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FULL PAPER

Synthesis and characterization of d^2 imido complexes of molybdenum. Crystal structure of $[MoCl_2\{N(mes)\}(PhC{\equiv}CPh)(PMe_3)_2]\cdot 0.5PhC{\equiv}CPh$ (mes = 2,4,6-trimethylphenyl)‡

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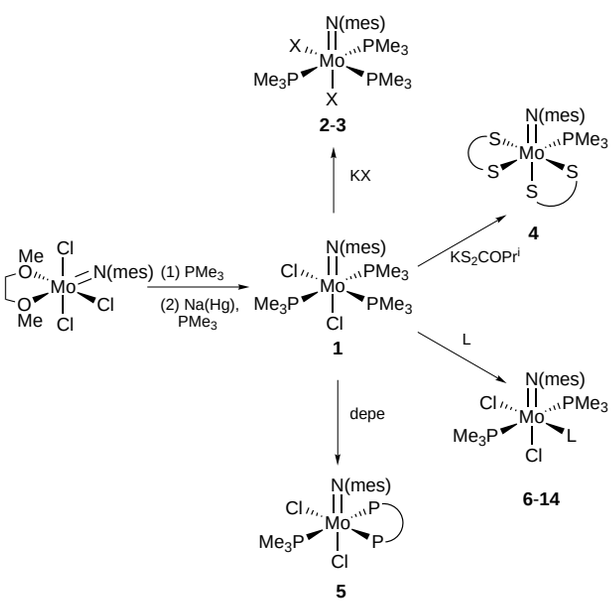
The compound $[MoCl_2\{N(mes)\}(PMe_3)_3]$ **1** (mes = 2,4,6-trimethylphenyl) has been prepared by the reaction of $[MoCl_3\{N(mes)\}(dme)]$ (dme = 1,2-dimethoxyethane) with 2 equivalents of PMe_3 and subsequent sodium amalgam reduction, in the presence of 1 additional equivalent of PMe_3. Metathesis reactions of **1** with KX gave $[MoX_2\{N(mes)\}(PMe_3)_3]$ (X = Br **2** or NCS **3**), whereas the anionic bidentate $Pr^iOCS_2^-$ ligand produced the monophosphine compound $[Mo\{N(mes)\}(S_2COPr^i)_2(PMe_3)]$ **4**. Substitution of two of the PMe_3 ligands to give $[MoCl_2\{N(mes)\}(PMe_3)(depe)]$ **5** (depe = $Et_2PCH_2CH_2PEt_2$) is also feasible, whilst phosphites and other π acceptors provided the corresponding $[MoCl_2\{N(mes)\}L(PMe_3)_2]$ compounds [L = $P(OMe)_3$ **6**, $P(OCH_2)_3CCH_2CH_3$ **7**, C_2H_4 **8**, $H_2C{=}CHCO_2Me$ **9**, CO **10**, $CNBu^t$ **11**, CNMe **12**, PhC≡CH **13** or PhC≡CPh **14**] by substitution of the unique PMe_3 group of **1**. Some of these arylimido complexes exhibit dynamic behaviour in solution, due to restricted rotation of the aryl group around the C–N bond. The molecular structure of **14** (as its PhC≡CPh hemisolvate, *i.e.* **14**·0.5PhC≡CPh) has been determined by an X-ray study.

Interest in compounds that contain metal–ligand multiple bonds[1] has increased enormously in the last two decades, in particular those of organoimides.[2] Low metal electronic configurations are commonly encountered, for example, an ample variety of d^2 organoimido derivatives of the Group 6 elements has been investigated.[3] As a continuation of our own work in this area,[4] we now report the synthesis of the d^2 mesitylimido complex $[MoCl_2\{N(mes)\}(PMe_3)_3]$ **1** (mes = 2,4,6-trimethylphenyl) along with its substitution chemistry. As shown in Scheme 1, this concerns both the replacement of the chloride groups by other anionic ligands, as well as that of the PMe_3 donors by phosphines, phosphites and other π acceptors. Variable-temperature NMR studies on some of these complexes indicate they exhibit fluxional behaviour, attributed to hindered aryl rotation around the C–N bond. While our work was in progress Nielson and co-workers reported a series of closely related d^2 imido compounds of tungsten.[5]

Results and Discussion

Synthesis and properties of the d^2 imido compound $[MoCl_2\{N(mes)\}(PMe_3)_3]$ 1

We have reported recently that the comproportionation reaction of the molybdenum-(VI) and -(IV) compounds $[MoCl_2\{N(mes)\}_2(dme)]$ and $[MoCl_4(thf)_2]$, respectively, constitutes a convenient entry into the chemistry of the d^1 $Mo\{N(mes)\}$ fragment, since it provides the molybdenum(V) imido complex $[MoCl_3\{N(mes)\}(dme)]$ in good yields.[4] Treatment of the latter compound with 2 equivalents of PMe_3 and subsequent Na–Hg reduction in the presence of one additional equivalent of PMe_3 gives $[MoCl_2\{N(mes)\}(PMe_3)_3]$ **1**. As shown in Scheme 1, this one-pot reaction, based on very simple synthetic methodology, provides easy access to the chemistry of the d^2 $Mo\{N(mes)\}$ moiety. The chloride ligand of **1** can be replaced by other halides or pseudo-halides; treatment with KX salts permits isolation of the expected $[MoX_2\{N(mes)\}(PMe_3)_3]$ derivatives (X = Br **2** or NCS **3**). Compound **1** is a blue solid whereas **2** and **3** can be isolated as red, also microcrystalline, materials. They show good solubility properties in Et_2O and other more polar organic solvents. Their spectroscopic properties are consistent with the proposed structures. For instance, complex **1** exhibits a typical AX_2 pattern of lines in the $^{31}P\text{-}\{^1H\}$ NMR spectrum and a virtually coupled triplet plus a doublet in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra. These observations indicate a meridional distribution of the PMe_3 groups, as has previously been found for other d^2 organoimido compounds of Group 6 elements.[6] Compounds **2** and **3** display similar NMR features. In addition, the IR spectrum of **3** contains two strong bands at 2083 and 2053 cm^{-1}, attributed to ν(NC) of the co-ordinated thiocyanate. These frequencies are very similar to those found



Scheme 1

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‡ *Non-SI unit employed*: atm = 101 325 Pa.

for the related oxo species $[MoO(NCS)_2(PMe_3)_3]$.[7] Free rotation around the N–C bond of the mesitylimido fragment takes place in solution; only one *o*-Me and one *m*-CH signal are observed in the ^1H and ^{13}C-$\{^1H\}$ NMR spectra of these complexes.

Earlier work from these laboratories showed that the molybdenum(IV) complex $[MoOCl_2(PMe_3)_3]$, that is the oxo analogue of **1**, exhibits an interesting reactivity toward *O*-alkyl dithiocarbonate ligands (*i.e.* xanthates).[8] Thus, upon reaction with the *O*-isopropyl salt, KS_2COPr^i, a compound of composition $MoO\{S_2C(PMe_3)OPr^i\}(S_2COPr^i)$ was isolated. Spectroscopic and X-ray studies demonstrated the presence of a trihapto *S*,*S*′,*C*-dithiocarbonate, along with the zwitterionic fragment $S_2C(PMe_3)OPr^i$.[8] In view of this result we have carried out the analogous reaction of **1** with KS_2COPr^i. A complex of the expected composition $Mo\{N(mes)\}(S_2COPr^i)_2(PMe_3)$ **4** has been obtained, but its spectroscopic properties indicate different structural features. Thus, the PMe_3 of **4** gives rise to a ^{31}P-$\{^1H\}$ NMR singlet at δ 0.1 and to a ^1H doublet (δ 1.24, $^2J_{HP} = 8.5$ Hz). Both the observed chemical shifts and the magnitude of this coupling are characteristic of co-ordinated PMe_3 groups and differ markedly from those expected for a quaternary phosphorus atom bearing a positive charge. For comparative purposes, the zwitterionic group of the above-mentioned oxo compound gives rise to a low-field ^{31}P-$\{^1H\}$ signal at δ 51 and to a ^1H doublet arising from a $^2J_{HP}$ coupling of *ca.* 13 Hz. The two dithiocarbonate ligands of **4** originate two different sets of signals. For example, four doublets and two heptets are respectively observed for the Me and CH groups in the ^1H NMR spectrum (see Experimental section), while the S*C*OR ^{13}C nuclei resonate at δ 215.3 and 194.4. Although ^{13}C NMR data for dithiocarbonate complexes are rather scarce, these chemical shifts seem to be in the range expected for bidentate dithiocarbonate ligands. On the basis of these data, the six-co-ordinate structure shown in Scheme 1 can be proposed for this complex.

