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Molybdenum tetracarbonyl complexes with functionalised aminophosphine ligands: *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$ (R = Ph, Bu^t) — molecular structures of $PMes_2NHPh$ (Mes = 2,4,6-$Me_3C_6H_2$), PPh_2NHBu^t and *cis*-$[Mo(CO)_4(PPh_2NHBu^t)_2]$

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Abstract

The aminophosphines PPh_2NHR [R = Ph (**1a**), Bu^t (**1b**)] react readily with *cis*-$[Mo(CO)_4(NCEt)_2]$ to give *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$ [R = Ph (**2**), Bu^t (**3**)] in high yield, while the bulky aminophosphine $PMes_2NHPh$ (**1c**) (Mes = 2,4,6-$Me_3C_6H_2$), obtained from LiNHPh and $PMes_2Cl$, does not react even at elevated temperature. Compounds **1c**, **2** and **3** were characterised spectroscopically (IR; ^1H, ^{31}P, ^{13}C NMR), **2** and **3** also by MS, and crystal structure determinations were carried out on **1b**, **1c** and **3**; for **3**, this showed the presence of the *cis* isomer. Complexes **2** and **3** do not react with $[Cp_2ZrCl_2]/NEt_3$ or with $[Cp_2ZrMe_2]$.

Keywords: Molybdenum; Aminophosphine ligands; *cis* Isomers; Molecular structures

1. Introduction

While tertiary phosphines have long been employed as ligands in the synthesis of transition metal complexes with catalytic properties [1], secondary phosphinoamines have received only limited attention [2,3], and only a few examples of heterodinuclear complexes in which a phosphinoamido or -amine ligand bridges two different metals have been reported to date [4]. Several transition metal [2d,e,5] and lanthanide complexes [6] with phosphinoamido ligands are known in which the anionic ligand can be terminal, chelating or bridging. Some of them have been employed in transition metal catalysed synthesis [2c]. Recently, we have shown that the homoleptic phosphinoamide complex $[Zr(NPhPPh_2)_4]$ and the related bisamido complex $[TiCl_2\{N(PPh_2)_2\}_2]$ are active catalysts for the formation of elastomeric polypropylene in the presence of methylalumoxane (MAO) [7]. In our investigations on phosphinoamides and -amines as potential mono- and bidentate ligands in transition metal complexes, we have also obtained the Ni(0) complex $[Ni(PPh_2NHPh)_4]$ [8] with bulky phosphinoamine ligands. We now report the synthesis of the molybdenum carbonyl complexes *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$ [R = Ph (**2**), Bu^t (**3**)] in high yield.

While numerous mononuclear and heterodinuclear molybdenum(0) tetracarbonyl complexes with *cis*-coordinated phosphine ligands have been structurally characterised [9], the number of corresponding compounds with bifunctional phosphine ligands, such as phosphinoamine ligands [3], is still rather small. Only a few examples for structurally characterised heterodinuclear complexes in which Mo and M′ (M′ = Ni [4a,b], Cu [4c]) are bridged by *P*,*N* ligands have been reported. As molybdenum bis(diphosphine) complexes also have catalytic potential [10], the use of mixed soft–hard *P*,*N* ligands in the preparation of heterodinuclear molybdenum complexes appears attractive, as early–late

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bridged transition metal complexes may show cooperative reactivity in catalytic processes, which stems from the possibility for the electron-poor early transition metal and the electron-rich late transition metal to create an ideal environment for heterolytic bond cleavage of polar substrates.

2. Synthesis and spectroscopic properties of phosphinoamines

Lithium amides LiNHR (R = Ph, Bu^t) react readily with diarylchlorophosphines PR'_2Cl [R′ = Ph, 2,4,6-$Me_3C_6H_2$ (Mes)] to give aminophosphines PPh_2NHR (R = Ph (**1a**) [11], Bu^t (**1b**) [12]) and $PMes_2NHPh$ (**1c**); Eq. (1)).

$$LiNHR + PR'_2Cl \rightarrow PR'_2NHR + LiCl \quad (1)$$

The P–N bond in aminophosphines is essentially a single bond [6,13], so the lone pairs on nitrogen and phosphorus are available for donor bonding towards metal atoms.

