ELSEVIER

Journal of Organometallic Chemistry 564 (1998) 85–92

Journal of Organometallic Chemistry

Synthesis, structure and reactivity of molybdenum imido and oxo complexes. X-ray structure of $MoCl_3(NAr)L_2$ (Ar = 2,6-diisopropyl phenyl; L = *N*-2',6'-diisopropyl phenyl-2,5-dimethyl benzamide)[1]

F. Javier de la Mata [a,*], Joseph W. Ziller [b]

[a] *Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain*
[b] *Department of Chemistry, University of California, Irvine, California 92717, USA*

Received 10 February 1998; received in revised form 24 April 1998

Abstract

The reaction of $MoCl_4(O)$ with ArNCO (Ar = 2,6-$^iPr_2Ph$) afforded a series of paramagnetic oxo and imido Mo(V) complexes depending on the nature of the solvent used in each case. An X-ray study of one of this complexes, $MoCl_3(NAr)L_2$ (L = *N*-2',6'-diisopropyl phenyl-2,5-dimethyl benzamide) (**3**) (orthorhombic, $P2_12_12_1$, $a = 10.8194(8)$, $b = 23.528(2)$, $c = 23.914(2)$ Å, $V = 6087.4(9)$ Å^3, $Z = 4$) supports a pseudo-octahedral structure with the imido group occupying one of the axial positions. Reduction of Mo(VI) and Mo(V) oxo and imido complexes in the presence of three equivalents of $P(OMe)_3$ yields complexes $MoCl_2(E)[P(OMe)_3]_3$ (E = O (**5**), NAr (**6**)). Spectroscopic data of **5** and **6** show a pseudo-octahedral structure with the oxo or imido ligand occupying one of the axial positions and the three phosphite ligands placed in the equatorial plane. Complexes **5** and **6** react with 3,3-diphenylcyclopropene leading to olefin complexes which are thermally unstable and decompose at room temperature affording 1,1,6,6 tetraphenyl hexatriene, presumably via intermediate molybdenum vinyl alkylidenes. © 1998 Elsevier Science S.A. Ltd. All rights reserved.

Keywords: Alkylidene; Cyclopropene; Imido; Molybdenum; Oxo; Tungsten

---

1. Introduction

Tungsten, molybdenum and rhenium are the three metals that show the greatest activity for metathesis of ordinary olefins in classical metathesis systems [1]. In the past several years well-characterised tungsten and molybdenum alkylidene complexes have been prepared and some of the most versatile and controllable catalyst are those of the type M(CHR')(NAr)$(OR)_2$ (M = Mo, W; Ar = 2,6-diisopropyl phenyl; OR = various alkoxides) [2].

Recently a number of tungsten imido [3] and oxo [4] vinyl alkylidene complexes of type $W({=}CH{-}CH{=}CPh_2)(E)(OR)_2(PX_3)$ (E = NAr, O; $PX_3{=}P(OMe)_3$, $PMePh_2$; R = $C(CH_3)(CF_3)_2$) have been prepared via the reaction of 3,3 diphenylcyclopropene with appropriate tungsten(IV) precursors and subsequent thermal ring-opening of the cyclopropene ligand. The tungsten(IV) precursors are complexes of type $WCl_2(E)(PX_3)_3$ (E = O [5], NAr [6], $PX_3 = P(OMe)_3$, $PMePh_2$) and their selection for this study was based upon their ability to form a variety of π-acceptor complexes of the form $WCl_2(L)(E)(PX_3)_2$ (L = π-acceptor ligand) via substitution of one phosphine or phosphite ligand [7]. It was thought that molybdenum vinyl alkylidene complexes of type $Mo({=}CH{-}CH{=}CPh_2)(OR)_2(E)(PX_3)$ (E = NAr, O; $PX_3{=}P(OMe)_3$, $PMePh_2$) should be accessible by an analogous approach. In general, molybdenum catalyst might have

---

* Corresponding author. Tel.: +34 1 8854654; fax: +34 1 8854683; e-mail: jmata@inorg.alcala.es

[1] Dedicated to Professor P. Royo on the occasion of his 60th birthday.