Compound **1** undergoes also substitution reactions in the presence of the neutral bidentate ligand $Et_2PCH_2CH_2PEt_2$, depe. Mixing solutions of **1** and depe allows isolation of the new imido derivative $[MoCl_2\{N(mes)\}(PMe_3)(depe)]$ **5**, which can alternatively be obtained by a one-pot procedure that involves the direct treatment of the molybdenum(V) compound $[MoCl_3\{N(mes)\}(dme)]$ with depe, followed by Na–Hg reduction, in the presence of 1 equivalent of PMe_3 (see Experimental section). The ^{31}P-$\{^1H\}$ NMR spectrum of **5** corresponds to an AMX spin system (X = PMe_3). The large $^2J_{AX}$ coupling constant of 191 Hz found for this compound indicates that the PMe_3 group is *trans* with respect to one of the P atoms of the diphosphine ligand.[9] Since, as detailed in the Experimental section, the four PCH_2CH_3 groups give rise to four independent signals in the ^1H NMR spectrum, the structure in Scheme 1 can be confidently assigned to this compound. This geometry, in which the three P-donor atoms avoid the co-ordination site *trans* to the N(mes) moiety, is similar to that previously proposed for the analogous oxo derivative $[MoOCl_2(PMe_3)(dmpe)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[10]

Characterisation of d² imido complexes of composition $MoCl_2\{N(mes)\}L(PMe_3)_2$ 6–14

Phosphine substitution reactions by π-acceptor ligands on complexes of the Group 6 elements with d^2 configuration [*i.e.* metal(IV) derivatives] that contain metal–ligand multiple bonds have been observed previously.[6c,11] Co-ordination of the π-acceptor ligand *cis* to the metal–ligand multiple bond is the geometry expected on the basis of simple MO arguments.[1c] In consonance, the interaction of **1** with different π-acceptor reagents (L) produces, through displacement of the unique PMe_3, compounds of general formulation $MoCl_2\{N(mes)\}L(PMe_3)_2$ **6**–**14**.

Treatment of complex **1** with the soft π-acceptor phosphites $P(OMe)_3$ and $P(OCH_2)_3CCH_2CH_3$ gives, after work-up, the new complexes $[MoCl_2\{N(mes)\}\{P(OMe)_3\}(PMe_3)_2]$ **6** and $[MoCl_2\{N(mes)\}\{P(OCH_2)_3CCH_2CH_3\}(PMe_3)_2]$ **7**. Their ^{31}P-$\{^1H\}$ NMR spectra consist of a pattern of lines typical of an AX_2 spin system, whereas ^1H NMR data are indicative of a *trans* geometrical disposition of the equivalent PMe_3 groups (δ 1.51, 18 H, virtually coupled triplet, $J_{HP_{app}} = 3.9$ Hz, for **6**). According to these observations, the general structure shown in Scheme 1 can be proposed for these complexes.

Olefins can also replace the unique phosphine ligand of complex **1**. Thus, **1** reacts with ethylene (2 atm, 20 °C) or $H_2C{=}CHCO_2Me$ (80 °C) to afford the corresponding imido derivatives $[MoCl_2\{N(mes)\}(C_2H_4)(PMe_3)_2]$ **8** and $[MoCl_2\{N(mes)\}(H_2C{=}CHCO_2Me)(PMe_3)_2]$ **9**, respectively, in the form of orange crystalline solids. The ^{31}P-$\{^1H\}$ NMR spectrum of **8** is a singlet at δ −6.0 while that of **9** consists of a strongly coupled AB quartet ($^2J_{AB} = 177$ Hz) due to the asymmetry introduced by the methyl acrylate ligand. The NMR parameters of both compounds are consistent with the expected perpendicular *cis* arrangement of the olefin with respect to the Mo–N(mes) bond, as has been found for other structurally characterized olefin complexes of Group 6, d^2 M=X functionalities, *e.g.* $[WOCl_2(C_2H_4)(PMePh_2)_2]$,[11a] $[WCl_2(NNCMe_2)(C_2H_4)(PMe_2Ph)_2]$,[11c] $[WCl_2(NPh)(H_2C{=}CMe_2)(PMe_3)_2]$[12] or $[WCl_2(PhC{\equiv}CPh)(C_2H_4)(PMe_3)_2]$.[13] Rotation of the olefin around the molybdenum–olefin bond appears to be restricted at room temperature in view of the presence of two multiplets in the ^1H NMR spectrum of **8** attributable to the C_2H_4 protons. As for **9**, stereomers due to the orientation of the CO_2Me group, either above or below the plane perpendicular to the Mo–N(mes) axis, are also possible. Despite this only one isomer has been detected but determination of the geometry of the $H_2C{=}CHCO_2Me$ fragment in this complex has not been attempted.

The interaction of complex **1** with CO, $CNBu^t$ or CNMe yields the corresponding $MoCl_2\{N(mes)\}L(PMe_3)_2$ compounds (L = CO **10**, $CNBu^t$ **11** or CNMe **12**) in the form of red (**10**) or blue crystalline materials, soluble in Et_2O and other more polar solvents and moderately stable to air. Their IR spectra exhibit a strong absorption in the proximity of 2000 cm^{-1} due to ν(CO) (**10**, 1961 cm^{-1}) or to ν(CN) (**11**, 2094; **12**, 2153 cm^{-1}) of the co-ordinated π acceptor. The energy of this band suggests substantial π donation from the d^2 molybdenum center to the CO and CNR ligands and compares well with those reported for related complexes {for instance the ν(CO) and ν(CN) respectively at 1968 and 2095 cm^{-1} for $[MoCl_2(NBu^t)(CO)(PMe_3)_2]$ and $[MoCl_2(NBu^t)(CNBu^t)(PMePh_2)_2]$[14]}. The NMR data for **10**–**12** are in accord with the proposed formulation.

