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Steric *versus* electronic effects in six-co-ordinate d^0 *cis*-bis(imido) molybdenum complexes†

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The previously reported molybdenum(VI) *cis*-bis(imido) complex $[Mo(Nmes)_2Cl_2(PMe_3)_2]$ **2** (mes = $C_6H_2Me_3$-2,4,6) displayed NMR properties consistent with a *cis*-chloride,*trans*-PMe_3 configuration at the metal centre. LSDA density functional calculations on the *cis*-bis(imido) models $[Mo(NR)_2Cl_2(PR'_3)_2]$ (R = H, Me or Ph for R′ = H and R = H for R′ = Me) were performed in order to establish the reason why **2** does not adopt the expected *trans*-chloride,*cis*-PMe_3 geometry. The relative stabilities of three different isomers (*cis*-chloride,*trans*-PR'_3; *trans*-chloride,*cis*-PR'_3 and *cis*-chloride,*cis*-PR'_3) of such species were examined. The actual stereochemistry of **2** was properly reproduced by the calculations as the most stable isomer, only when no simplification of PMe_3 ligand by PH_3 was considered in the model. The use of PH_3 yields the *cis*-chloride,*trans*-PH_3 configuration as the most unstable isomer. The inversion in the trend of relative stabilities of the three isomers is discussed on the basis of steric considerations. The tendency of π-donor chloride ligands to occupy *cis* positions with respect to the d^0 bis(imido) moiety was overcome by the steric incompatibility of two *cis*-PMe_3 ligands. The molecular structure of $[Mo(Nmes)_2Cl_2(dme)]$ **1** was determined by an X-ray study and the reaction of **1** with PMe_3 to yield **2** revised.

The relative orientation of two multiple bonded π-donor ligands in octahedral transition metal complexes is known to be strongly governed by the electron configuration of the metal centre.[1,2] The consideration of metal–ligand π interactions and competition for d_π orbitals dictate the stereochemistry of such types of complexes.[3] The abundance of molybdenum(VI) dioxo compounds made possible, as early as 1979,[4] the generalisation of several rules to predict the precise arrangement of ligands. Several studies have analysed theoretically the disposal of d^0 dioxo transition metal compounds.[3a,5] These species are characterised by a distorted octahedral structure containing a *cis*-dioxo moiety in order to favour the π donation into the empty d_π set of orbitals. Analogously, on the basis of electronic effects, a *trans* geometry can be rationalised in d^2 dioxo compounds.[6]

On the basis of the bonding properties, an imido ligand is comparable to the oxo group. They are isoelectronic, acting as 4e π donor ligands. A large amount of experimental work has established well the preferential *cis* arrangement of a π-donor co-ligand in d^0 imido complexes.[7,8] In particular, the *cis*-bis(imido) moiety is a general feature for a d^0 six-co-ordinate complex,[1,8] that can be rationalised by the same arguments outlined above for dioxo compounds. Cundari and co-workers have explored profusely,[9] from a theoretical point of view, the area of transition metal imido complexes. Recently, we have reported MO calculations for d^0 imido vanadium complexes that show the preferential *cis* situation of π-donor chloride co-ligands.[10]

As a continuation of our own work,[11] we have revised the preparation of the complex $[Mo(Nmes)_2Cl_2(PMe_3)_2]$ (mes = $C_6H_2Me_3$-2,4,6), previously reported by Sundermeyer and co-workers,[12] and we describe here LSDA density functional calculations on the d^0 *cis*-bis(imido) models $[Mo(NR)_2Cl_2(PR'_3)_2]$ (R = H, Me or Ph for R′ = H and R = H for R′ = Me). The relative stabilities of three different isomers (*cis*-chloride, *trans*-PR'_3; *trans*-chloride,*cis*-PR'_3 and *cis*-chloride,*cis*-PR'_3) of such species were examined. The *cis*-chloride,*trans*-PMe_3 structure of $[Mo(Nmes)_2Cl_2(PMe_3)_2]$ is properly reproduced by the calculations, as the most stable isomer, only when the model contains the actual PMe_3 ligand. On the contrary, this isomer is the most unstable of the models in which the PMe_3 ligand is described as the simplest PH_3 group. The inversion in the trend of the relative stabilities of the three isomers is discussed on the basis of steric considerations. The tendency of π-donor chloride ligands to occupy *cis* positions with respect to the d^0 bis(imido) moiety was overcome by the steric incompatibility of two *cis*-PMe_3 ligands. On the other hand, the reaction of compound $[Mo(Nmes)_2Cl_2(dme)]$ **1** (dme = 1,2-dimethoxyethane) with PMe_3 to yield the above complex is revised. During the course of our studies we have obtained crystals of **1** suitable for an X-ray study, the results of which are also reported.