In the ^{1}H NMR spectra, the N–H signals were observed as doublets at 4.38 ppm ($^2J_{PH}$ = 7.8 Hz) for **1a** [14], 1.96 ppm ($^2J_{PH}$ = 11.6 Hz) for **1b** [12,15], and 4.34 ppm ($^2J_{PH}$ = 9.0 Hz) for **1c**. The $^{31}P\{^1H\}$ NMR spectra of the aminophosphines in $CDCl_3$ show singlets at 28.6 ppm (**1a**), 22.5 ppm (**1b**), and 19.4 ppm (**1c**). No $^2J_{PH}$ coupling was observed in the ^{31}P NMR spectra. The chemical shifts in the $^{31}P\{^1H\}$ NMR spectra are in accordance with the electronic properties of the substituents on nitrogen and phosphorus. Thus, substitution of mesityl for phenyl on phosphorus results in the expected high-field shift of **1c** ($\Delta\delta$ = 9.2 ppm) due to the increased electron density on phosphorus. The same effect, but to a higher degree, is observed when the Mes* substituent (Mes* = 2,4,6-$Bu^t_3C_6H_2$, 48.6 ppm [13]) on nitrogen is substituted for phenyl (28.6 ppm) or Bu^t (22.5 ppm). 1,2-Bis(diphenylphosphinoamino)-benzene (32.5 ppm) and 3,4-bis(diphenylphosphinoamino)toluene (33.3, 30.4 ppm) also fit into this series [3e].

In the IR spectra (KBr), the ν(NH) band is observed at 3295 cm^{-1} (**1a**), 3400 cm^{-1} (**1b**) [12], and 3364 cm^{-1} (**1c**). The ν(PN) vibration is tentatively assigned to a very strong absorption at 892 cm^{-1} (**1a**) and 979 cm^{-1} (**1b**). 1,2-Bis(diphenylphosphinoamino)benzene and 3,4-bis(diphenylphosphinoamino)toluene have ν(NH) bands at 3328 and 3329 cm^{-1} and ν(PN) bands at 904 and 887 cm^{-1}, respectively [3e].

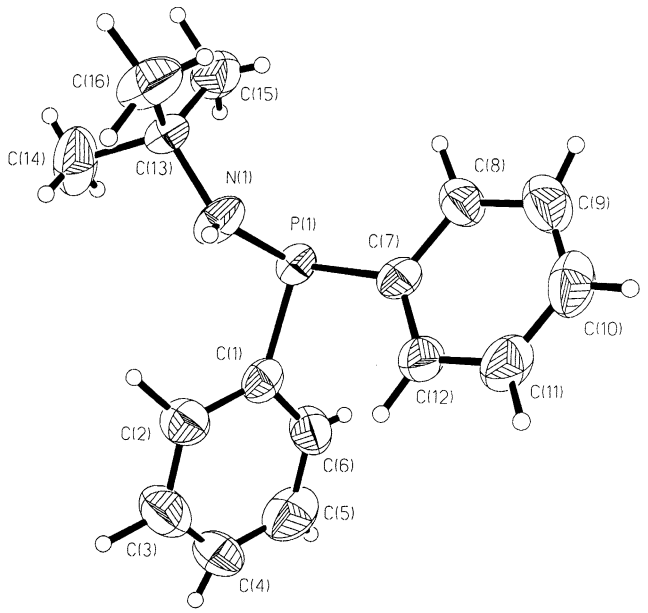


Fig. 1. Molecular structure of **1b** (ORTEP, 50% probability, SHELXTL PLUS; XP) [26]. Only one of the two independent molecules is shown.