Finally, the interaction of complex **1** with the alkynes PhC≡CH and PhC≡CPh has been studied and the new compounds $[MoCl_2\{N(mes)\}(PhC{\equiv}CH)(PMe_3)_2]$ **13** and $[MoCl_2\{N(mes)\}(PhC{\equiv}CPh)(PMe_3)_2]\cdot 0.5PhC{\equiv}CPh$ **14** isolated and the latter structurally characterized. Whilst the reaction of **1** with PhC≡CH proceeds at 85 °C, with complete conversion into **13** in 5 h, the analogous interaction with PhC≡CPh does not proceed beyond *ca.* 15% yield, after heating at 70 °C overnight. Both compounds are isolated as orange crystals, soluble in common organic solvents. The proposed *trans*-PMe_3 geometry is once again based on the observation of a strongly coupled AB spin system ($^2J_{AB} = 197$ Hz) in the ^{31}P-$\{^1H\}$ NMR spectrum of **13**. The resonances of the acetylenic carbons appear in the range characteristic of two-electron-donor alkyne ligands.[15,16]

Molecular structure of the diphenylacetylene complex $[MoCl_2\{N(mes)\}(PhC{\equiv}CPh)(PMe_3)_2]\cdot 0.5PhC{\equiv}CPh$ 14

The molecular structure of complex **14** has been determined by an X-ray study and is shown in Fig. 1. Selected bond distances and angles are collected in Table 1. The complex has a distorted octahedral structure with a *cis*, *trans* disposition of the chloro

Table 1 Selected bond lengths (Å) and angles (°) for $[MoCl_2\{N(mes)\}(PhC{\equiv}CPh)(PMe_3)_2]\cdot 0.5PhC{\equiv}CPh$ **14**

Mo–Cl(1)	2.557(2)	Mo–P(2)	2.565(2)
Mo–Cl(2)	2.491(2)	Mo–C(1)	2.132(6)
Mo–N	1.751(4)	Mo–C(2)	2.142(6)
Mo–P(1)	2.556(2)	C(1)–C(2)	1.251(8)
Cl(1)–Mo–Cl(2)	81.0(1)	N–Mo–P(2)	97.0(1)
Cl(1)–Mo–P(1)	91.79(7)	N–Mo–C(1)	102.1(2)
Cl(1)–Mo–P(2)	80.34(7)	N–Mo–C(2)	95.4(2)
Cl(2)–Mo–P(1)	77.2(1)	C(1)–Mo–C(2)	34.2(2)
Cl(2)–Mo–P(2)	81.4(1)	Mo–N–C(15)	176.9(4)
P(1)–Mo–P(2)	158.2(2)	Mo–C(2)–C(3)	148.1(5)
N–Mo–Cl(1)	176.3(2)	Mo–C(1)–C(9)	145.8(5)
N–Mo–Cl(2)	96.1(2)	C(1)–C(2)–C(3)	139.3(6)
N–Mo–P(1)	89.8(2)	C(2)–C(1)–C(9)	140.6(6)

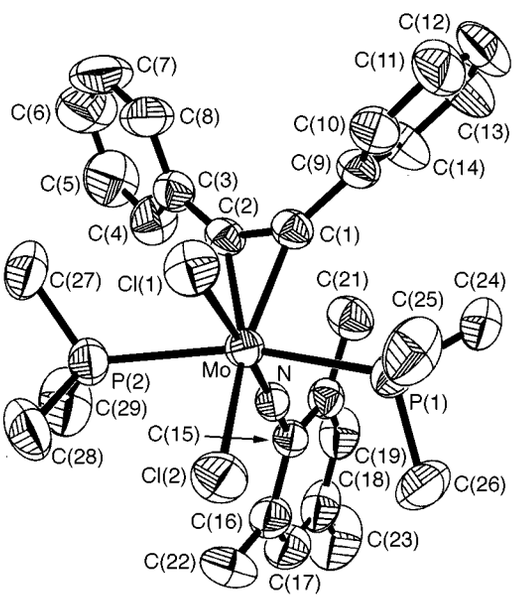

Fig. 1 Molecular structure of $[MoCl_2\{N(mes)\}(PhC{\equiv}CPh)(PMe_3)_2]$

and PMe_3 ligands as already suggested by the spectroscopic data. The Mo–N–C(15) part of the imido functionality is linear [176.9(4)°] and the Mo–N distance of 1.751(4) Å compares well with the analogous distances found in related d^2 W(NR) (R = aryl) complexes that have been structurally authenticated, *e.g.* $[WCl_2(NPh)(PMe_3)_3]$ [1.755(3) Å],[6a] $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$ [1.77(1) Å],[17] $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC{\equiv}CH)(PMe_3)_2]$ [1.757(4) Å][5] and $[WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2]$ [1.78(1) Å].[12] The two Mo–Cl bond lengths, 2.557(2) and 2.491(2) Å, are significantly different. Since the longer of the two corresponds to the Mo–Cl bond *trans* to the imido group, this difference can be attributed to the *trans* influence of the imide ligand.[18] However, the value of Δ(Mo–Cl) for **14** [0.066(3) Å], although similar to those found in other related compounds that have Mo–Cl bonds *trans* to oxo or imido functionalities,[4,19] can be considered as indicative of a small *trans* influence.[18] As pointed out elsewhere,[4] it appears that the rather hard Cl donor experiences a smaller *trans* influence from the imido group than the soft P-donors. The Mo–C bond distances within the Mo–PhC≡CPh linkage [Mo–C(1) 2.132(6), Mo–C(2) 2.142(6) Å] and the C(1)–C(2) separation of 1.251(8) Å are similar to those found in the related complex $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$.[17] The C(1)–C(2) bond length of the co-ordinated PhC≡CPh is larger than the C≡C bond distance found for the solvate PhC≡CPh molecule. The distortions from the octahedral geometry are close to those reported for $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$[17] and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC{\equiv}CH)(PMe_3)_2]$,[4] the main feature being the P(1)–Mo–P(2) angle [158.2(2)°] bending from the acetylene ligand more than from the arylimido group.

Rotation of the arylimide ligand about the C–N bond in some $[MoCl_2\{N(mes)\}L(PMe_3)_2]$ compounds

The signal due to the *o*-methyl groups of the mesitylimide ligand in the ^{1}H NMR spectra of some $[MoCl_2\{N(mes)\}L(PMe_3)_2]$ compounds deserves an additional comment. For example, in the 500 MHz spectra of the isocyanide derivatives **11** and **12**, recorded at 298 K, this resonance appears as a broad singlet, whereas in the 300 MHz spectra of **13** and **14**, also at 298 K, the Me groups are not observed and the *m*-C*H* protons give a broad hump. Conversely, the same *o*-methyl resonance is seen as a sharp singlet in the corresponding spectra of complexes **1** and **6**–**10**. Variable-temperature ^{1}H NMR (300 MHz, $[^2H_6]$acetone) studies have been carried out for **11**, **13** and **14**. For **11** the spectrum obtained at 203 K contains two singlets of equal intensity for the *o*-methyl groups of the arylimide ligand. The splitting indicates the non-equivalence of the two sides of the aryl ring and suggests hindered rotation of the arylimido group around the C–N bond. Accordingly, at the same temperature, the ^{13}C-{^{1}H} NMR spectrum shows six signals for the aromatic carbon atoms of the aryl functionality, and two resonances for the *o*-methyl groups. The exchange process responsible for the magnetic equivalence of the two sides of the ring, observed at room temperature, is rotation of the aryl group of the arylimide ligand. Based on the behaviour of the resonances of the methyl groups, the activation energy for the fluxional process was calculated by line shape analysis[20] at the coalescence temperature. A value of $\Delta G^{\ddagger}$ (249 K) = 51 kJ mol^{-1} was found for **11**. For both **13** and **14**, cooling to around 233 K resulted in two sharp singlets in the *o*-Me region while the broad resonance due to the *m*-hydrogens split into two well defined singlets. The low-temperature spectrum is consistent with rigid conformation of the arylimido group. For both complexes an approximate value of $\Delta G^{\ddagger} = 57$ kJ mol^{-1} was calculated for rotation of the arylimide ligand around the C–N bond (the coalescence temperature was 270 K for the *m*-CH resonances and 298 K for the *o*-Me signals). The NMR behaviour of **13** and **14** is in accord with the data reported for Grubbs and co-workers[6c] for the complex $[WCl_2(NC_6H_3Me_2\text{-}2,6)(PhC{\equiv}CPh)(PEt_2Ph)_2]$ and with those of Nielson and co-workers[5] for the related derivatives $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC{\equiv}CH)(PMe_3)_2]$ and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PhC{\equiv}CPh)(PMe_3)_2]$. In these cases the presence of sterically more demanding groups results in a rigid conformation of the arylimide ligand, at room temperature.

