo(CO)_6$ first bond dissociation energies were found to be in the range of about 35 to 40 kcal/mol.[8]

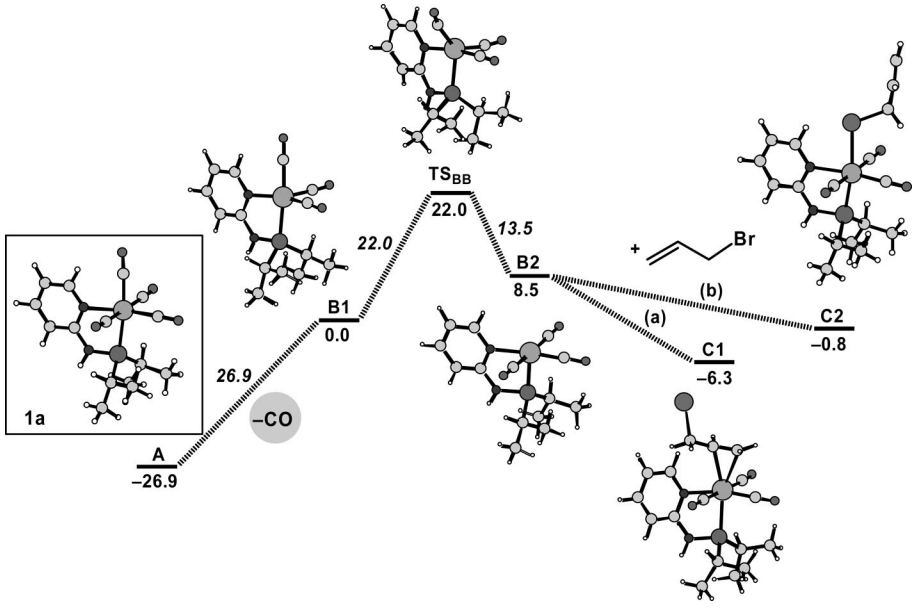


Figure 6. Profile of the B3LYP potential energy surfaces (free energies in kcal/mol) for the formation and interconversion of tricarbonyl complexes **B1** and **B2** and addition of allyl bromide via (a) an initial η^2 π complex and via (b) a direct Br attack to give **C1** and **C2**, respectively.

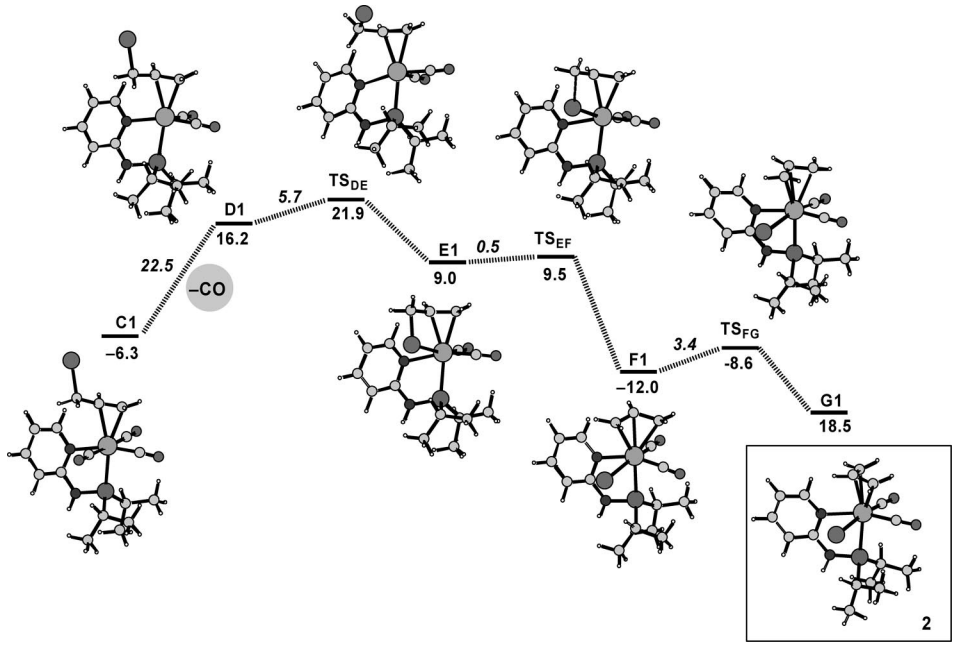


Figure 7. Profile of the B3LYP potential energy surfaces (free energies in kcal/mol) for the conversion of **C1** to the final η^3-allyl complex **G1**.