PII S0022-328X(98)00626-3

certain advantages such as a greater tolerance of functional groups. However, possible disadvantages could be a greater tendency to be reduced and a lower activity.

In this paper we described the synthesis of oxo and imido molybdenum complexes of type $MoCl_2(E)[P(OMe)_3]_3$ (E = O, NAr; Ar = 2,6-^{i}Pr$_2$–Ph) and their reactivity with 3,3 diphenylcyclopropene.

2. Results and discussion

2.1. Synthesis and characterization of starting materials

Our first choices as precursors for the synthesis of $MoCl_2(E)[P(OMe)_3]_3$ (E = O, NAr; Ar = 2,6-^{i}Pr$_2$–Ph), were $MoCl_4(O)$ and $MoCl_4(NAr)$, given the good results observed in the analogous chemistry of tungsten [3,5](b). However, $MoCl_4(NAr)$ was not know at the outset of this work. Schrock and coworkers reported [2](c) that it is not possible to prepare this compound using a synthetic protocol similar to that described for $MoCl_4(Ntol)(THF)$ (prepared from $MoCl_4$ and tolyl azide [8]) or by reaction of $MoCl_4(O)$ and ArNCO in octane (analogous to the synthesis of $WCl_4(NAr)$ from $WCl_4(O)$ [9]).

Nevertheless, we decided to re-examine this last reaction and carried it out in different solvents. In all cases, paramagnetic yellow solids with different compositions depending on the solvent used in the reaction were obtained—the composition of these new compounds was proposed on the basis of their reactivity (see next section in this paper).

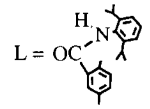
The reaction of $MoCl_4(O)$ and ArNCO in refluxing benzene, toluene and octane over 2–3 days gave '$MoCl_3(O)$' (**1**). We believe that this result is a consequence of the great tendency of molybdenum to be reduced and the necessity of higher reaction temperatures in the case of benzene and toluene. In the case of octane, the same result was obtained—despite the fact that the temperature could be high enough—presumably due to solubility problems.

Other solvents were then examined, such as chlorobenzene and p-xylene, where the solubility of $MoCl_4(O)$ and the boiling temperature are high enough. In chlorobenzene a mixture of '$MoCl_3(O)$' and '$MoCl_3(NAr)$' (**2**) was obtained. The amount of **2** increased slowly with increasing reaction times but could not be driven to complexion (Eq. 1).

$$MoCl_4(O) + ArNCO \xrightarrow[\text{reflux}]{\text{chlorobenzene}} \underset{\mathbf{1}}{\text{"}MoCl_3(O)\text{"}} + \underset{\mathbf{2}}{\text{"}MoCl_3(NAr)\text{"}}$$

The reaction in p-xylene is particularly interesting due to the nature of the product obtained. $MoCl_4(O)$ reacted with an excess of ArNCO in refluxing p-xylene to give $MoCl_3(NAr)(L_2)$ (**3**) in a 40–50% yield (Eq. 2).

$$MoCl_4(O) + 3\,ArNCO \xrightarrow[\text{reflux} \atop -CO_2]{\text{p-Xylene}} \underset{\mathbf{3}}{MoCl_3(NAr)L_2}$$



In this particular case the imido molybdenum complex was obtained without oxo impurities, perhaps due to stabilisation of the final product by the new ligand, N-2',6'-diisopropyl phenyl-2,5-dimethyl benzamide. ArNCO and p-xylene do not react in refluxing p-xylene by themselves, which means that the formation of this new ligand is likely due to electrophilic attack of the isocyanate to a p-xylene molecule in a metal-catalysed reaction.

Complex **3** reacted with THF giving paramagnetic species (presumably $MoCl_3(NAr)(THF)_2$) and liberating two molecules of the benzamide ligand that could now be characterised by NMR spectroscopy [10].