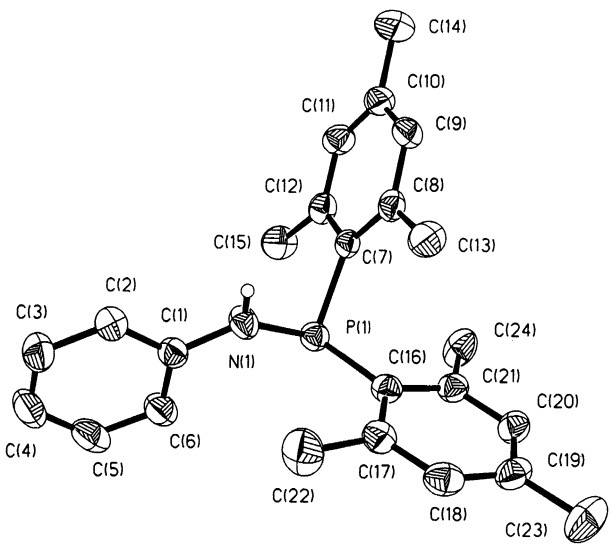


Fig. 2. Molecular structure of **1c** (ORTEP, 50% probability, SHELXTL PLUS; XP) [26]. Hydrogen atoms (other than N–H) omitted for clarity.

3. Molecular structures of PPh_2NHBu^t (1b) and $PMes_2NHPh$ (1c)

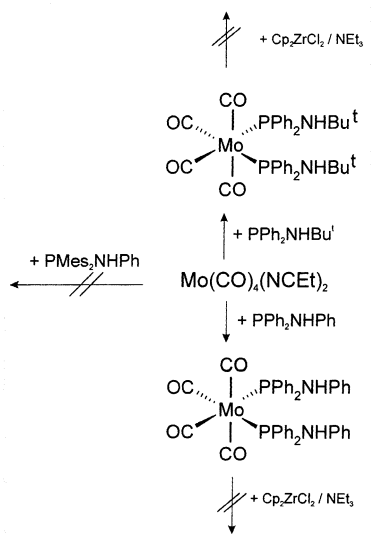
PPh_2NHBu^t (**1b**) (Fig. 1) crystallises monoclinic in the space group $P2_1$ (no. 4) with two independent molecules in the asymmetric unit and four molecules in the unit cell, $PMes_2NHPh$ (**1c**) (Fig. 2) crystallises monoclinic in the space group $P2_1/c$ (no. 14) with four molecules in the unit cell. A comparison of selected bond lengths and angles in **1b** and **1c** with those of related aminophosphines is shown in Table 1.

In both molecules, the phosphorus atom is coordinated in a distorted tetrahedral fashion by a nitrogen atom, two carbon atoms of the phenyl [C(1), C(7), and C(17), C(23)] or mesityl [C(7) and C(16)] substituents,

Table 1
Comparison of selected bond lengths and angles in aminophosphines

Complex	P–N (Å)	C–P–N (°)	P–N–C (°)
PPh_2NHPh[6]	1.696(3)	[b]	[b]
PPh_2NHMes[13]	1.730(2)	99.7(1), 102.1(1)	114.6(1)
PPh_2NHBu^t (**1b**) [a]	1.673(5), 1.701(5)	101.8(2), 104.9(2)	120.9(4), 127.0(4)
$PMes_2NHPh$ (**1c**)	1.703(2)	96.83(9), 108.80(9)	126.1(2)

[a] Two independent molecules.
[b] No values reported.



Scheme 1.

and the electron lone pair. In **1c**, two of the three bond angles between the substituents [N(1)–P(1)–C(16) 108.80(9) and C(16)–P(1)–C(7) 105.17(9)°] are near to the tetrahedral angle of 109.5°, while the third bond angle [N(1)–P(1)–C(7) 96.83(9)°] is significantly smaller. This effect is less pronounced in the less crowded molecule **1b** [N–P–C 101.8(2)–104.9(2), C–P–C 98.8(2), 100.5(2)°]. The P–C bond lengths of 1.829(5)–1.845(5) (**1b**) and 1.847(2)–1.853(2) Å (**1c**) and the P–N bond lengths of 1.673(5), 1.701(5) (**1b**) and 1.703(2) Å (**1c**) are in the expected range.

The nitrogen atom in **1b**, **c** has a trigonal-planar environment formed by H(1N) [or H(2N)], C(13) [or C(29)] and P(1) [or P(2)] (**1b**), or H(1), C(1) and P(1) (**1c**) (sum of bond angles at N: 359.0, 347.9° for **1b**; 359.1° for **1c**). In **1b**, the P–N–H [126(6), 126(4)°] and P–N–C [120.9(4), 127.0(4)°] angles are larger than the C–N–H bond angles [101(7), 106(4)°]. In **1c**, the bond angle C(1)–N(1)–P(1) of 126.1(2)° is slightly larger than expected. The conformation about the P–N bond in **1b** and **1c** is staggered.