Results and discussion

Sundermeyer and co-workers reported[12] the synthesis and characterisation of the complex $[Mo(Nmes)_2Cl_2(PMe_3)_2]$ **2**, prepared by the reaction of $[Mo(Nmes)_2Cl_2(dme)]$ **1** with PMe_3. More recently,[13] we used **1** as the starting material for the synthesis of other imido compounds of molybdenum. One of our findings[14] was that the treatment of **1** with bidentate phosphine ligands gave complex reaction mixtures, in which reduction to molybdenum(V) and molybdenum(IV) species occurs through an imido transfer reaction. With these data we decided to revise the reaction of **1** with PMe_3 in order to establish if an imido-transfer reaction occurs. Following the synthetic methodology reported by Sundermeyer, compound $[Mo(Nmes)_2Cl_2(PMe_3)_2]$ was obtained in the reaction of **1** with two equivalents of PMe_3. NMR data, in agreement with those reported previously, are consistent with the *cis*-chloride,*trans*-PMe_3 structure.

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† Electronic supplementary information (ESI) available: computational data. See http://www.rsc.org/suppdata/dt/b0/b003998p/

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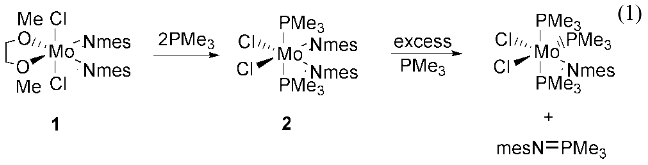
However, the situation changes if an excess of PMe_3 is employed in the reaction. If the reaction is analysed by $^{31}P-\{^1H\}$ NMR, at the initial stage, only one signal is observed for complex **2**. Gradually, this signal slightly decreases in intensity and two patterns of resonances appeared simultaneously. These signals correspond to the phosphinimine mesN=PMe_3 and to the complex $[Mo(Nmes)Cl_2(PMe_3)_3]$, previously reported by us,[11a] eqn. (1). This complex has an intense blue colour and probably



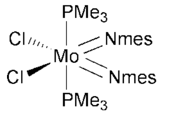
(1)

1 **2**

was also formed in small quantities in the Sundermeyer preparation of **2** (blue colour reported for the reaction mixture).

Molybdenum mediated imido transfer reactions were studied, some years ago, by Harlan and Holm[15] and Maatta and co-workers.[16] More recently, related imido-transfer reactions to phosphines have been reported for Group 6 imido derivatives.[17] In our case, the imido-transfer reaction is not complete at room temperature and, after 4 days, only 30% conversion into mesN=PMe_3 and $[Mo(Nmes)Cl_2(PMe_3)_3]$ was observed. Other bis(imido) derivatives behave similarly.[15] This slow process is different with respect to the fast oxo-transfer reaction observed[18] in the reaction of the related $[Mo(O)_2Cl_2(dme)]$ with PMe_3, for which the formation of $OPMe_3$ and $[Mo(O)Cl_2(PMe_3)_3]$ proceeds readily.

Complex **2** attracts our attention due to the *cis*-chloride, *trans*-PMe_3 structure (**I**). Other possible isomers containing the *cis*-imido moiety are displayed in **II** (*trans*-chloride,*cis*-PMe_3) and **III** (*cis*-chloride,*cis*-PMe_3). The *cis* configuration of two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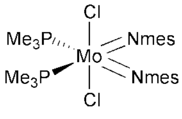
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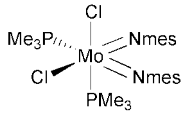
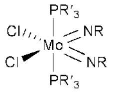
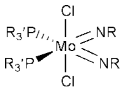
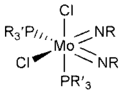