Hindered rotation of the arylimido group has been reported recently in other systems[6c,21] and is usually explained on the basis of steric factors.[5,6c,22] However, very recently Gibson and co-workers[23] have attributed to electronic effects the conformation of the aryl group observed in the solid-state structure of $[MoCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NBu^t)(dme)]$. A simple molecular model of **14** shows that rotation of the phenylimide ligand about the C–N bond is hindered due to the phenyl substituents of the alkyne ligand and this favours the explanation of the dynamic behaviour of our compounds on the basis of only steric factors.

Finally, for comparative purposes, a variable-temperature ^{1}H NMR study (300 MHz, $[^2H_6]$acetone) of the carbonyl compound **10**, that contains a non-sterically demanding coligand L has been performed. At room temperature the spectrum shows only sharp signals, but they broaden significantly at lower temperatures. Even though the slow-exchange regime was not reached at 203 K from the shape of the *o*-Me signals, an approximate value of $\Delta G^{\ddagger}$ (226 K) ≈ 46 kJ mol^{-1} can be suggested for this fluxional process. In this case the C–N rotation is obviously not blocked by the carbonyl groups, hence the steric hindrance arises from the PMe_3 ligands. In accord with this,

$\Delta G^{\ddagger}$ for L = CO (**10**) is lower than for **11** (L = $CNBu^t$), **13** (L = PhC≡CH) or **14** (L = PhC≡CPh).

Experimental

Microanalyses were by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin-Elmer model 883 spectrophotometer, ^1H, ^{13}C and ^{31}P NMR spectra on Bruker AMX-300 or AMX-500 spectrometers. The ^{31}P shifts were measured with respect to external 85% H_3PO_4, ^{13}C were referenced using the resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40–60 °C. The compound [$MoCl_3$-{N(mes)}(dme)] was prepared according to the literature.[4] Only selected data are reported for the low-temperature NMR spectra.

Syntheses

[$MoCl_2${N(mes)}(PMe_3)$_3$] 1. Over a solution of [$MoCl_3$-{N(mes)}(dme)] (0.64 g, 1.5 mmol) in thf (35 cm^3) were added 2 equivalents of PMe_3 and allowed to react for 30 min at room temperature. The resulting solution was then reduced with Na–Hg amalgam (50 mg of Na, 4.7 g Hg) and treated with an additional equivalent of PMe_3, the stirring being continued for 2 h. The deep blue solution was filtered and removal of the volatiles gave a blue solid residue. Crystallization from a mixture of Et_2O–thf at −20 °C gave **1** as blue needle crystals (0.51 g, 65%). ^{31}P-{^1H} NMR ([$^2H_6$]acetone, AX_2 spin system): δ 3.2 (t, $^2J_{PP}$ = 17 Hz) and −9.2 (d). ^1H NMR (300 MHz, C_6D_6): δ 6.51 (s, 2 H, *m*-CH), 2.43 (s, 6 H, *o*-CH_3), 1.94 (s, 3 H, *p*-CH_3), 1.41 (t, $J_{HP_{app}}$ = 3.6, 18 H, PMe_3), 1.28 (d, J_{HP} = 7.5 Hz, 9 H, PMe_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 151.0 (s, *ipso*-C of C_6H_2), 134.8, 134.75 (s, *p*- and *o*-C of C_6H_2), 128.7 (s, *m*-C of C_6H_2), 21.9 (d, J_{CP} = 23, PMe_3), 20.8 (s, *p*-CH_3), 19.7 (s, *o*-CH_3) and 16.8 (t, J_{CP} = 11.5 Hz, PMe_3) (Found: C, 42.5; H, 7.7; N, 2.6. $C_{18}H_{38}Cl_2MoNP_3$·0.5Et_2O requires C, 42.5; H, 7.6; N, 2.5%).

[MoX_2{N(mes)}(PMe_3)$_3$] (X = Br 2 or NCS 3). A mixture of complex **1** (0.15 g, 0.28 mmol) and 2 equivalents of KBr was stirred in thf (25 cm^3) at ambient temperature overnight. Volatiles were then removed, the residue extracted with Et_2O (30 cm^3) and filtered to separate KCl. Concentration of the solution and cooling to −20 °C afforded red microcrystals of **2** (55%). ^{31}P-{^1H} NMR (C_6D_6, AX_2 spin system): δ −2.5 (t, $^2J_{PP}$ = 18.2 Hz) and −16.4 (d). ^1H NMR (500 MHz, C_6D_6): δ 6.47 (s, 2 H, *m*-CH), 2.39 (s, 6, *o*-CH_3), 1.90 (s, 3 H, *p*-CH_3), 1.50 (t, $J_{HP_{app}}$ = 3.6, 18 H, PMe_3) and 1.29 (d, J_{HP} = 7.6 Hz, 9 H, PMe_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 151.0 (s, *ipso*-C of C_6H_2), 135.2, 134.4 (s, *p*- and *o*-C of C_6H_2), 128.9 (s, *m*-C of C_6H_2), 22.1 (d, J_{CP} = 24.1, PMe_3), 20.9 (s, *p*-CH_3), 20.0 (s, *o*-CH_3) and 18.2 (t, J_{CP} = 11.8 Hz, PMe_3) (Found: C, 35.2; H, 6.2; N, 3.1. $C_{18}H_{38}Br_2MoNP_3$ requires C, 35.0; H, 6.2; N, 2.3%).

Complex **3** was obtained by using KNCS and employing a similar procedure (69%). IR (Nujol): 2083 and 2053 cm^{-1}, ν(NC). ^{31}P-{^1H} NMR (C_6D_6, AX_2 spin system); δ 1.2 (t, $^2J_{PP}$ = 16.8 Hz) and −4.6 (d). ^1H NMR (500 MHz, C_6D_6): δ 6.46 (s, 2 H, *m*-CH), 2.22 (s, 6 H, *o*-CH_3), 1.92 (s, 3 H, *p*-CH_3), 1.16 (t, $J_{HP_{app}}$ = 3.4, 18 H, PMe_3) and 1.13 (d, J_{HP} = 7.5 Hz, 9 H, PMe_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 156.3 (s, NCS), 150.9 (s, *ipso*-C of C_6H_2), 142.2 (s, NCS), 135.9, 135.0 (s, *p*- and *o*-C of C_6H_2), 129.0 (s, *m*-C of C_6H_2), 21.0 (d, J_{CP} = 23.4, PMe_3), 20.8 (s, *p*-CH_3), 19.5 (s, *o*-CH_3) and 16.6 (t, J_{CP} = 11.6 Hz, PMe_3) (Found: C, 41.8; H, 6.6; N, 7.7. $C_{19}H_{38}MoN_2P_3S$ requires C, 41.9; H, 6.6; N, 7.3%).

[Mo{N(mes)}(S_2COPr^i)$_2$(PMe_3)] 4. To a mixture of complex **1** (0.19 g, 0.36 mmol) and KS_2COPr^i (0.13 g, 0.72 mmol) was added thf (30 cm^3). The resulting suspension was stirred at room temperature and the KS_2COPr^i salt dissolved gradually, while the solution became dark red. After 14 h the reaction was complete (by ^{31}P-{^1H} NMR) and the volatiles were removed under reduced pressure. The red residue was extracted with light petroleum and filtered to remove KCl. The filtrate was concentrated and cooled to −20 °C. Orange crystals of **4** were obtained (0.14 g, 68%). ^{31}P-{^1H} NMR (C_6D_6): δ 0.1 (s). ^1H NMR (300 MHz, C_6D_6): δ 6.49 (s, 2 H, *m*-CH), 5.26, 5.36 (quintet, $^3J_{HH}$ = 6.2, 1 H, C*H*Me_2), 2.40 (s, 6 H, *o*-CH_3), 1.93 (s, 3 H, *p*-CH_3), 1.24 (d, J_{HP} = 8.5, 9 H, PMe_3), 1.13, 1.03, 1.01, 0.90 (d, $^3J_{HH}$ = 6.2 Hz, 3, CH*Me*$_2$). ^{13}C-{^1H} NMR (75 MHz, C_6D_6): δ 215.3 (d, J_{CP} = 4.3, S_2C), 194.4 (s, S_2C), 154.0 (s, *ipso*-C of C_6H_2), 135.3, 134.7 (s, *p*- and *o*-C of C_6H_2), 128.7 (s, *m*-C of C_6H_2), 75.9, 75.3 (d, *C*HMe_2), 21.7 (s, *p*-CH_3), 20.9 (s, *o*-CH_3), 19.9, 18.9 (s, CH*Me*$_2$) and 15.6 (d, J_{CP} = 25.8 Hz, PMe_3) (Found: C, 42.2; H, 6.1; H, 2.5. $C_{20}H_{34}MoNO_2PS_4$ requires C, 41.7; H, 5.9; N, 2.4%).