4. Synthesis and spectroscopic properties of *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$ (R = Ph, Bu^t)

The aminophosphines **1a**, **b** react readily with *cis*-$[Mo(CO)_4(NCEt)_2]$ [16] to give *cis*-$[Mo(CO)_4(PPh_2NHR)_2]$ (R = Ph (**2**), Bu^t (**3**)) in high yield (Scheme 1). Compound **1c** does not react even at elevated temperature, only decomposition of *cis*-$[Mo(CO)_4(NCEt)_2]$ occurs.

Apparently, the greater steric hindrance of the mesityl substituent in **1c** compared with the phenyl substituent in **1a**, **b** is the reason for this. A similar behaviour was observed for the organic triphos ligand $CH_3C(CH_2PR_2)_3$ (R = *o*-tolyl), in which the *o*-tolyl substituent causes a significant decrease in the ligating strength of the triphos ligand relative to the phenyl-substituted ligand [17].

In the $^{31}P\{^1H\}$ NMR spectra, **2** and **3** exhibit singlets which show the expected low-field shifts relative to the uncoordinated ligands [**2**: 70.8 ppm ($\Delta\delta = 42.2$ ppm), **3**: 69.2 ppm ($\Delta\delta = 46.7$ ppm)]. In addition, satellites indicative of an ABX spin system are visible, but at a resolution too poor to determine the ^{31}P–^{31}P coupling constant. In the $^{13}C\{^1H\}$ NMR spectrum of **2** the pattern of an ABX spin system is clearly visible for the *trans*-CO carbon atoms at 214.8 ppm and the *ipso*-C atoms of the phenyl rings on phosphorus at 136.8 ppm, respectively.

The IR spectra of **2** and **3** show the typical pattern for *cis*-$[Mo(CO)_4(phosphine)_2]$ complexes (local symmetry C_{2v}) in the carbonyl region. In these and related complexes [3,9,18] usually only three of the four expected absorptions are observed in the range of 1870–2025 cm^{-1}. In addition, **2** and **3** exhibit a ν(NH) band at 3383 and 3385 cm^{-1}, respectively, which is shifted to higher wavenumbers for **2** ($\Delta\nu = 85$ cm^{-1}), but to lower wavenumbers for **3** ($\Delta\nu = -15$ cm^{-1}) compared with **1a**, **b**. The ν(PN) vibration in **2** and **3** is tentatively assigned to strong absorptions at 906 cm^{-1} (**2**) and 1010 cm^{-1} (**3**). In *cis*-$[Mo(CO)_4(PPh_2NR_2)_2]$ (R = Me, Et, Pr, Bu), the ν(PN) band is observed in the same range (at 926–985 cm^{-1}) [3l].

5. Molecular structure of *cis*-$[Mo(CO)_4(PPh_2NHBu^t)_2]$ (3)

Cis-$[Mo(CO)_4(PPh_2NHBu^t)_2]$ (Fig. 3) crystallises monoclinic in the space group $P2_1$ (no. 4) with two molecules in the unit cell. Selected bond lengths and angles are given in Table 2.

The molybdenum atom is octahedrally coordinated by four carbonyl groups and the two phosphorus atoms of the two *cis*-oriented aminophosphine ligands. The P–Mo–P bond angle of 95.44(3)° is slightly larger than the ideal angle of 90°. The Mo–P bond lengths in **3** are

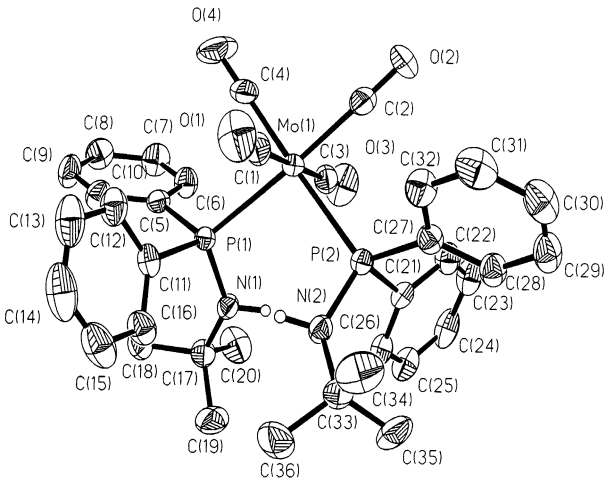


Fig. 3. Molecular structure of **3** (ORTEP, 50% probability, SHELXTL PLUS; XP) [26]. Hydrogen atoms (other than N–H) omitted for clarity.