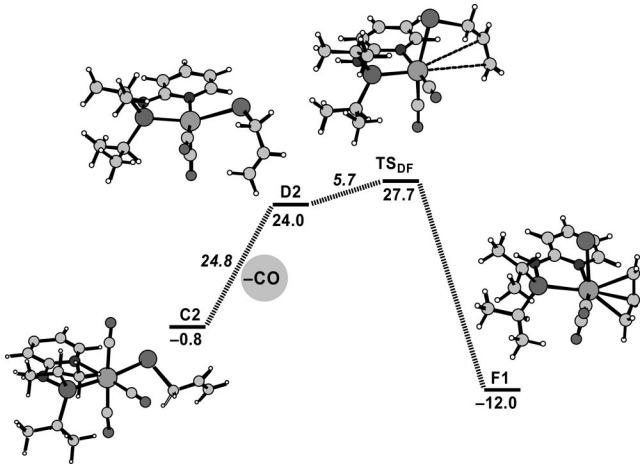
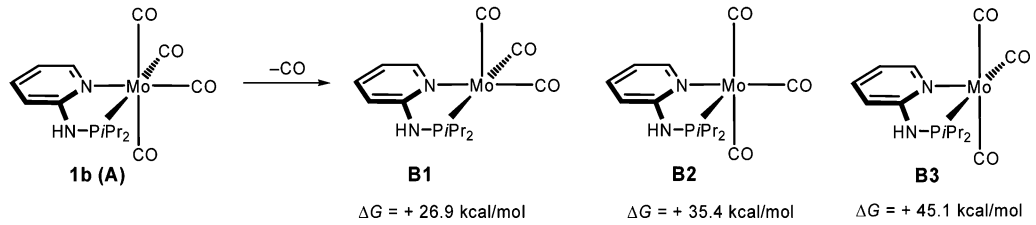


Figure 8. Profile of the B3LYP potential energy surfaces (free energies in kcal/mol) for the conversion of **C2** to the intermediate η^3-allyl complex **E2**.

Since CO has a higher *trans* influence and *trans* effect than phosphanes and pyridine, dissociation of one of the two CO ligands which are coordinated *trans* to one another is strongly favored. This is also in line with DFT calculations showing that the formation of square pyramidal intermediate **B1** is strongly favored over **B2** and **B3** (Scheme 3). The free energy of formation for **B1** is 26.9 kcal/mol, whereas **B2** and **B3** require free energies of formation of 35.4 and 45.1 kcal/mol, respectively. It has to be noted however that experimentally this is not an equilibrium situation since CO will at least partially escape from solution and **A** will not be reformed completely. We therefore have chosen **B1** arbitrarily as zero energy point. Due to the high free energies of formation the direct formation of **B2** and particularly **B3** is unlikely. However, **B1** is able to isomerize to **B2** via $\mathbf{TS_{BB}}$ with an energy barrier of 22.0 kcal/mol (Figure 6). As it turns out, **B2** is the crucial intermediate on the pathway to the final η^3-allyl complex **G1**. The oxidative addition of allyl bromide leads to the formation of the preliminary η^2-π complex **C1** where the terminal C=C double bond interacts with the metal center (pathway a). In an alternative pathway, the oxidative addition can follow a different mechanism where the bromine atom directly attacks the molybdenum center to give intermediate **C2** (pathway b). Similar pathways have been established recently by DFT calculations for the oxidative addition of allyl bromide to $Ni(CO)_4$.[9] Both intermediates are formed without any barrier lying 14.8 and 9.3 kcal/mol, respectively, lower in energy than **B2** + free allyl bromide. The octahedral intermediates **C1** and **C2** contain *trans* CO ligands which is an essential prerequisite for rendering the subsequent CO dissociation step feasible. Accordingly, the calculated free energy required to form **D1** and **D2** of 22.5 and 24.8 kcal/mol, respectively, is experimentally accessible (Figures 7 and 8) and is associated with the cleavage of a Mo–C bond. **D1** reacts via $\mathbf{TS_{DE}}$ to afford **E1** where the allyl ligand is coordinated in an η^3-C,C,Br fashion. This is essentially a rotation about the C–C single bond by about 180° thereby forming a new Mo–Br bond. **E1** is an unstable intermediate which undergoes facile C–Br bond cleavage with a barrier of merely 0.5 kcal/mol to form the η^3-allyl complex **F1**. Counter-clockwise rotation of the η^3-allyl moiety by roughly 80° leads to the final product **G1**.

In the case of the second pathway, the conversion of **D2** to **F1** involves migration of the η^1-Br allyl ligand *trans* to a CO ligand with concomitant coordination of the terminal C=C double bond and C–Br bond cleavage as shown in Figure 8. The free activation energy for this process is



Scheme 3.

5.7 kcal/mol. It has to be noted that in contrast to the oxidative addition of allyl bromide to $Ni(CO)_4$[9] an η^1-allyl intermediate as a result of an oxidative addition via a S_N2 type mechanism is not a stable entity in this particular system and no stationary point could be located. This may largely be attributed to steric reasons.