[$MoCl_2${N(mes)}(PMe_3)(depe)] 5. To a solution of complex **1** (0.1 g, 0.19 mmol) in thf (35 cm^3) was added 1 equivalent of depe (1 M solution in thf) and the mixture stirred overnight. Completion of the reaction was checked by ^{31}P-{^1H} NMR. The volatiles were pumped off and the residue was extracted with Et_2O. Cooling to −20 °C afforded green crystals of **5**.

The following is an alternative, one-pot procedure: to a solution of [$MoCl_3${N(mes)}(dme)] (0.21 g, 0.5 mmol) in thf (25 cm^3) was added 1 equivalent of depe (1 M solution in thf) and the mixture stirred for 90 min at room temperature. The resulting solution was transferred to a flask containing Na–Hg amalgam (15 mg of Na, 1.3 g Hg) and treated immediately with 1 equivalent of PMe_3. The mixture was stirred for 3 h and the pale greenish suspension filtered. Removal of the volatiles gave a green residue. Crystallization from Et_2O at −20 °C gave **5** as green crystals (0.18 g, 62%). ^{31}P-{^1H} NMR (C_6D_6, AMX spin system): δ 58.2 (d, P_A, depe, $^2J_{PP}$ = 17), 45.6 (d, P_M, depe, $^2J_{PP}$ = 191 Hz) and −8.1 (dd, P_X, PMe_3). ^1H NMR (500 MHz, C_6D_6): δ 6.55 (s, 2 H, *m*-CH), 2.56 (s, 6 H, *o*-CH_3), 1.95 (s, 3 H, *p*-CH_3), 1.47 (d, J_{HP} = 8, 9 H, PMe_3), 1.26 (dt, J_{HP} = 14.0, $^3J_{HH}$ = 7.7, 3 H, CH_2CH_3), 1.07 (dt, J_{HP} = 13.6, $^3J_{HH}$ = 7.7, 3 H, CH_2CH_3), 0.76 (dt, J_{HP} = 13.9, $^3J_{HH}$ = 7.6, 3 H, CH_2CH_3), 0.63 (dt, J_{HP} = 12.3, $^3J_{HH}$ = 7.6 Hz, 3 H, CH_2CH_3), 2.7–0.9 (9 multiplets, CH_2 groups, depe). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 151.2 (s, *ipso*-C of C_6H_2), 135.6, 134.9 (s, *p*- and *o*-C of C_6H_2), 128.6 (s, *m*-C of C_6H_2), 25.1 (d, J_{CP} = 24, CH_2, depe), 25.0 (d, J_{CP} = 24, CH_2, depe), 22.1 (d, J_{CP} = 19, CH_2, depe), 20.9 (s, *p*-CH_3), 20.3 (d, J_{CP} = 17, CH_2, depe), 19.5 (s, *o*-CH_3), 19.0 (d, J_{CP} = 15.7, CH_2, depe), 18.3 (d, J_{CP} = 20.5, CH_2, depe), 16.2 (d, J_{CP} = 22, PMe_3), 8.8 (d, J_{CP} = 4, CH_3, depe), 8.3 (d, J_{CP} = 3, CH_3, depe), 8.0 (s, CH_3, depe) and 7.9 (d, J_{CP} = 4 Hz, CH_3, depe) (Found: C, 45.3; H, 7.6. $C_{22}H_{44}Cl_2MoNP_3$ requires C, 45.3; H, 7.6%).

[$MoCl_2${N(mes)}{$P(OMe)_3$}(PMe_3)$_2$] 6. The compound $P(OMe)_3$ (0.30 mmol; 1 M solution in thf) was added to a solution of complex **1** (0.13 g, 0.25 mmol) in thf (25 cm^3) and the mixture stirred at room temperature for 1 d. The solvent was removed in vacuum, the crude product extracted with Et_2O (15 cm^3) and the resulting solution cooled to −20 °C. Blue crystals of **6** were collected (42%). ^{31}P-{^1H} NMR (C_6D_6, AX_2 spin system): δ 173.1 [t, J_{PP} = 30.5 Hz, $P(OMe)_3$] and −8.6 (d, PMe_3). ^1H NMR (500 MHz, C_6D_6): δ 6.54 (s, 1 H, *m*-CH), 3.37 [d, J_{HP} = 9.9, 9 H, $P(OMe)_3$], 2.58 (s, 6 H, *o*-CH_3), 1.94 (s, 3 H, *p*-CH_3) and 1.51 (t, $J_{HP_{app}}$ = 3.9 Hz, 18 H, PMe_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 151.2 (s, *ipso*-C of C_6H_2), 136.8, 134.8 (s, *p*- and *o*-C of C_6H_2), 128.8 (s, *m*-C of C_6H_2), 52.7 [d, J_{CP} = 8.4, $P(OMe)_3$], 20.8 (s, *p*-CH_3), 19.6 (s, *o*-CH_3) and 16.8 (t, J_{CP} = 11.3 Hz, PMe_3).

[$MoCl_2${N(mes)}{$P(OCH_2)_3CCH_2CH_3$}(PMe_3)$_2$] 7. A mixture of complex **1** (0.15 g, 0.28 mmol) and $P(OCH_2)_3CCH_2CH_3$ (0.28 mmol; 1 M solution in thf) in thf (25 cm^3) was stirred at ambient temperature overnight. The volatiles were removed under vacuum and the residue dissolved in an Et_2O–thf mixture. The solution was concentrated and cooled to −20 °C. The desired compound **7** was isolated as a violet crystalline solid (0.09 g, 54%). ^{31}P-{^1H} NMR ($CDCl_3$, AX_2 spin system): δ 162.7 [t, $^2J_{PP}$ = 31.5 Hz, P_A, $P(OCH_2)_3CCH_2CH_3$] and −8.9 (d, P_X, PMe_3). ^1H NMR (500 MHz, $CDCl_3$): δ 6.63 (s, 2 H, *m*-CH), 4.22 [d, $^3J_{HP}$ = 4.4, 6 H, $P(OCH_2)_3CCH_2CH_3$], 2.44 (s, 6 H, *o*-CH_3), 2.11 (s, 3 H, *p*-CH_3), 1.48 (pseudo t, $J_{HP_{app}}$ = 3.4, 18 H, PMe_3), 1.22 (q, J_{HH} = 7.6, 2 H, CH_2CH_3) and 0.82 (t, J_{HH} = 7.6 Hz, 3 H, CH_2CH_3). ^{13}C-{^1H} NMR (125 MHz, $CDCl_3$): δ 150.3 (s, *ipso*-C of C_6H_2), 137.1, 135.9 (s, *p*- and *o*-C of C_6H_2), 128.6 (s, *m*-C of C_6H_2), 73.8 [d, J_{CP} = 6.7, $P(OCH_2)_3CCH_2CH_3$], 34.8 [d, J_{CP} = 30 Hz, $P(OCH_2)_3CCH_2CH_3$], 23.5 (s, CH_2CH_3), 21.1 (s, *p*-CH_3), 19.4 (s, *o*-CH_3), 15.7 (t, J_{CP} = 12.4 Hz, PMe_3) and 7.0 (s, CH_2CH_3) (Found: C, 41.0; H, 7.0; N, 3.0. $C_{21}H_{40}Cl_2NMoO_3P_3$ requires C, 41.0; H, 6.5; N, 2.3%).