similar to those in related complexes (Table 2). Another general feature is that the Mo–C bond lengths of the carbonyl groups *trans* to the aminophosphine ligands (*trans* effect) are slightly shorter [**3**: Mo(1)–C(2) 1.984(4), Mo(1)–C(4) 1.995(4) Å] than those of the other two carbonyl groups [**3**: Mo–C 2.048(4) Å]. The phosphorus atoms of the aminophosphines show distorted tetrahedral coordination. Here the N–P–Mo bond angles are markedly larger than 109.5° [113.0(1) and 112.4(1)°], and the other bond angles are correspondingly smaller. The smallest bond angle at phosphorus is that between the two phenyl substituents [C–P–C 102.9(2) and 102.2(2)°]. The nitrogen atom is coordinated in a trigonal-planar fashion by phosphorus, the carbon atom of the Bu^t substituent, and a hydrogen atom. The sum of the bond angles is 358.8° (N1) and 355.7° (N2). The bond angles between the two bulky substituents (P–N–C) are larger (136.8(2) and 133.7(2)°) than the ideal angle of 120°, whereas those angles involving the hydrogen atom are correspondingly smaller (109–113°). As in [Ni($PPh_2NHPh)_4$] [8], the overall structure of PPh_2NHPh [6] is almost uninfluenced by coordination to the Mo atoms.

6. Attempted formation of heterodinuclear complexes

Several attempts to employ **2** and **3** in the synthesis of heterobimetallic ligand-bridged dinuclear complexes were unsuccessful. Thus, *cis*-[$Mo(CO)_4(PPh_2NHR)_2$] (R = Ph, Bu^t) does not react with [Cp_2ZrCl_2] in the presence of NEt_3 as an auxiliary base, and no CH_4 elimination occurred when *cis*-[$Mo(CO)_4(PPh_2NHR)_2$] (R = Ph, Bu^t) was treated with [Cp_2ZrMe_2]. Apparently, the acidity of the N–H group in coordinated aminophosphines is too low.

The phosphinoamine PPh_2NHPh [11] is readily deprotonated by BuLi to give $LiNPhPPh_2$ [19]. Two mesomeric structures can be formulated for these anions in which the negative charge is localised at the N (phosphinoamide) or P atom (iminophosphide). According to theoretical calculations [20], the phosphinoamide structure is dominant. However, while lithiation of **3** with BuLi was successful, no further reaction with [Cp_2ZrCl_2] was observed.

7. Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. NMR spectra: Avance DRX 400 (Bruker), standards: ^{1}H NMR (400.1 MHz): trace amounts of protonated solvent, C_6D_6, ^{13}C NMR (100.6 MHz): internal solvent, ^{31}P NMR (161.9 MHz): external 85% H_3PO_4. The IR spectra were recorded as KBr mulls on a Perkin–Elmer FT-IR spectrometer system 2000 in the range 350–4000 cm^{-1}. The mass spectra were recorded with a Sektorfeldgerät AMD 402 (AMD Intectra GmbH; EI, 70 eV). The melting points were determined in sealed capillaries under argon and are uncorrected. PPh_2NHR (R = Ph (**1a**) [11], Bu^t (**1b**) [12]), [$Mo(CO)_4(NCEt)_2$] [16], LiNHPh [21], $PMes_2Cl$ [22], [Cp_2ZrCl_2] [23] and [Cp_2ZrMe_2] [24] were prepared by literature procedures.