The overall reaction sequence **A** + allyl bromide → **G1** + 2CO in the gas phase is endergonic by 14.9 kcal/mol. The rate-determining step is the dissociation of CO. Noteworthy, solvation effects were evaluated with the polarized continuum model (PCM) method leading to similar results with only 2–3 kcal/mol differences. Under experimental conditions, however, one can expect that once CO has dissociated from the metal complexes, it will at least partially escape from solution with minimal chances for recombination with the metal complex to reform **A**. Accordingly, the equilibrium will be shifted towards the formation of the η^3-allyl complex **G1** Moreover, the increase of entropy in this particular case appears to be underestimated by DFT calculations.[10]

Conclusion

Tetracarbonyl complexes of the type $Mo(PN)(CO)_4$ are readily available upon treatment of $Mo(CO)_6$ with several phosphanylamine ligands based on 2-aminopyridine at elevated temperatures. In the case of $Mo(PN\text{-}iPr)(CO)_4$ we have studied the oxidative addition of allyl bromide to give the η^3-allyl complex $Mo(PN\text{-}iPr)(\eta^3\text{-}CH_2CHCH_2)(CO)_2Br$. Two reasonable reaction pathways for this process have been established by means of DFT calculations proceeding via a preliminary η^2-π complex where the terminal C=C double bond interacts with the metal center and where the bromine directly attacks the molybdenum atom.

Experimental Section

General: All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures.[11] The ligands 2-(diphenylphosphanylamino)pyridine (PN-Ph),[4e,5] 2-amino-*N*-(diisopropylphosphanyl)pyridine (PN-*i*Pr),[2] 2-[(2-pyridyl)amino]dibenzo[*d*,*f*][1,2,3]dioxaphosphepine (PN-BIPOL),[2] and dimethyl (4*S*,5*S*)-2-[(2-pyridyl)amino]-1,3,2-dioxaphospholane-4,5-dicarboxylate (PN-TAR^{Me})[2] and $Mo(\eta^3\text{-}CH_2CHCH_2)(CO)_2(CH_3CN)_2Br$[12] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried with 4-Å molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively.

2-Amino-*N*-(di-*tert*-butylphosphanyl)pyridine (PN-*t*Bu): A solution of 2-aminopyridine (0.50 g, 5.31 mmol) and NEt_3 (0.81 mL, 5.844 mmol) in 10 mL of anhydrous toluene was cooled to 0 °C and treated with *n*BuLi (5.31 mmol, 2.3 mL of a 2.3 M solution in *n*-hexane). After 15 min of stirring at this temperature $ClPtBu_2$ (1.01 mL, 5.31 mmol) was slowly added and the solution was heated to 90 °C and stirred for 15 h. The solution was then filtered and the solvent was removed under vacuum; yield 0.86 g (68%). $C_{13}H_{23}N_2P$ (238.31): calcd. C 65.52, H 9.73, N 11.76; found C 65.12, H 9.77, N 11.80. ^1H NMR ($CDCl_3$, 20 °C): δ = 8.03 (d, J = 4.1 Hz, 1 H, py^6), 7.43 (vt, J = 7.9 Hz, 1 H, py^4), 7.13 (d, J = 8.4 Hz, 1 H, py^3), 6.62 (vt, J = 5.9 Hz, 1 H, py^5), 5.02 (d, J = 9.6 Hz, 1 H, N*H*), 1.16 and 1.11 [2s, 9H each, C(CH_3)$_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 160.9 (d, J_{CP} = 18.2 Hz, py^2), 147.9 (d, J_{CP} = 0.8 Hz, py^6), 137.6 (d, J_{CP} = 1.5 Hz, py^4), 114.2 (d, J_{CP} = 0.8 Hz, py^5), 109.0 (d, J_{CP} = 18.4 Hz, py^3), 34.2 and 33.9 [2s, *C*(CH$_3$)$_3$], 28.2 and 27.9 [2s, C(*C*H$_3$)$_3$] ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 71.3 ppm.

2-Amino-*N*-(1,3,2-dioxaphospholane-1-yl)pyridine (PN-ETOL): A solution of 2-aminopyridine (0.50 g, 5.31 mmol) in 15 mL of anhydrous toluene was treated with NEt_3 (0.81 mL, 5.84 mmol) and cooled to 0 °C. A solution of 2-chloro-1,3,2-dioxaphospholane (0.48 mL, 5.31 mmol) in toluene (5 mL) was added dropwise and the mixture was allowed to reach room temperature and stirred for 15 h. The solution was then filtered and the solvent removed under vacuum; yield 0.83 g (85%). $C_7H_9N_2O_2P$ (184.13): calcd. C 45.66, H 4.93, N 15.21; found C 45.76, H 4.80, N 15.12. ^1H NMR ($CDCl_3$, 20 °C): δ = 8.03 (d, J = 4.1 Hz, 1 H, py^6), 7.43 (td, J = 7.7, J = 1.5 Hz, 1 H, py^4), 6.79–6.74 (m, 2 H, py^{3,5}), 6.06 (s, 1 H, N*H*), 4.22–4.10 (m, 2 H, CH_2), 4.03–3.94 (m, 2 H, CH$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 155.9 (d, J_{CP} = 13.8 Hz, py^2), 148.1 (d, J_{CP} = 1.2 Hz, py^6), 137.9 (d, J_{CP} = 1.5 Hz, py^4), 116.1 (s, py^5), 109.7 (d, J_{CP} = 10.7 Hz, py^3), 63.6 (d, J_{CP} = 1.3 Hz, *C*H$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 140.0 ppm.