[$MoCl_2${N(mes)}(C_2H_4)(PMe_3)$_2$] 8. Over a solution of [$MoCl_3${N(mes)}(dme)] (0.20 g, 0.47 mmol) in thf (30 cm^3) was added 2 equivalents of PMe_3 (1 M solution in toluene) and the mixture allowed to react for 30 min at room temperature. The resulting solution was transferred to a flask containing Na–Hg amalgam (12 mg of Na, 1.3 g Hg) under an atmosphere of C_2H_4 (1 atm), stirred for 90 min and then centrifuged. Removal of the volatiles gave an orange solid. Extraction with Et_2O and cooling at −20 °C afforded **8** as orange crystals (0.09 g, 41%).

A pressure vessel was charged with a solution of complex **1** (0.07 g, 0.13 mmol) in thf (20 cm^3) and C_2H_4 (2 atm). The solution was stirred at ambient temperature overnight. After depressurization, a ^{31}P-{^1H} NMR spectrum of the resulting solution indicated completion of the reaction. The solution was evaporated to dryness and worked up as above. ^{31}P-{^1H} NMR (C_6D_6): δ −6.0 (s). ^1H NMR (300 MHz, C_6D_6): δ 6.31 (s, 2 H, *m*-CH), 2.81 (m, 2 H, HCH=CHCH), 2.64 (m, 2 H, HCH=CHCH), 2.25 (s, 6 H, *o*-CH_3), 1.85 (s, 3 H, *p*-CH_3) and 1.37 (pseudo t, $J_{HP_{app}}$ = 3.8 Hz, 18 H, PMe_3). ^{13}C-{^1H} NMR (75 MHz, C_6D_6): δ 150.6 (s, *ipso*-C of C_6H_2), 139.5, 136.6 (s, *p*- and *o*-C of C_6H_2), 129.1 (s, *m*-C of C_6H_2), 48.3 (s, C_2H_4), 20.6 (s, *p*-CH_3), 19.7 (s, *o*-CH_3) and 14.1 (t, J_{CP} = 13 Hz, PMe_3) (Found: C, 42.8; H, 7.0; N, 3.3. $C_{17}H_{33}Cl_2MoNP_2$ requires C, 42.5; H, 6.9; N, 2.9%).

[$MoCl_2${N(mes)}(H_2C=$CHCO_2Me$)(PMe_3)$_2$] 9. To a solution of complex **1** (0.15 g, 0.3 mmol) in thf (25 cm^3) was added an excess of H_2C=$CHCO_2Me$ (0.2 cm^3). The mixture was heated at 80 °C, with stirring, for 3 h. After this period it was centrifuged and volatiles removed *in vacuo*. The residue was extracted with Et_2O and crystallized to give orange crystals of **9** (68%, isolated product). ^{31}P-{^1H} NMR (C_6D_6, AB spin system): δ −5.7 (d, $^2J_{AB}$ = 177 Hz) and −8.8 (d). ^1H NMR (300 MHz, C_6D_6): δ 6.38 (s, 2 H, *m*-CH), 3.73 (td, 1 H, *J* = 11, 9, H_2C=CH), 3.28 (m, 1 H, H_2C=CH), 3.13 (s, 3 H, CO_2Me), 3.02 (td, 1 H, *J* = 10, 3.3, H_2C=CH), 2.58 (s, 6 H, *o*-CH_3), 1.87 (s, 3 H, *p*-CH_3), 1.61 (d, $^2J_{HP}$ = 8.9, 9 H, PMe_3) and 1.39 (d, $^2J_{HP}$ = 9.1 Hz, 9 H, PMe_3). ^{13}C-{^1H} NMR (75 MHz, C_6D_6): δ 175.5 (s, CO_2Me), 149.5 (s, *ipso*-C of C_6H_2), 139.6, 137.4 (s, *p*- and *o*-C of C_6H_2), 129.1 (s, *m*-C of C_6H_2), 56.1 (d, J_{CP} = 6.5, H_2C=CH), 55.2 (d, J_{CP} = 7.8, H_2C=CH), 49.9 (s, CO_2Me), 20.7 (s, *p*-CH_3), 20.1 (s, *o*-CH_3), 14.3 (d, J_{CP} = 24.4, PMe_3) and 13.7 (d, J_{CP} = 26.2 Hz, PMe_3) (Found: C, 42.6; H, 6.7; N, 2.6. $C_{19}H_{35}Cl_2MoNO_2P_2$ requires C, 42.4; H, 6.5; N, 2.6%).

[$MoCl_2${N(mes)}(CO)(PMe_3)$_2$] 10. To a solution of [$MoCl_3$-{N(mes)}(dme)] (0.21 g, 0.5 mmol) in thf (30 cm^3) were added 2 equivalents of PMe_3 (1 M solution in toluene) and the mixture allowed to react for 30 min at room temperature. The resulting solution was transferred to a pressure vessel containing Na–Hg amalgam (15 mg of Na, 1.3 g Hg) and, immediately, charged with CO (2 atm). The mixture was stirred for 2 h and then depressurized and centrifuged. The removal of the volatiles gave an oily reddish residue. Extraction with light petroleum–Et_2O (1 : 1) and cooling at −20 °C gave complex **10** as dark red crystals (0.10 g, 43%).

An alternative procedure involves the direct reaction of complex **1** (0.06 g, 0.11 mmol) in thf (20 cm^3) with CO (2 atm), as described for **8**. Work-up as above gave **10** in 70% isolated yield. IR (Nujol): 1961 cm^{-1}, ν(CO). ^{31}P-{^1H} NMR (C_6D_6): δ −10.7 (s). ^1H NMR (500 MHz, C_6D_6): δ 6.42 (s, 2 H, *m*-CH), 2.40 (s, 6, *o*-CH_3), 1.89 (s, 3 H, *p*-CH_3) and 1.27 (pseudo t, $J_{HP_{app}}$ = 4 Hz, 18 H, PMe_3). ^1H NMR (300 MHz, [$^2H_6$]acetone, 203 K): δ 2.39 (br s, 3 H, *o*-CH_3) and 2.24 (br, s, 3 H, *o*-CH_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 248.2 (t, J_{CP} = 8.9, CO), 150.1 (s, *ipso*-C of C_6H_2), 137.6, 136.9 (s, *p*- and *o*-C of C_6H_2), 129.0 (s, *m*-C of C_6H_2), 20.8 (s, *p*-CH_3), 19.8 (s, *o*-CH_3) and 14.4 (t, J_{CP} = 12.7 Hz, PMe_3). ^{13}C-{^1H} NMR (75 MHz, [$^2H_6$]acetone, 213 K): δ 150.5 (s, *ipso*-C of C_6H_2), 139.9 (br s, *o*-C of C_6H_2), 138.5 (s, *p*-C of C_6H_2), 137.8 (br s, *o*-C of C_6H_2), 130.0 (br s, *m*-C of C_6H_2) and 20.7 (br, *o*-CH_3) (Found: C, 41.0; H, 6.3; N, 2.8. $C_{16}H_{29}Cl_2MoNOP_2$ requires C, 41.2; H, 6.0; N, 2.9%).