Table 2
Selected bond lengths (Å) and bond angles (°) in *cis*-[$Mo(CO)_4L_2$] (L = phosphinoamine, L_2 = 3,4-$(PPh_2NH)_2C_6H_3Me$)

L or L_2	PPh_2NHPh (**3**)	PPh_2NH_2 [3b]	PPh(Cl)NHPr^i [3c]	3,4-$(PPh_2NH)_2C_6H_3Me$ [3e]
Mo–P	2.5386(8), 2.5503(8)	2.5218(7), 2.5290(7)	2.459(1), 2.463(1)	2.516(2), 2.471(2)
P–N	1.665(3)	1.677(3), 1.682(2)	1.637(2), 1.639(2)	1.688(6), 1.717(6)
Mo–C_{ax}	2.048(4), 2.048(4)	2.031(3), 2.051(2)	2.035(2), 2.043(3)	[a]
Mo–C_{eq}	1.984(4), 1.995(4)	2.002(3), 1.987(3)	1.999(3), 2.013(3)	[a]
P–Mo–P	95.44(3)	90.06(2)	90.5(1)	84.6(1)
Mo–P–N	113.0(1), 112.4(1)	111.6(1), 112.0(1)	116.5(1), 116.9(1)	113.9(2), 115.6(2)
P–Mo–C_{trans}	175.3(1), 178.1(1)	176.71(8), 178.36(8)	178.9(1), 179.7(1)	[a]
P–Mo–C_{cis}	86.4(1)–91.9(1)	85.8(1)–94.3(1)	89.6(1)–91.3(1)	[a]

[a] No values reported.

7.1. Preparation of $PMes_2NHPh$ (**1c**)

At −78°C, 9.23 ml (13.85 mmol) of a 1.5 M BuLi solution in hexane was added with a dropping funnel to a solution of 1.45 ml (13.85 mmol) $PhNH_2$ in 30 ml thf. The solution was slowly warmed to room temperature (r.t.) and stirred for 1 h. The solution was then transferred into a dropping funnel and added dropwise to a solution of 5.4 g (13.85 mmol) $Mes_2PCl{\cdot}C_6H_{14}$ in 50 ml thf at −78°C. The solution was stirred for 2 h and then slowly warmed to r.t. The solvent was removed in vacuo, the off-white residue dissolved in hexane and LiCl filtered off. After concentration of the hexane solution, beige crystals of **1c** formed. Yield: 4.0 g (80%). M.p.: 124–126°C.

^{1}H NMR ($CDCl_3$, ppm): 7.21 (m, 3 H, *o*,*p*-H in Ph), 7.00 (m, 2 H, *m*-H in Ph), 6.80 (d, $^4J_{PH} = 1.9$ Hz, 2 H, $C_6H_2(CH_3)_3$), 4.34 (d, $^2J_{PH} = 9.0$ Hz, 1 H, NH), 2.30 (s, 12 H, *o*-CH_3 in Mes), 2.26 (s, 6 H, *p*-CH_3 in Mes). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): 19.4 (s). IR (KBr, cm^{-1}): 3364 cm^{-1} (vst, NH). Elemental analysis: $C_{24}H_{28}NP$ (361.45 g): C, 79.53 (79.75); H, 7.94 (7.81); N, 4.01 (3.88); P, 8.65 (8.57).

7.2. Preparation of cis-$[Mo(CO)_4(PPh_2NHPh)_2]$ (**2**)

PPh_2NHPh (5.54 g, 20 mmol) and 3.18 g (10 mmol) $[Mo(CO)_4(NCEt)_2]$ were stirred in 50 ml CH_2Cl_2 for 2 h. The solution was concentrated in vacuo, and the white product was precipitated with 30 ml hexane. Crystals were obtained from the mother liquor at −20°C. Yield: 6.55 g (86%). M.p.: 190–191°C.