2-Amino-*N*-(3,5,8,10-tetra-*tert*-butyldibenzo[*d*,*f*]-1,3,2-dioxaphosphepine-1-yl)pyridine (PN-BIPOL^{2tBu}): To a solution of 2-aminopyridine (0.80 mg, 8.4 mmol) in 20 mL of toluene NEt_3 (1.2 mL, 8.4 mmol) and 4,6,9,11-tetra-*tert*-butyl-2-chlorodibenzo[*d*,*f*]-1,3,2-dioxaphosphepine (4.0 g, 8.4 mmol) were added at 0 °C. The reaction mixture was allowed to reach room temperature and heated at 90 °C for 15 h. The solution was then filtered and the solvent removed under vacuum; yield 0.99 g (88%). $C_{33}H_{45}N_2O_2P$ (532.70): calcd. C 74.41, H 8.51, N 5.26; found C 74.50, H 8.65, N 5.60. ^1H NMR ($CDCl_3$, 20 °C): δ = 8.17 (d, J = 4.0 Hz, 1 H, py^6), 7.93 (d, J = 4.7 Hz, py^4), 7.43 (d, J = 2.4 Hz, 2 H, Ph), 6.89 (d, J = 8.2 Hz, 1 H, py^3), 6.78 (dd, J = 6.8, J = 5.4 Hz, 1 H, py^5), 6.62 (vt, J = 6.5 Hz, 1 H, Ph), 6.55 (d, J = 8.4 Hz, 1 H, Ph), 6.15 (s, 1 H, N*H*), 1.37–1.19 [m, 36 H, C(*C*H$_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C):

δ = 156.3 (Ph), 155.7 (d, J_{CP} = 17.2 Hz, py^2), 148.3 (py^6), 146.6 (Ph), 137.7 (py^4), 133.2 (d, J_{CP} = 18.2 Hz, Ph), 126.3 (Ph), 124.3 (Ph), 112.1 (py^5), 112.1 (Ph), 110.1 (d, J_{CP} = 14.4 Hz, py^3), 35.5 [*C*(CH$_3$)$_3$], 34.7 [C(*C*H$_3$)$_3$], 31.6 [C(*C*H$_3$)$_3$], 31.3 [C(*C*H$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ = 151.0 ppm.