III

imido ligands in six-co-ordinate complexes allows all three d_π orbitals to accept π donation from these ligands. The three first empty MOs (a_1, a_2 and b_2) are the π* combinations of d_π orbitals and π-type imido orbitals.[4] Conversely, in a *trans* geometry the π-type orbitals have to share two d_π orbitals. Under the considerations mentioned above, the stabilisation of the *cis* geometry for d^0 complexes can easily be rationalised. The preferential orientation of an additional π-donor co-ligand in *cis*-bis(imido) complexes can qualitatively be explained on the basis of the same reasons. This co-ligand will occupy a site where it will not be competing for the available d_π orbitals. Consequently, the two π-donor chlorides would prefer a *cis* position with respect to the multiple bonded ligands. In agreement with this statement, a CSD[19] search showed that the *cis*-imido, *trans*-chloride configuration (structure of type **II**) is a general attribute of d^0 six-co-ordinate Group 6 bis(imido) complexes containing two halide ligands. A possible exception is the complex[20] $[W(NC_6H_3{}^iPr_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)Cl_2(OPMe_3)(PMe_3)]$, that shows a structure of type **III**, but contains one imido and one acylimido ligand.

In order to explain the structure of type **I** observed for complex **2** we have performed MO studies of the DFT type on the models $[Mo(NR)_2Cl_2(PR'_3)_2]$ (R = H, Me or Ph for R′ = H and R = H for R′ = Me). Initially, with the aim to speed the calculations, the analysis was undertaken using a model in which the trimethylphosphine ligands were replaced by PH_3 groups. We designed a series of models in which the complexity of the imido ligand was gradually increased (R = H, Me or Ph).

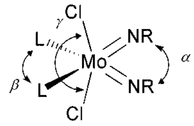
Table 1 Relative energies (kcal mol^{-1}) of $[Mo(NR)_2Cl_2(PR'_3)_2]$ (R = H, Me or Ph for R′ = H and R = H for R′ = Me) isomers **I**–**III**

R	R′	 **I**	 **II**	 **III**
H	H	2.4	0.0	1.6
Me	H	1.6	0.0	0.7
Ph	H	1.1	0.0	−2.5
H	Me	0.0	11.0	8.1

Three different arrangements were considered for these model compounds, corresponding to the isomers **I**–**III** of the parent compound **2**. These models were fully optimised at C_1 symmetry and their relative energies are reported in Table 1. The calculated bond and angle parameters are available as Supplementary Information.

Inspection of Table 1 shows that when PH_3 ligands are used in the models the energy differences between the three isomers are small, whatever the imido substituent is. For R = H and Me the preferred isomer is of type **II**; as we stated above, this is the structure observed for six-co-ordinate Group 6 d^0-bis(imido-halide) complexes. For R = Ph the most stable form is of type **III**, observed in $[W(NC_6H_3{}^iPr_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)Cl_2(OPMe_3)(PMe_3)]$.[20] However, our results do not fit the experimentally deduced structure of **2**, which is precisely the most unstable isomer (**I**).

It is known that the main distortion from the octahedral geometry in these complexes is the opening of the bond angle between the two *cis*-imido ligands (α angle in **IV**).[1,8] This bond



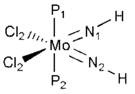
IV

angle opening is accompanied by a closure from 180° of the axial ligands (γ angle) and from 90° of the equatorial ones (β angle). These distortions would lead to an acute β angle (lower than 90°) and in this case some congestion takes place between L ligands (**IV**). Remarkably, CSD searches show that the β angle range in these bis(imido) derivatives goes from *ca.* 67 to 84°, while the lowest angle reported for two *cis*-PMe_3 ligands is 86.6° in a six-co-ordinate transition metal complex.[21] Therefore, some kind of steric repulsion can qualitatively be anticipated for a *cis* disposition of the PMe_3 ligands in **2**. The importance of steric factors in closely related dioxomolybdenum systems has been pointed out recently by Lledos, Jean and co-workers[22] in an integrated MO-MM theoretical study. Furthermore, Parkin and Friesner have shown quite recently that the use of PH_3 as a substitute of PMe_3 ligands gave a poor description in theoretical calculations in $[MX_2(PMe_3)_4]$ (M = Mo or W) systems.[23]

With the above considerations in mind, we decided to increase the complexity of the model by considering the use of PMe_3 ligands for the simplest imido ligand (R = H) and geometry optimisation of the three isomers **I**–**III** was performed at C_1 symmetry. Concerning the energetics of the system (see Table 1), not only the relative energy differences between the three isomers are larger than in the case of PH_3 models, but the trend has dramatically changed. In fact, isomer **I** is the most stable, which is in accordance with the experimentally observed structure of **2**. The final optimised geometry of this isomer is depicted in Fig. 1 and selected bond and angle parameters have been included in Table 2.