^{1}H NMR ($CDCl_3$, ppm): 7.56 (br, 8 H, *m*-H in P–Ph), 7.34 (t, $^3J_{HH} = 5.1$ Hz, 12 H, *o*,*p*-H in P–Ph), 6.76 (t, $^3J_{HH} = 7.7$, 4 H, *m*-H in N–Ph), 6.58 (t, $^3J_{HH} = 7.3$ Hz, 2 H, *p*-H in N–Ph), 5.93 (d, $^3J_{HH} = 8.0$ Hz, 4 H, *o*-H in N–Ph), 4.34 (d, $^2J_{PH} = 22.2$ Hz, 2 H, NH). ^{13}C NMR ($CDCl_3$, ppm): 214.81 (m, CO *trans* to P), 209.78 (t, $^2J_{PC} = 9.9$ Hz, CO *cis* to P), 142.51 (t, $^2J_{PC} = 5.5$ Hz, *ipso*-C in N–Ph), 136.76 (m, *ipso*-C in P–Ph), 131.51 (d, $^2J_{PC} = 6.2$ Hz, *o*-C in P–Ph), 131.45 (d, $^2J_{PC} = 6.6$ Hz, *o*-C in P–Ph), 130.45 (s, *p*-C in P–Ph), 129.26 (d, $^3J_{PC} = 4.6$ Hz, *m*-C in Ph), 129.21 (d, $^3J_{PC} = 4.6$ Hz, *m*-C in Ph), 129.07 (s, *m*-C in N–Ph), 120.91 (s, *p*-C in N–Ph), 118.58 (t, $^3J_{PC} = 2.6$ Hz, *o*-C in N–Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): 70.84 (s, P), ^{13}C satellites at 70.96 (s), 70.77 (s), 70.60 (s), 70.41 (s). MS [*m*/*z*, %]: 514 $[(OC)_5Mo(PPh_2NHPh)^+$, 3], 486 $[(OC)_4Mo(PPh_2NHPh)^+$, 3], 430 $[(OC)_2Mo(PPh_2NHPh)^+$, 12], 374 $[Mo(PPh_2NHPh)^+$, 24], 277 $(PPh_2NHPh^+$, 100), 200 $(PPh_2NH^+$, 66), and fragmentation products thereof. IR (KBr, cm^{-1}): 3383 (m, NH), 2022 (vst, CO), 1929 (vst, CO), 1902 (vst, CO), 906 (st, PN). Elemental analysis: $C_{40}H_{32}MoN_2O_4P_2$ (762.58 g): C, 61.31 (63.00); H, 4.13 (4.23); N, 3.43 (3.67); O, 8.49 (8.39); P, 8.21 (8.12).

7.3. Preparation of cis-$[Mo(CO)_4(PPh_2NHBu^t)_2]$ (**3**)

PPh_2NHBu^t (0.89 g, 3.47 mmol) and 0.55 g (1.73 mmol) $[Mo(CO)_4(NCEt)_2]$ were stirred in 30 ml CH_2Cl_2 for 2 h. The solution was then concentrated in vacuo and the light brown product precipitated by adding 30 ml hexane. Crystals were obtained from the mother liquor at −20°C. Yield: 1.04 g (83%). M.p.: 117–120°C.

^{1}H NMR ($CDCl_3$, ppm): 7.34–7.70 (m, 4 H, *m*-H in Ph), 7.40–7.38 (m, 6 H, *o*,*p*-H in Ph), 2.15 (d, $^2J_{PH} = 20.0$ Hz, 2 H, NH), 0.85 (s, 18 H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 216.89 (d, $^2J_{PC} = 8.1$ Hz, CO *trans* to P), 216.80 (d, $^2J_{PC} = 8.7$ Hz, CO *trans* to P), 210.31 (t, $^2J_{PC} = 9.9$ Hz, CO *cis* to P), 139.83 (d, $^1J_{PC} = 18.2$ Hz, *ipso*-C in Ph), 139.65 (d, $^1J_{PC} = 18.0$ Hz, *ipso*-C in Ph), 132.62 (d, $^2J_{PC} = 6.5$ Hz, *o*-C in Ph), 132.55 (d, $^2J_{PC} = 6.5$ Hz, *o*-C in Ph), 129.87 (s, *p*-C in Ph), 128.45 (d, $^3J_{PC} = 4.3$ Hz, *m*-C in Ph), 128.41 (d, $^3J_{PC} = 4.3$ Hz, *m*-C in Ph), 56.33 (d, $^2J_{PC} = 6.7$ Hz, $C(CH_3)_3$), 56.27 (d, $^2J_{PC} = 6.7$ Hz, $C(CH_3)_3$), 32.69 (s, $C(CH_3)_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): 69.2 (s). IR (cm^{-1}): 3385 (m, NH), 2018 (vst, CO), 1905 (vst, CO), 1872 (vst, CO), 1010 (st, PN).