Mo(PN-Ph)(CO)$_4$ (1a): A mixture of PN-Ph (0.50 g, 1.80 mmol) and $Mo(CO)_6$ (0.46 g, 1.80 mmol) was stirred in toluene at 90 °C for 6 h. After that time the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (neutral Al_2O_3, eluent CH_2Cl_2); yield 0.59 g (68%). $C_{21}H_{15}MoN_2O_4P$ (486.27): calcd. C 51.87, H 3.11, N 5.76; found C 51.99, H 3.02, N 5.61. ^{1}H NMR (δ = , CD_2Cl_2, 20 °C): 8.51 (d, *J* = 5.4 Hz, 1 H, py^6), 7.66–7.50 (m, 11 H, py^4, and Ph), 6.91 (d, *J* = 8.4 Hz, 1 H, py^3), 6.69 (t, *J* = 6.6 Hz, 1 H, py^5), 6.18 (d, *J* = 5.8 Hz, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 220.7 (d, J_{CP} = 7.0 Hz, *C*O), 216.1 (d, J_{CP} = 34.9 Hz, *C*O), 208.1 (d, J_{CP} = 9.5 Hz, *C*O), 160.0 (d, J_{CP} = 15.5 Hz, py^2), 153.6 (d, J_{CP} = 4.5 Hz, py^6), 139.0 (py^4), 137.7 (d, J_{CP} = 39.4 Hz, Ph), 130.6 (d, J_{CP} = 15.5 Hz, Ph), 130.6 (d, J_{CP} = 2.0 Hz, Ph), 128.7 (d, J_{CP} = 10.0 Hz, Ph), 115.7 (py^5), 111.2 (d, J_{CP} = 6.0 Hz, py^3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 95.9 ppm. IR (ATR): $\tilde{\nu}$ = 2075 (s, $\nu_{C=O}$), 1895 (s, $\nu_{C=O}$), 1807 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-*i*Pr)(CO)$_4$ (1b): This compound was prepared analogously to **1a** with PN-*i*Pr (0.50 g, 2.39 mmol) and $Mo(CO)_6$ (0.63 g, 2.39 mmol) as the starting materials; yield 0.66 g (66%). $C_{15}H_{19}MoN_2O_4P$ (418.24): calcd. C 43.08, H 4.58, N 6.70; found C 43.12, H 4.62, N 6.61. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 8.41 (d, *J* = 4.9 Hz, 1 H, py^6), 7.49 (vt, *J* = 7.3 Hz, 1 H, py^4), 6.75 (d, *J* = 8.2 Hz, 1 H, py^3), 6.58 (vt, *J* = 6.2 Hz, 1 H, py^5), 5.45 (d, *J* = 4.4 Hz, 1 H, N*H*), 2.44–2.23 [m, 2 H, C*H*(CH$_3$)$_2$], 1.34–1.20 [m, 12 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 221.5 (d, J_{CP} = 7.0 Hz, *C*O), 215.7 (d, J_{CP} = 33.4 Hz, *C*O), 209.6 (d, J_{CP} = 9.5 Hz, *C*O), 161.0 (d, J_{CP} = 12.0 Hz, py^2), 153.4 (d, J_{CP} = 4.5 Hz, py^6), 138.8 (py^4), 114.8 (py^5), 110.6 (d, J_{CP} = 5.0 Hz, py^3), 30.6 and 30.3 [2s, *C*H(CH$_3$)$_2$], 18.2 and 18.1 [2s, CH(*C*H$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 124.1 ppm. IR (ATR): $\tilde{\nu}$ = 2019 (s, $\nu_{C=O}$), 1879 (s, $\nu_{C=O}$), 1818 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-*t*Bu)(CO)$_4$ (1c): This compound was prepared analogously to **1a** with PN-*t*Bu (0.41 g, 1.74 mmol) and $Mo(CO)_6$ (0.46 g, 1.74 mmol) as the starting materials; yield 0.57 g (74%). $C_{17}H_{23}MoN_2O_4P$ (446.29): calcd. C 45.75, H 5.19, N 6.28; found C 45.69, H 5.02, N 6.39. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 8.39 (d, *J* = 5.4 Hz, 1 H, py^6), 7.49 (vt, *J* = 7.6 Hz, 1 H, py^4), 6.87 (d, *J* = 8.2 Hz, 1 H, py^3), 6.59 (vt, *J* = 6.3 Hz, 1 H, py^5), 5.54 (d, *J* = 3.9 Hz, 1 H, N*H*), 1.42 and 1.36 [s, 9H each, C(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 222.2 (d, J_{CP} = 6.9 Hz, *C*O), 216.4 (d, J_{CP} = 34.9 Hz, *C*O), 211.4 (d, J_{CP} = 8.3 Hz, *C*O), 161.5 (d, J_{CP} = 10.6 Hz, py^2), 153.2 (d, J_{CP} = 4.6 Hz, py^6), 138.9 (py^4), 115.0 (py^5), 111.1 (d, J_{CP} = 4.6 Hz, py^3), 37.7 [d, J_{CP} = 9.2 Hz, *C*(CH$_3$)$_3$], 28.8 and 28.7 [s, C(*C*H$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 138.2 ppm. IR (ATR): $\tilde{\nu}$ = 2010 (s, $\nu_{C=O}$), 1903 (s, $\nu_{C=O}$), 1880 (s, $\nu_{C=O}$), 1812 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-ETOL)(CO)$_4$ (1d): This compound was prepared analogously to **1a** with PN-ETOL (0.37 g, 2.02 mmol) and $Mo(CO)_6$ (0.53 g, 2.02 mmol) as the starting materials; yield 0.63 g (80%). $C_{11}H_9MoN_2O_6P$ (392.12): calcd. C 33.69, H 2.31, N 7.14; found C 33.58, H 2.22, N 7.12. ^{1}H NMR (δ = , CD_2Cl_2, 20 °C): 8.42 (d, *J* = 4.7 Hz, 1 H, py^6), 7.56 (vt, *J* = 7.5 Hz, 1 H, py^4), 6.75–6.69 (m, 3 H, py^{3,5}, N*H*), 4.35–4.30 (m, 4 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 219.1 (d, J_{CP} = 11.5 Hz, *C*O), 214.8 (d, J_{CP} = 53.4 Hz, *C*O), 206.1 (d, J_{CP} = 