The origin of the larger stability of isomer **I** with respect to **II** can be rationalised in terms of the steric congestion caused by

Table 2 Selected bond lengths (Å) and angles (°) obtained for the *cis*-chloride,*trans*-PMe_3-$[Mo(NH)_2Cl_2(PMe_3)_2]$ model



Isomer **I**

Mo–N1	1.778	Mo–Cl2	2.511
Mo–N2	1.786	Mo–P1	2.506
Mo–Cl1	2.566	Mo–P2	2.506
N1–Mo–N2	104.9	Cl1–Mo–Cl2	82.4
N1–Mo–Cl1	169.3	Cl1–Mo–P1	76.8
N1–Mo–Cl2	87.0	Cl1–Mo–P2	76.8
N1–Mo–P1	101.7	Cl2–Mo–P1	81.8
N1–Mo–P2	101.7	Cl2–Mo–P2	81.8
N2–Mo–Cl1	85.7	P1–Mo–P2	150.5
N2–Mo–Cl2	168.1	Mo–N1–H1	128.6
N2–Mo–P1	95.5	Mo–N2–H2	127.5
N2–Mo–P2	95.5		

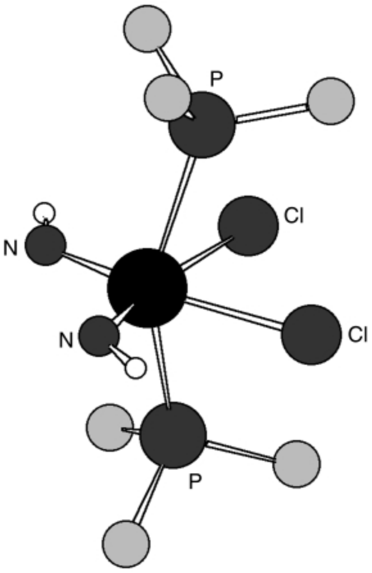


Fig. 1 Final optimised geometry of the *cis*-chloride,*trans*-PMe_3-$[Mo(NH)_2Cl_2(PMe_3)_2]$ model (hydrogen atoms of Me groups are not shown).

two *cis* PMe_3 ligands with an acute P–Mo–P bond angle (computed value: 81.7°). Also the destabilisation of isomer **III** originates in the existence of important steric interactions due to acute Cl–Mo–P angles (for example, computed values of 73.7 and 75.6°, in comparison with the lowest Cl–Mo–P angle of 75.3° found[24] in a mononuclear molybdenum six-co-ordinate complex).

Group 6 d^2-bis(imido) complexes containing phosphine ligands are known to have co-ordination numbers four and five.[12,25] Likewise, examples of analogous d^0 systems are the four-co-ordinate complex[26] $[W(NC_6H_3{}^iPr_2\text{-}2,6)_3(PMe_3)]$, the five-co-ordinate $[MoMe_2(NC_6H_3{}^iPr_2\text{-}2,6)_2(PMe_2Ph)]$[27] and the above mentioned six-co-ordinate $[W(NC_6H_3{}^iPr_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)Cl_2(OPMe_3)(PMe_3)]$.[20] However, to our knowledge, no structurally characterised example has been reported of six-co-ordinate bis(imido-phosphine) d^0 derivatives. Consequently, we have not performed precise comparisons with experimental structural data. The calculated parameters are reasonable and compare well with other data found in related d^0 molybdenum imido complexes. Nevertheless, although no six-co-ordinate bis(imido-phosphine) d^0 derivatives are structurally characterised, related bis[hydrazido(2−)] complexes $[Mo(NNPh_2)_2Cl_2(PR_3)_2]$ ($R = Me$[28] or Ph[29]) have been reported. They have the *cis*-chloride,*trans*-PR_3 geometry of type **I**. The computed Mo–Cl and Mo–P bond distances and N–Mo–N and Cl–Mo–Cl bond angles for **I** agree well with the experimental values found in the hydrazido derivatives. What seems abnormal is the low computed value found for the imido Mo–N–H angle. However, this value was checked for the PH_3 models and the replacement of the imido substituent from H to Ph groups produces a substantial improvement in the description of the Mo–N–R angle. This result suggests that such a simple model could not be suitable. Actually, when the NH imido ligand is replaced by NPh, a relaxation of the Mo–N bond and a concomitant alleviation of the *trans* influence is observed, leading to a better agreement with the experimental values. This trend was also evident in a related imidovanadium system.[10]