[$MoCl_2${N(mes)}($CNBu^t$)(PMe_3)$_2$] 11. Over a solution of [$MoCl_3${N(mes)}(dme)] (0.21 g, 0.5 mmol) in thf (30 cm^3) was added 2 equivalents of PMe_3 and the mixture allowed to react for 30 min at room temperature. The resulting solution was transferred to a Na–Hg amalgam (16 mg of Na, 1.5 g Hg) and, immediately, 1 equivalent of $CNBu^t$ (0.5 M solution in thf) added. The mixture was stirred for 90 min at room temperature. The pale violet solution was centrifuged and taken to dryness. The oily residue was washed with light petroleum and extracted with Et_2O. Crystallization at −20 °C yielded **11** as blue crystals (0.08 g, 31%). IR (Nujol): 2094 cm^{-1} ν(CN). ^{31}P-{^1H} NMR (C_6D_6): δ −8.8 (s). ^1H NMR (500 MHz, C_6D_6): δ 6.54 (s, 2 H, *m*-CH), 2.46 (br s, 6 H, *o*-CH_3), 1.96 (s, 3 H, *p*-CH_3), 1.40 (pseudo t, $J_{HP_{app}}$ = 3.8 Hz, 18 H, PMe_3), 1.22 (s, 9 H, CMe_3). ^1H NMR (300 MHz, [$^2H_6$]acetone, 203 K): δ 2.37 (s, 3 H, *o*-CH_3) and 2.24 (s, 3 H, *o*-CH_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ; 187.5 (br s, $CNBu^t$), 151.2 (s, *ipso*-C of C_6H_2), 137.1, 134.9 (s, *p*- and *o*-C of C_6H_2), 128.7 (s, *m*-C of C_6H_2), 57.6 (s, CMe_3), 30.1 (s, CMe_3). 20.9 (s, *p*-CH_3), 20.4 (s, *o*-CH_3) and 15.0 (t, J_{CP} = 11.7 Hz, PMe_3). ^{13}C-{^1H} NMR (75 MHz, [$^2H_6$]acetone, 203 K): δ 151.5 (s, *ipso*-C of C_6H_2), 138.9 (s, *p*-C of C_6H_2), 137.0 (s, *o*-C of C_6H_2), 136.3 (s, *o*-C of C_6H_2), 129.8 (s, *m*-C of C_6H_2), 129.3 (s, *m*-C of C_6H_2), 21.5 (s, *o*-CH_3) and 20.8 (s, *o*-CH_3) (Found: C, 45.3; H, 7.2; N, 5.4. $C_{20}H_{38}Cl_2MoN_2P_2$ requires C, 44.9; H, 7.1; N, 5.2%).

[$MoCl_2${N(mes)}(CNMe)(PMe_3)$_2$] 12. To a solution of complex **1** (0.14 g, 0.26 mmol) in thf (20 cm^3) was added an excess of CNMe (0.1 cm^3). The mixture was stirred at room temperature overnight. The volatiles were removed, the residue was extracted with Et_2O (50 cm^3), centrifuged and the solution then concentrated. Cooling to −20 °C gave blue crystals of **12**. IR (Nujol): 2153 cm^{-1}, ν(CN). ^{31}P-{^1H} NMR (C_6D_6): δ −7.9 (s). ^1H NMR (300 MHz, C_6D_6): δ 6.52 (s, 2 H, *m*-CH), 2.93 (s, 3 H, CNMe), 2.47 (br s, 6 H, *o*-CH_3), 1.95 (s, 3 H, *p*-CH_3) and 1.40 (pseudo t, $J_{HP_{app}}$ = 3.6 Hz, 18 H, PMe_3). ^{13}C-{^1H} NMR (125 MHz, C_6D_6): δ 191.7 (s, CNMe), 150.6 (s, *ipso*-C of C_6H_2), 137.2, 135.6 (s, *p*- and *o*-C of C_6H_2), 128.5 (s, *m*-C of C_6H_2), 31.9 (s, CN*Me*), 20.9 (s, *p*-CH_3), 19.8 (s, *o*-CH_3) and 15.2 (t, J_{CP} = 11.7 Hz, PMe_3) (Found: C, 41.4; H, 6.6; N, 6.2. $C_{17}H_{32}Cl_2MoN_2P_2$ requires C, 41.4; H, 6.5; N, 5.7%).

[$MoCl_2${N(mes)}(PhC≡CH)(PMe_3)$_2$] 13. To a solution of complex **1** (0.08 g, 0.15 mmol) in toluene (20 cm^3) was added PhC≡CH (0.1 cm^3). A change from blue to orange was observed after stirring at 85 °C for 5 h. The mixture was cooled to room temperature, volatiles were removed under vacuum and the

Table 2 Crystallographic data for complex **14**

Formula	$C_{29}H_{39}Cl_2MoNP_2 \cdot 0.5C_{14}H_{10}$
Crystal system	Monoclinic
M	719.5
Space group	$P2_1/c$
a/Å	19.310(0)
b/Å	9.163(1)
c/Å	20.526(6)
β/°	94.40(5)
U/Å^3	3621(1)
Z	4
D_c/g cm^{-3}	1.32
μ(Mo-Kα)/cm^{-1}	6.13
T/K	295
λ(Mo-Kα)/Å (graphite monochromated)	0.710 69
2θ Range/°	2–56
Unique reflections, $I \geqslant 2\sigma(I)$	3990
R^a	0.044
R'^b	0.046

^{a} $R = \Sigma||\Delta F|/\Sigma|F_o||$. ^{b} $R' = (\Sigma w \Delta^2 F/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

residue was extracted with Et_2O. Compound **13** was obtained as an orange solid by cooling at −20 °C (83%). ^{31}P-{^{1}H} NMR (C_6D_6, AB spin system): δ 9.0 (d, J_{AB} = 197 Hz) and 3.4 (d). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.41 (dd, $^3J_{HP}$ = 20.7, 5.3, 1 H, ≡CH), 7.62 (d, J_{HH} = 7.2, 2 H, *o*-CH, PhC≡), 7.16 (t, J_{HH} = 7.6, 2 H, *m*-CH, PhC≡), 7.04 (t, J_{HH} = 7.2, 1 H, *p*-CH, PhC≡), 6.42 (s, 2 H, *m*-CH), 1.91 (s, 3 H, *p*-CH_3), 1.40 (d, $^2J_{HP}$ = 9.7, 9 H, PMe_3) and 1.26 (d, $^2J_{HP}$ = 9.5 Hz, 9 H, PMe_3). ^{1}H NMR (300 MHz, [$^2H_6$]acetone, 218 K): δ 6.78 (s, 1 H, *m*-CH), 6.69 (s, 1 H, *m*-CH), 2.62 (s, 3 H, *o*-CH_3) and 1.92 (s, 3 H, *o*-CH_3). ^{13}C-{^{1}H} NMR (75 MHz, [$^2H_6$]acetone): δ 155.7 (br s, *ipso*-C of C_6H_2), 146.5 (t, J_{CP} = 4.4, *ipso*-C of C_6H_5), 144.5 (dd, J_{CP} = 14.2, 4, Ph*C*≡), 143.5 (s, *p*-CH), 134.6 (s, *m*-CH), 133.7 (dd, J_{CP} = 24, 4, ≡*C*H), 133.2, 132.7, 131.9 (s, Ph), 19.9 (s, *p*-CH_3), 19.0 (d, J_{CP} = 25, PMe_3) and 18.95 (d, J_{CP} = 27 Hz, PMe_3) (Found: C, 49.6; H, 6.4; N, 2.8. $C_{23}H_{35}Cl_2MoNP_2$ requires C, 49.8; H, 6.3; N, 2.5%).