13.2 Hz, *C*O), 157.8 (d, J_{CP} = 19.0 Hz, py^2), 153.4 (d, J_{CP} = 5.2 Hz, py^6), 139.1 (py^4), 116.3 (py^5), 110.9 (d, J_{CP} = 5.7 Hz, py^3), 65.5 (d, J_{CP} = 7.5 Hz, *C*H$_2$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 190.6 ppm. IR (ATR): $\tilde{\nu}$ = 2025 (s, $\nu_{C=O}$), 1920 (s, $\nu_{C=O}$), 1887 (s, $\nu_{C=O}$), 1850 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-BIPOL)(CO)$_4$ (1e): This compound was prepared analogously to **1a** with PN-BIPOL (0.76 g, 2.45 mmol) and $Mo(CO)_6$ (0.65 g, 2.45 mmol) as the starting materials; yield 1.03 g (81%). $C_{21}H_{13}MoN_2O_6P$ (516.26): calcd. C 48.86, H 2.54, N 5.43; found C 48.79, H 2.52, N 5.38. ^{1}H NMR (δ = , CD_2Cl_2, 20 °C): 8.52 (d, *J* = 4.7 Hz, 1 H, py^6), 7.64–7.08 (m, 9 H, py^4 and Ph), 6.82–6.79 (m, 2 H, py^3, and py^5), 6.60–6.52 (m, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 218.5 (d, J_{CP} = 10.9 Hz, *C*O), 214.4 (d, J_{CP} = 55.7 Hz, *C*O), 206.2 (d, J_{CP} = 13.8 Hz, *C*O), 157.8 (d, J_{CP} = 20.7 Hz, py^2), 153.9 (d, J_{CP} = 4.6 Hz, py^6), 148.8 (d, J_{CP} = 9.2 Hz, Ph), 139.4 (py^4), 130.3 (d, J_{CP} = 2.3 Hz, Ph), 129.9 (d, J_{CP} = 1.7 Hz, Ph), 129.8 (d, J_{CP} = 1.7 Hz, Ph), 126.2 (d, J_{CP} = 1.7 Hz, Ph), 121.9 (d, J_{CP} = 2.9 Hz, Ph), 116.8 (py^5), 111.2 (d, J_{CP} = 6.9 Hz, py^3) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 196.5 ppm. IR (ATR): $\tilde{\nu}$ = 2022 (s, $\nu_{C=O}$), 1944 (s, $\nu_{C=O}$), 1885 (s, $\nu_{C=O}$), 1860 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-BIPOL$^{2t\mathrm{Bu}}$)(CO)$_4$ (1f): This compound was prepared analogously to **1a** with PN-BIPOL$^{2t\mathrm{Bu}}$ (0.381 g, 0.728 mmol) and $Mo(CO)_6$ (0.192 g, 0.728 mmol) as the starting materials; yield 0.352 g (65%). $C_{37}H_{45}MoN_2O_6P$ (740.69): calcd. C 60.00, H 6.12, N 3.78; found C 59.89, H 6.08, N 3.81. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 8.52 (s, 1 H, py^6), 7.55–7.12 (m, 5 H, py^4, and Ph), 6.74–6.59 (m, 3 H, py^3, py^5, and N*H*), 1.54–1.24 [m, 36 H, C(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 219.2 (d, J_{CP} = 10.9 Hz, *C*O), 215.2 (d, J_{CP} = 56.9 Hz, *C*O), 206.7 (d, J_{CP} = 12.1 Hz, *C*O), 157.5 (d, J_{CP} = 19.5 Hz, py^2), 153.7 (d, J_{CP} = 4.6 Hz, py^6), 147.6 (Ph), 145.7 (d, J_{CP} = 10.9 Hz, Ph), 140.6 (d, J_{CP} = 3.4 Hz, Ph), 139.4 (d, J_{CP} = 3.4 Hz, py^4), 131.6 (d, J_{CP} = 2.9 Hz, Ph), 127.2 (Ph), 124.9 (Ph), 116.4 (py^5), 111.0 (d, J_{CP} = 6.3 Hz, py^3), 35.4 [*C*(CH$_3$)$_3$], 34.6 [C(*C*H$_3$)$_3$], 31.2 [C(*C*H$_3$)$_3$], 30.9 [C(*C*H$_3$)$_3$] ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 194.2 ppm. IR (ATR): $\tilde{\nu}$ = 2028 (s, $\nu_{C=O}$), 1959 (s, $\nu_{C=O}$), 1915 (s, $\nu_{C=O}$), 1877 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-TAR$^{\mathrm{Me}}$)(CO)$_4$ (1g): This compound was prepared analogously to **1a** with PN-TAR$^{\mathrm{Me}}$ (0.40 g, 1.33 mmol) and $Mo(CO)_6$ (0.35 g, 1.33 mmol) as the starting materials; yield 0.51 g (75%). $C_{15}H_{13}MoN_2O_{10}P$ (508.19): calcd. C 35.45, H 2.58, N 5.51; found C 35.38, H 2.53, N 5.60. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 8.44 (br. s, 1 H, py^6), 7.59 (br. s, 2 H, py^4 and py^3), 6.84–6.74 (m, 2 H, py^5 and N*H*), 5.33–5.10 (m, 2 H, C*H*), 3.93 (s, 3 H, COOC*H*$_3$), 3.90 (s, 3 H, COOC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 218.5 (d, J_{CP} = 11.5 Hz, *C*O), 214.8 (d, J_{CP} = 55.7 Hz, *C*O), 205.8 (d, J_{CP} = 13.8 Hz, *C*O), 205.6 (d, J_{CP} = 13.8 Hz, *C*O), 170.9 (s, *C*OOCH$_3$), 168.3 (d, J_{CP} = 2.3 Hz, *C*OOCH$_3$), 157.4 (d, J_{CP} = 20.1 Hz, py^2), 153.3 (d, J_{CP} = 5.2 Hz, py^6), 139.2 (py^4), 116.6 (py^5), 111.4 (d, J_{CP} = 6.3 Hz, py^3), 78.1 (d, J_{CP} = 8.0 Hz, *C*H), 76.7 (d, J_{CP} = 10.3 Hz, *C*H), 53.8 (s, COO*C*H$_3$), 53.7 (s, COO*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 202.9 ppm. IR (ATR): $\tilde{\nu}$ = 2030 (s, $\nu_{C=O}$), 1900 (s, $\nu_{C=O}$), 1857 (s, $\nu_{C=O}$) cm^{-1}.