An X-ray study of complex **3** confirmed the nature proposed for this complex and provided information about the structure of some of these paramagnetic molybdenum(V) complexes. This complex has a pseudo-octahedral structure around the Mo atom with the imido group occupying one of the axial positions and the three chloride ligands placed in the equatorial plane. The remaining axial and equatorial positions are occupied by the benzamide ligands (Fig. 1).Selected bond distances and angles are listed in Table 1.

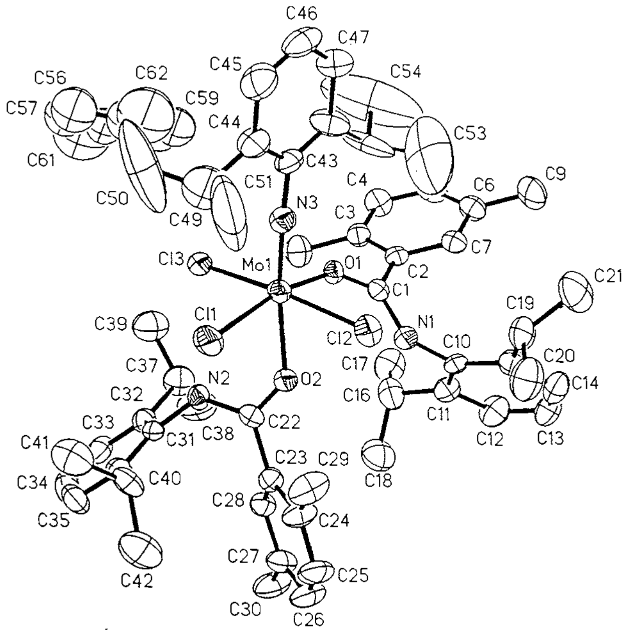
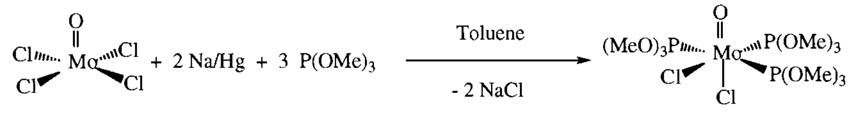


Fig. 1.

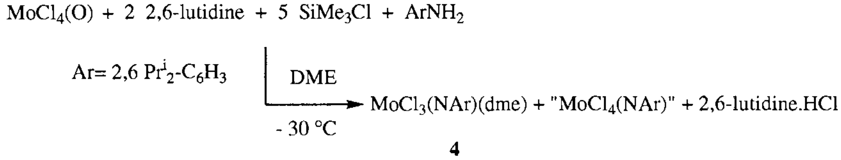


5

The distances Mo–N(3) (1.731(7) Å), Mo–Cl(1), Mo–Cl(2) and Mo–Cl(3) (2.367(2), 2.408(2) and 2.413(2) Å, respectively) are in the expected range. The distances Mo–O(1) and Mo–O(2) (2.102(5) and 2.239(5) Å) are shorter than the Mo–O distances found for the coordination of an oxygen-containing ligand to a molybdenum centre [11] and in particular the Mo–O(1) bond length is considerably shorter. The different length of both Mo–O distances could be due to the strong *trans* influence of the imido ligand over the Mo–O(2) bond [12].

Despite the possible use of this new imido molybdenum(V) complex (**3**) as precursor for the synthesis of imido complexes of molybdenum(IV), it was decided to explore other ways to synthesize the desired product $MoCl_4(NAr)$. Schrock and co-workers have shown that $MoCl_2(NAr)_2(dme)$ can be prepared from $MoCl_2O_2$ and $ArNH_2$ in high yield [2](c). We tried a similar reaction for the synthesis of $MoCl_4(NAr)$ from $MoCl_4(O)$.