[$MoCl_2${N(mes)}(PhC≡CPh)(PMe_3)$_2$]·0.5PhC≡CPh 14. To a mixture of complex **1** (0.13 g, 0.25 mmol) and PhC≡CPh (0.085 g, 0.5 mmol) was added thf (25 cm^3). The solution was heated at 70 °C overnight, after which time the ^{31}P-{^{1}H} NMR spectrum showed only *ca.* 15% conversion. The mixture was centrifuged and then evaporated to dryness. The orange oily residue was extracted with Et_2O and **14** was separated from **1** by fractional crystallization. Dark orange crystals of **14** were collected in low yield (10%). ^{31}P-{^{1}H} NMR (C_6D_6): δ −6.2 (s). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.57–7.43 (m, 5 H, C*H*, PhC≡CPh), 7.1–6.96 (m, 5 H, CH, PhC≡CPh), 6.47 (br s, 2 H, *m*-CH), 1.93 (s, 3 H, *p*-CH_3) and 1.30 (t, $J_{HP_{app}}$ = 4.5 Hz, 18 H, PMe_3). ^{1}H NMR (300 MHz, C_6D_6, 223 K): δ 6.36 (s, 1 H, *m*-CH), 6.30 (s, 1 H, *m*-CH), 2.92 (s, 3 H, *o*-CH_3) and 1.83 (s, 3 H, *o*-CH_3). ^{13}C-{^{1}H} NMR (75 MHz, C_6D_6, 298 K); δ 151.4 (s, *ipso*-C of C_6H_2), 143.8 (t, Ph*C*≡*C*Ph), 140.8, 137.9 (s, *p*- and *o*-C of C_6H_2), 131.6, 129.1 (s, *Ph*C≡C*Ph*), 128.6 (s, *m*-C of C_6H_2), 128.4, 127.0, 123.6 (s, *Ph*C≡C*Ph*), 20.8 (s, *p*-CH_3) and 14.9 (t, J_{CP} = 13 Hz, PMe_3) (Found: C, 55.2; H, 6.4; N, 1.3. $C_{29}H_{39}Cl_2MoNP_2$ requires C, 54.0; H, 6.2; N, 2.2%).

Crystallography

A summary of the fundamental crystal data for complex **14** is given in Table 2. A prismatic orange crystal was coated with an epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections with a 2θ range of 11–26°. The intensities were corrected for Lorentz-polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, Cl and P were taken from ref. 24. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[25] was applied at the end of the isotropic refinements.

A final refinement, based on F, was undertaken with unit weights and anisotropic thermal motion for the non-hydrogen atoms. Hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in ΔF *vs.* F_o or (sin θ)/λ was observed. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-RAY 80 System.[26]

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References

1 (*a*) W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; (*b*) W. A. Herrmann, *Polyhedron*, 1987, **6**, 1165; (*c*) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988; (*d*) F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339.
2 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
3 For example, D. S. Williams, M. H. Schofield, J. T. Anhaus and R. R. Schrock, *J. Am. Chem. Soc.*, 1990, **112**, 6728; L. K. Johnson, M. Frey, T. A. Ulibarri, S. C. Virgil, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 8167; G. Hogarth, R. L. Mallors and T. Norman, *J. Chem. Soc., Chem. Commun.*, 1993, 1721; U. Radius, J. Sundermeyer and H. Pritzkow, *Chem. Ber.*, 1994, **127**, 1827; M. L. H. Green, P. C. Konidaris, D. M. Michaelidou and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1995, 155; A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1995, 2111; P. W. Dyer, V. C. Gibson, J. A. K. Howard, B. Whittle and C. Wilson, *Polyhedron*, 1995, **14**, 103; P. W. Dyer, V. C. Gibson and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1995, 3313; A. J. Nielson, P. A. Hunt, C. E. F. Rickard and P. Schwerdtfeger, *J. Chem. Soc., Dalton Trans.*, 1997, 3311; J. E. McCusker, K. A. Abboud and L. McElwee-White, *Organometallics*, 1997, **16**, 3863; N. J. Bailey, J. A. Cooper, H. Gailus, M. L. H. Green, J. T. James and M. A. Leech, *J. Chem. Soc., Dalton Trans.*, 1997, 3579.
4 A. Galindo, F. Montilla, A. Pastor, E. Carmona, E. Gutiérrez-Puebla, A. Monge and C. Ruiz, *Inorg. Chem.*, 1997, **36**, 2379.
5 G. R. Clark, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.*, 1995, 1907.
6 (*a*) D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651; (*b*) C. Y. Chou, D. D. Devore, S. C. Huckett, E. A. Maatta, J. C. Huffman and F. Takusagawa, *Polyhedron*, 1986, **5**, 301; (*c*) L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 8130; (*d*) C. Redshaw, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *Polyhedron*, 1993, **12**, 2013; (*e*) M. L. H. Green, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1994, 2851.
7 E. Carmona, A. Galindo, L. Sanchez, A. J. Nielson and G. Wilkinson, *Polyhedron*, 1984, **3**, 347.
8 E. Carmona, A. Galindo, E. Gutiérrez-Puebla, A. Monge and C. Puerta, *Inorg. Chem.*, 1986, **25**, 3804.
9 P. S. Pregosin, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, eds. J. G. Verkade and L. D. Quin, VCH, Weinheim, 1987.
10 E. Carmona, A. Galindo, C. Guille-Photin and L. Sánchez, *Polyhedron*, 1988, **7**, 1767.
11 See, for example, (*a*) F.-M. Su, C. Cooper, S. J. Geib, A. L. Rheinfold and J. M. Mayer, *J. Am. Chem. Soc.*, 1986, **108**, 3545; (*b*) F.-M. Su, J. C. Bryan, S. Jang and J. M. Mayer, *Polyhedron*, 1989, **8**, 1261; (*c*) T. Aoshima, T. Tamura, Y. Mizobe and M. Hidai, *J. Organomet. Chem.*, 1992, **435**, 85; (*d*) H. Oshita, Y. Mizobe and M. Hidai, *Organometallics*, 1992, **11**, 4116; (*e*) A. J. Nielson and D. C. Ware, *Polyhedron*, 1990, **9**, 603; (*f*) J. de la Mata and R. H. Grubbs, *Organometallics*, 1996, **15**, 577.
12 G. R. Clark, A. J. Nielson, C. E. F. Rickard and D. C. Ware, *J. Chem. Soc., Dalton Trans.*, 1990, 1173.

13 G. R. Clark, A. J. Nielson, A. D. Rae and C. E. F. Rickard, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1069; *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1783.
14 K. A. Hall and J. M. Mayer, *J. Am. Chem. Soc.*, 1992, **114**, 10 402.
15 See, for example, G. R. Clark, M. W. Glenny, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1147 and refs. therein; A. J. Nielson, P. D. W. Boyd, G. R. Clark, P. A. Hunt, J. B. Metson, C. E. F. Rickard and P. Schwerdtfeger, *Polyhedron*, 1995, **14**, 1255.
16 J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **27**, 1.
17 G. R. Clark, A. J. Nielson, C. E. F. Rickard and D. C. Ware, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 343.
18 P. D. Lyne and D. M. P. Mingos, *J. Organomet. Chem.*, 1994, **394**, 213.
19 A. A. Danopoulos, C. Redshaw, A. Vaniche, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1993, **12**, 1061.
20 J. Sandstrom, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
21 See, for example, T. A. Coffey, G. D. Forster and G. Hogarth, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2337; J. M. Boncella, M. L. Cajigal, A. S. Gamble and K. A. Abboud, *Polyhedron*, 1996, **15**, 2071.
22 See, for example, H. E. Selnau and J. S. Merola, *Organometallics*, 1993, **12**, 1583; G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron*, 1988, **7**, 117.
23 R. C. B. Copley, P. W. Dyer, V. C. Gibson, J. A. K. Howard, E. L. Marshall, W. Wang and B. Whittle, *Polyhedron*, 1996, **15**, 3001; V. C. Gibson, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1607.
24 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–98.
25 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
26 J. M. Stewart, X-RAY 80 System, Computer Science Center, University of Maryland, College Park, MD, 1985.

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