Table 3 Selected bond lengths (Å) and angles (°) for $[Mo(Nmes)_2Cl_2(dme)]$ **1**

Mo–N(2)	1.744(4)	Mo–N(1)	1.747(5)
Mo–O(2)	2.351(4)	Mo–O(5)	2.385(4)
Mo–Cl(2)	2.404(2)	Mo–Cl(1)	2.420(2)
N(2)–C(16)	1.405(6)	N(1)–C(7)	1.402(8)
N(2)–Mo–N(1)	105.2(2)	N(2)–Mo–O(2)	92.8(2)
N(1)–Mo–O(2)	162.0(2)	N(2)–Mo–O(5)	162.4(2)
N(1)–Mo–O(5)	92.3(2)	O(2)–Mo–O(5)	69.66(12)
N(2)–Mo–Cl(2)	96.4(2)	N(1)–Mo–Cl(2)	96.2(2)
O(2)–Mo–Cl(2)	81.02(11)	O(5)–Mo–Cl(2)	80.10(11)
N(2)–Mo–Cl(1)	96.8(2)	N(1)–Mo–Cl(1)	96.9(2)
O(2)–Mo–Cl(1)	81.17(11)	O(5)–Mo–Cl(1)	82.17(11)
Cl(2)–Mo–Cl(1)	158.31(5)	C(16)–N(2)–Mo	164.7(4)
C(7)–N(1)–Mo	163.3(4)		

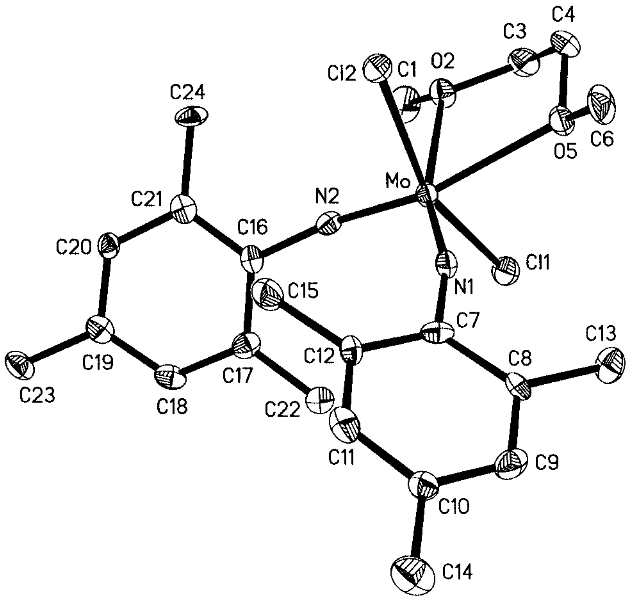


Fig. 2 Molecular structure of $[Mo(Nmes)_2Cl_2(dme)]$ **1**.

Molecular structure of complex 1

While this work was in progress, crystals of $[Mo(Nmes)_2Cl_2(dme)]$ **1** suitable for an X-ray study were obtained. The molecular geometry of **1** is represented in Fig. 2. Selected bond length and angle values are collected in Table 3. Two independent molecules are contained in the asymmetric unit, only one of which is shown. The complex has a distorted octahedral structure with the expected *cis* distribution of the imido ligands and the two chloro atoms *cis* with respect to these groups. Both imido groups are almost linear with Mo–N–C angles from 163.3(4) to 164.7(4)°, in the range expected for such linear linkages. The angle between these ligands (N(1)–Mo–N(2), 105.2(2)°) compares well with the mean value found in octahedral d^0-bis(imido) complexes of molybdenum and tungsten (104.6(4)°, CSD search). The Mo–N distances measure

1.747(5) and 1.744(4) Å. The structure is not significantly different from those found in related bis(imido) complexes of molybdenum(VI) containing dme reported by Gibson,[30] Sundermeyer[31] and co-workers and needs no additional comments.

Conclusion

Our calculations have shown that in six-co-ordinate d^0 bis(imido) molybdenum complexes the steric properties of the co-ligands (in the present case PMe_3) govern a specific disposition of ligands, even when this configuration is the most unstable from an electronic point of view. In other related transition metal complexes with largely distorted six-co-ordinate geometries special attention must be devoted to steric factors because they can induce a particular geometry. The use of PH_3 as a model ligand in these cases gave poor results in theoretical calculations.