The addition of two equivalents of 2,6-lutidine, five equivalents of Me_3SiCl and one equivalent of $ArNH_2$ to a solution of $MoCl_4(O)$ in dimethoxyethane cooled to − 30°C, leads the formation of a orange–red solution from which yellow crystalline, paramagnetic $MoCl_3(NAr)(dme)$ (**4**) could be isolated. It was identified on the basis of its reactivity (see next section) and its elemental analysis (see experimental part). Complex **4** reacted with THF, forming a new organometallic species (presumably $MoCl_3(NAr)(THF)_2$) and liberating dimethoxyethane which can be observed by ^1H-NMR. Complex **4** was not the only product obtained in this reaction and the presence of a more soluble diamagnetic complex, probably $MoCl_4(NAr)$ [13], that decreased the yield of **4**, was also noticed (Eq. 3).



$$MoCl_4(O) + 2\ 2,6\text{-lutidine} + 5\ SiMe_3Cl + ArNH_2 \xrightarrow[-30\ ^\circ C]{DME} \underset{\mathbf{4}}{MoCl_3(NAr)(dme)} + \text{"}MoCl_4(NAr)\text{"} + 2,6\text{-lutidine.HCl}$$

$Ar = 2,6\ Pr^i_2\text{-}C_6H_3$

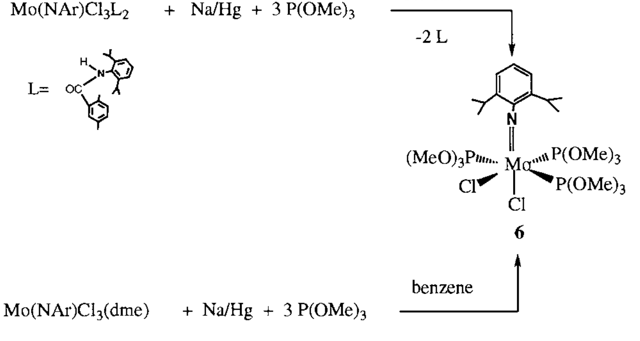
We have tried to isolate this Mo(VI) complex from the reaction mixture several times but significant amounts of complex **4** were always found, that we have not been able to remove so far.

2.2. Synthesis of complexes of type $MoCl_2(E)[P(OMe)_3]_3$ (E = O, NAr)

Complex $MoCl_2(O)[P(OMe)_3]_3$ (**5**) was prepared by direct reduction of $MoCl_4(O)$ with two equivalents of Na amalgam in the presence of trimethyl phosphite [14] (Eq. 4).

Complex **5** is a diamagnetic green solid, soluble in aromatic hydrocarbons, tetrahydrofuran and chlorinated solvents. The ^1H and ^{13}C-NMR spectra in deuterated benzene show a triplet and a doublet that correspond, respectively, to two mutually *trans* phosphite ligands and one phosphite ligand *trans* to a chloride ligand. The ^{31}P-NMR spectrum shows coupling between the unequivalent phosphite ligands that gives rise to two resonances that appear as a doublet and a triplet in a 2:1 ratio. These data are similar to those of analogous complexes such as $WCl_2(O)[P(OMe)_3]_3$ [5](a) and are consistent with the expected meridional arrangement of the phosphite ligands [3].

The corresponding imido complex $MoCl_2(NAr)[P(OMe)_3]_3$ (**6**) could be prepared by reduction of the mixture $MoCl_3(NAr)(dme)$ and '$MoCl_4(NAr)$' with Na/Hg in the presence of $P(OMe)_3$. Since the exact ratio of these complexes was unknown, it was not possible to calculate which is the stochiometric amount of sodium that was necessary for the reduction which could decrease the overall yield. Nevertheless, using 1.5 equivalents of a 6% Na amalgam it was possible to obtain **6** as a yellow solid in ≈ 60% yield. There are other ways to synthesize **6** (Eq. 5) but final yields were always lower than using the synthetic route described above [15].