Mo(PN-*i*Pr)(η^3-allyl)(CO)$_2$Br (2). Method 1: A solution of **1b** (0.23 g, 0.54 mmol) in 10 mL of anhydrous toluene was treated with a slight excess of allyl bromide (51 μL, 0.60 mmol) and heated at 90 °C for 15 h. After removal of the solvent under reduced pressure the product was washed twice with *n*-pentane and dried under vacuum; yield 0.22 g (82%). **Method 2:** A solution of Mo(η^3-allyl)(CO)$_2$(CH$_3$CN)$_2$Br (0.300 g, 0.845 mmol) was treated with PN-*i*Pr (0.178 g, 0.845 mmol) in 10 mL of CH_2Cl_2. The deep red solution was stirred for 2 h. After removal of the solvent, the product was dried under vacuum; yield 0.342 g (83.8%). $C_{16}H_{24}BrMoN_2O_2P$ (483.20): calcd. C 39.77, H 5.01, N 5.80; found C 39.70, H 5.06, N

Table 1. Details for the crystal structure determinations of compounds PN-*i*Pr, **1a**·CH_2Cl_2, **1b**, **1c**, **1d**, and **2**.

	PN-*i*Pr	**1a**·CH_2Cl_2	**1b**	**1c**	**1d**	**2**
Formula	$C_{11}H_{19}N_2P$	$C_{21}H_{15}MoN_2O_4P{\cdot}CH_2Cl_2$	$C_{15}H_{19}MoN_2O_4P$	$C_{17}H_{23}MoN_2O_4P$	$C_{11}H_9MoN_2O_6P$	$C_{16}H_{24}BrMoN_2O_2P$
Fw	210.25	571.19	418.23	446.28	392.11	483.19
Crystal size [mm]	0.35×0.30×0.12	0.65×0.45×0.40	0.54×0.40×0.38	0.58×0.55×0.53	0.59×0.12×0.11	0.56×0.24×0.22
Color, shape	colorless plate	yellow oval	yellow oval	yellow oval	yellow prism	orange prism
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$(no. 2)	$C2/c$ (no. 15)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a [Å]	16.6403(15)	8.8999(2)	20.9340(3)	9.0235(2)	8.7014(6)	33.2832(16)
b [Å]	7.7974(7)	11.4108(2)	10.3981(2)	13.3324(2)	12.4996(8)	8.5131(4)
c [Å]	9.2521(9)	13.3360(2)	16.8091(3)	16.0575(3)	13.2883(9)	13.7154(7)
α [°]	90	108.005(1)	90	90	90	90
β [°]	93.968(1)	94.390(1)	99.173(1)	90	92.385(1)	101.252(2)
γ [°]	90	109.668(1)	90	90	90	90
V [Å^3]	1197.6(2)	1187.96(4)	3612.11(11)	1931.80(6)	1444.0(2)	3811.5(3)
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Z	4	2	8	4	4	8
ρ_{calc} [g cm^{-3}]	1.166	1.597	1.538	1.534	1.804	1.684
μ [mm^{-1}] (Mo-K_α)	0.196	0.875	0.834	0.785	1.046	2.878
F(000)	456	572	1696	912	776	1936
Number of reflections measured	16297	24509	23511	24308	19512	26966
R_{int}	0.031	0.018	0.017	0.021	0.023	0.028
Number of reflections unique	3471	6884	5266	5613	4187	5533
Number of reflections $I>2\sigma(I)$	3211	6529	5087	5582	3738	4979
Number of parameters	131	266	215	235	190	217
R_1 [$I>2\sigma(I)$][a]	0.0301	0.0227	0.0185	0.0144	0.0267	0.0232
R_1 (all data)	0.0323	0.0237	0.0193	0.0146	0.0314	0.0272
wR_2 [$I>2\sigma(I)$]	0.0826	0.0608	0.0485	0.0386	0.0641	0.0576
wR_2 (all data)	0.0854	0.0615	0.0489	0.0388	0.0674	0.0590
Min./max. resid. electron density [e Å^{-3}]	–0.40/0.45	–0.40/0.66	–0.32/0.56	–0.41/0.26	–0.97/1.14	–0.58/0.69