MS [*m*/*z*, %]: 723 (M^+, 0.01), 695 ($M^+ - CO$, 0.02), 667 ($M^+ - 2$ CO, 0.4), 495 $[(OC)_5Mo(PPh_2NBu^tH)^+$, 2], 467 ($M^+ - PPh_2NHBu^t$, 5), 439 ($M^+ - CO - PPh_2NHBu^t$, 1), 411 ($M^{+-}2CO - PPh_2NHBu^t$, 10), 383 ($M^{+-}3CO - PPh_2NHBu^t$, 0.5), 355 $(Mo(PPh_2NBu^tH)^+$, 25), 257 $(PPh_2NHBu^{t+}$, 93), 200 $(PPh_2NH^+$, 100), 185 $(PPh_2^+$, 75), and fragmentation products thereof. Elemental analysis: $C_{36}H_{40}MoN_2O_4P_2$ (722.58 g): C, 58.76 (59.84); H, 5.61 (5.58); N, 3.65 (3.88); O, 8.95 (8.86); P, 8.65 (8.57).

7.4. Data collection and structure refinement of **1b**,**c** and **3**

Data were collected on a Siemens CCD (SMART) diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) (Table 3). All observed reflections were used for determination of the unit cell parameters. Absorption correction with SADABS [25].

The structure of compound **1b** could be solved only in the monoclinic space group $P2_1$ ($\beta = 90°$). The R_{int} value for the monoclinic crystal system was 0.04 and that for the orthorhombic system 0.12. The normal refinement procedure for the space group $P2_1$ gave a wR_2 value of 0.289 with anisotropic temperature factors for all non-hydrogen atoms. The refinement procedure for a pseudo-merohedral twin with the matrix 100 0 −10 00−1 and BASF = 0.30 gave a better convergence ($wR_2 = 0.131$ and $R_1 = 0.050$).

Positions of non-hydrogen atoms were located by using direct methods (SHELXTL PLUS) [26]. Subsequent least-squares refinement and difference electron density

Table 3
Crystal data and structure refinement for **1b**, **1c** and **3**

	1b	**1c**	**3**
Formula	$C_{16}H_{20}NP$	$C_{24}H_{28}NP$	$C_{36}H_{40}MoN_2O_4P_2$
M_r	257.30	361.45	722.58
Temperature (K)	213(2)	220(2)	220(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)
a (Å)	10.085(2)	13.4020(3)	9.7956(1)
b (Å)	9.560(2)	7.2409(1)	20.7138(1)
c (Å)	15.650(3)	21.4066(2)	10.0850(1)
α (°)	90	90	90
β (°)	90.00(3)	92.138(1)	115.879(1)
γ (°)	90	90	90
V [Å^3]	1508.9(5)	2075.09(6)	1841.08(3)
Z	4	4	2
ρ_{calcd} (Mg m^{-3})	1.133	1.156	1.303
$F(000)$	552	776	748
Crystal size (mm)	$0.3\times0.3\times0.2$	$0.5\times0.4\times0.2$	$0.2\times0.4\times0.5$
Absorption coefficient (mm^{-1})	0.166	0.139	0.481
$2\Theta_{max}$ (°)	2.6–57.6	3.4–56.0	4.0–54.4
Reflections collected	9864	11457	9883
Independent reflections	6073	4551	5819
R_{int}	0.0438	0.0447	0.0281
Parameters	486	347	566
R ($I>2\sigma(I)$)	0.0498	0.0527	0.0273
wR_2 (all data)	0.1316	0.1241	0.0690
Absolute structure parameter			−0.07(3)
$(\Delta/\rho)_{min}$ (e Å^{-3})	0.331	0.273	0.355
$(\Delta/\rho)_{max}$ (e Å^{-3})	−0.200	−0.267	−0.490

map calculations revealed the positions of the H atoms (non-hydrogen atoms anisotropic approximation, H atoms isotropic approximation).

8. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC nos. 145916 (**1b**), 145918 (**1c**), 145917 (**3**)). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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