Experimental

All preparations and other operations were carried out under a dry oxygen-free nitrogen atmosphere following conventional Schlenk techniques. Solvents were dried and degassed before use. Infrared spectra were recorded on Perkin-Elmer Model 883 spectrophotometer, ^1H, ^{13}C and ^{31}P NMR spectra on Bruker AMX-300 and AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. The light petroleum used had bp 40–60 °C. Complex $[Mo(Nmes)_2Cl_2(dme)]$ was prepared according to the literature.[12,13]

Computational

The electronic structure and geometries of the models $[Mo(NR)_2Cl_2(PR'_3)_2]$ (R = H, Me or Ph for R′ = H and R = H for R′ = Me) were computed within the density functional theory under no symmetry constraint. In particular, the Slater exchange[32] and the Vosko–Wilk–Nusair correlation functional[33] were employed (LSDA in the Gaussian 98 notation). The effective core potential (ECP) approximation of Stevens *et al.* was used.[34] For a Mo atom the electrons described by the ECP were those of 1s, 2s and 2p shells, while for 3s, 3p and valence electrons a basis set of sp type was used with the contraction (8s8p6d)/[4s4p3d]. For N, P, Cl and C the inner electrons were also described through an ECP, and valence electrons were accounted for using a (4s4p)/[2s2p] basis set. This basis set was enlarged with d polarisation functions on N, P and Cl atoms; d polarisation functions were also included in C atoms for R = Me, R′ = H and R = H and R′ = Me. For H atoms, the standard (4s)/[2s] DZ basis set was used. The calculations were performed using the Gaussian 98 package.[35] For the most stable isomers of the models $[Mo(NH)_2Cl_2(PR'_3)_2]$ (R′ = H or Me) frequency analyses were carried out and no imaginary frequencies were found.

Reactivity of complex 1 towards PMe_3

An NMR tube was charged with a solution of $[Mo(Nmes)_2Cl_2(dme)]$ **1** (0.054 g, *ca.* 0.10 mmol) in C_6D_6 (0.5 ml). An excess of PMe_3 (0.04 ml) was added and the reaction monitored periodically by $^{31}P\text{-}\{^1H\}$ NMR at 25 °C. At the initial stage only one signal was observed for the complex[12] $[Mo(Nmes)_2Cl_2(PMe_3)_2]$. After 4 days, at room temperature, only 30% conversion into mesN=PMe$_3$ and $[Mo(Nmes)Cl_2(PMe_3)_3]$[11a] (AX_2 spin system, δ_A 2.5, δ_X 9.3, $^2J_{AX} = 17$ Hz) was achieved. Selected spectroscopic data for mesN=PMe$_3$ were: $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6) δ 31.7 (s); ^1H NMR (300 MHz, C_6D_6) δ 6.71 (s, 2, CH, Ph), 2.18 (s, 3, *p*-CH_3), 2.10 (s, 6, *o*-CH_3) and 0.92 (d, $J_{HP} = 12.9$ Hz, PMe_3).

Table 4 Crystallographic data for complex **1**

Formula	$C_{22}H_{32}Cl_2MoN_2O_2$
M	523.34
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/Å	15.5279(11)
b/Å	14.2292(10)
c/Å	21.811(2)
U/Å^3	4819.1(6)
Z	8
D_c/g cm^{-3}	1.443
μ(Mo-Kα)/mm^{-1}	0.786
T/K	153(2)
λ(Mo-Kα)/Å	0.71073
Unique reflections, $I \geq 2\sigma(I)$	5116
R	0.0292
R'	0.0606

Crystallography

A summary of the fundamental crystal data is given in Table 4. A red crystal was mounted on a Brucker-Siemens Smart CCD detector diffractometer equipped with a low temperature device. The unit cell dimensions were determined by a least squares refinement. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and Cl were taken from ref. 36. The structure was solved by the MULTAN and Fourier methods. Full matrix least-squares refinement was carried out. Hydrogen atoms were included in their calculated positions. Refinement on F^2 for all reflections. Weighted R factor (R') based on F^2, conventional R on F. Most of the calculations were carried out with SMART[37] software for data collection and reduction and SHELXTL[37] for structure solution and refinements.

CCDC reference number 186/2004.

See http://www.rsc.org/suppdata/dt/b0/b003998p/ for crystallographic files in .cif format.

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