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

5.76. ^{1}H NMR (CD_2Cl_2, 20 °C): δ = 7.96 (d, *J* = 5.2 Hz, 1 H, py^6), 7.49 (vt, *J* = 7.5 Hz, 1 H, py^4), 6.83–6.76 (m, 2 H, py^3, and py^5), 5.70 (d, *J* = 5.4 Hz, 1 H, N*H*), 4.37–4.24 (m, 1 H, C*H*), 4.10 (br. s, 1 H, C*H*), 3.58 (br. s, 1 H, C*H*), 3.14–2.98 [m, 1 H, C*H*(CH_3)$_2$], 2.88–2.72 [m, 1 H, C*H*(CH_3)$_2$], 1.81 (d, *J* = 9.5 Hz, 1 H, C*H*), 1.70–1.61 (m, 4 H, C*H* and CH_3), 1.49–1.33 (m, 9 H, CH_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): δ = 226.3 (d, J_{CP} = 13.2 Hz, *C*O), 223.1 (d, J_{CP} = 8.0 Hz, *C*O), 160.7 (d, J_{CP} = 10.9 Hz, py^2), 147.9 (py^6), 138.7 (py^4), 120.6 (*C*H), 115.7 (py^5), 111.5 (d, J_{CP} = 5.7 Hz, py^3), 77.2 (*C*H^2), 62.0 (*C*H^2), 29.3 [d, J_{CP} = 20.1 Hz, *C*H(CH_3)$_2$], 27.9 [d, J_{CP} = 22.4 Hz, *C*H(CH_3)$_2$], 19.3 [d, J_{CP} = 8.0 Hz, CH-(*C*H$_3$)$_2$], 17.3 [d, J_{CP} = 4.3 Hz, CH(*C*H$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR ([D$_6$]acetone, 20 °C): δ = 106.6 ppm. IR (ATR): $\tilde{\nu}$ = 1925 (s, $\nu_{C=O}$), 1835 (s, $\nu_{C=O}$) cm^{-1}.

X-ray Structure Determination for PN-*i*Pr, 1a–d, and 2: X-ray data of the ligand PN-*i*Pr and the complexes **1a** (as the solvate **1a**·CH_2Cl_2), **1b**, **1c**, **1d**, and **2** were collected at *T* = 100 K on a Bruker Smart APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space with θ_{max} = 30°. After data integration with program SAINT+ corrections for absorption, λ/2 effects, and crystal decay were applied with program SADABS.[13] The structures were solved by direct methods (SHELXS97) and refined on F^2 with program SHELXL97.[14] All non-H atoms were refined anisotropically. H atoms were placed in calculated positions and thereafter treated as riding. The disordered solvent in **1a**·CH_2Cl_2 was squeezed with program PLATON.[15] The bromine Br1 of compound **2** was modestly disordered by interchanging position with the *trans*-located carbonyl

Table 2. Selected geometric data (Å and °) of compounds **1a**·CH_2Cl_2, **1b**, **1c**, and **1d**.

	1a·CH_2Cl_2	**1b**	**1c**	**1d**
Mo–N1	2.282(1)	2.296(1)	2.287(1)	2.273(2)
Mo–P	2.4803(3)	2.4912(3)	2.5596(3)	2.4092(6)
Mo–C_I[a]	1.968(1)	1.963(1)	1.979(1)	1.965(2)
Mo–C_{II}	1.982(1)	1.995(1)	1.967(1)	1.997(2)
Mo–C_{III}	2.026(1)	2.035(1)	2.028(1)	2.031(2)
Mo–C_{IV}	2.064(1)	2.051(1)	2.057(1)	2.050(2)
N1–Mo–P	75.89(3)	76.31(2)	75.22(2)	76.64(6)
N1–Mo–C_I	173.41(4)	176.38(4)	172.33(4)	175.18(9)
N1–Mo–C_{II}	94.83(4)	94.53(4)	95.25(4)	94.18(8)
N1–Mo–C_{III}	89.43(5)	92.42(4)	90.97(4)	92.70(8)
N1–Mo–C_{Iv}	94.98(4)	94.55(4)	98.00(4)	92.60(7)
P–Mo–C_{ii}	170.01(4)	170.46(4)	170.35(3)	170.81(6)
C_{III}–Mo–C_{IV}	174.19(5)	172.52(4)	166.49(5)	174.43(8)

[a] C_I through C_{IV} are the four carbonyl C atoms, with C_I *trans* to N1, C_{II} *trans* to P1, and C_{III} and C_{IV} *cis* to N1 and P1.

group at a level of ca. 7%, whereas the allyl group – usually prone to orientation disorder – was fully ordered. Crystal data and experimental details are given in Table 1. Selected geometric data of **1a** through **1d** are presented in Table 2, while for PN-*i*Pr and **2** they are reported in the Figure captions.

CCDC-735385 (for PN-*i*Pr), -735386 (for **1a**·CH_2Cl_2), -735387 (for **1b**), -735388 (for **1c**), -735389 (for **1d**), -735390 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: All calculations were performed using the Gaussian03 software package on the Phoenix Linux Cluster of the Vienna University of Technology.[16] The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[17] with the Stuttgart/Dresden ECP (SDD) basis set[18] to describe the electrons of the molybdenum atom. For all other atoms atoms the 6-31g** basis set was employed.[19] Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel and co-workers.[20] Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides, and obtaining the minima presented on the reaction energy profile. All geometries were optimized without symmetry constraints. Solvation effects were evaluated with the polarized continuum model (PCM) method.[21]

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