The ^{1}H-NMR spectrum of **6** presents resonances at $\delta = 6.99$ (m, $H_{aromatic}$), $\delta = 4.62$ (sp, 2, $J_{H-H} = 6.6$ Hz, $C\underline{H}$-CMe_2) and $\delta = 1.32$ (d, 12, $J_{H-H} = 6.6$ Hz, CH-$C\underline{Me_2}$) corresponding to the protons of the imido group and resonances at $\delta = 3.69$ (t, 18, $J_{PH} = 5.1$ Hz) and $\delta = 3.59$ (d, 9, $J_{PH} = 10.5$ Hz) corresponding to the three phosphite ligands. These data are consistent with the expected meridional arrangement of the phosphite ligands. Accordingly, we propose for complexes **5** and **6** the same pseudo-octahedral structure found in analogous tungsten complexes $WCl_2(E)[P(OMe)_3]_3$ [3,5] (E = O, NAr).

2.3. *Reactivity of $MoCl_2(E)[P(OMe)_3]_3$ with 3,3-diphenylcyclopropene*

Complexes of type $MoCl_2(E)[P(OMe)_3]_3$ (E = O (**5**), E = NAr (**6**)) react with one equivalent of 3,3-diphenylcyclopropene to give η^2-cyclopropene derivatives similar to those obtained for the analogous tungsten(IV) complexes.

Reaction of **5** and 3,3-diphenylcyclopropene gave rise to the formation of Mo(η^2-diphenylcyclopropene)$Cl_2(O)[P(OMe)_3]_2$ (**7**). Spectroscopic data of **7** (See experimental part) are analogous to those of W(η^2-diphenylcyclopropene)$Cl_2(O)[P(OMe)_3]_2$ [4]. These data suggest a distorted octahedral structure for **7** with the olefin carbons occupying one position in the equatorial plane and the oxygen atom occupying one of the axial positions *cis* to the cyclopropene ligand. The two phosphite groups have to be mutually *trans* and the two chloride ligands occupy the remaining equatorial and axial positions. Complex **7** is thermally unstable, has a half-live time of 3 h at room temperature, and decomposes leading to the dimerization product of the diphenylcyclopropene ($Ph_2C{=}CH{-}CH{=}CH{-}CH{=}CPH_2$) and recovering some of the starting material **5** (See Scheme 2). Recently it has been shown [4] that the same result is obtained with analogous tungsten complexes and the presence of carbene species in the dimerization process was demonstrated. In the tungsten case, it was also probed that the change of $P(OMe)_3$ by phosphines such as PMe_2Ph or $PMePh_2$ gives rise to more stable η^2-cyclopropene complexes. We infer similar behaviour for analogous phosphine molybdenum complexes, which are currently under investigation.

Complex **6** also reacts with 3,3-diphenylcyclopropene at room temperature to yield Mo(η^2-diphenylcyclopropene)$Cl_2(NAr)[P(OMe)_3]$ (**8**), which presents again a low thermal stability and decomposes over 40°C, generating once again the dimerization product of 3,3-diphenylcyclopropene, $Ph_2C{=}CH{-}CH{=}CH{-}CH{=}CPh_2$ (Scheme 1).

Table 1
Selected bond lengths and angles for **3**

Bond lengths (Å)			
Mo(1)–Cl(1)	2.367(2)	Mo(1)–Cl(2)	2.408(2)
Mo(1)–Cl(3)	2.413(2)	Mo(1)–O(1)	2.102(5)
Mo(1)–O(2)	2.239(5)	Mo(1)–N(3)	1.731(7)
O(1)–C(1)	1.258(9)	O(2)–C(22)	1.253(9)
N(1)–C(1)	1.311(10)	N(1)–C(10)	1.461(10)
N(2)–C(22)	1.327(10)	N(2)–C(31)	1.443(10)
N(3)–C(43)	1.390(10)		
Bond angles (°)			
Cl(1)–Mo(1)–Cl(2)	92.7(1)	Cl(1)–Mo(1)–Cl(3)	91.1(1)
Cl(2)–Mo(1)–Cl(3)	170.5(1)	Cl(1)–Mo(1)–O(1)	162.7(2)
Cl(2)–Mo(1)–O(1)	89.7(1)	Cl(3)–Mo(1)–O(1)	84.2(1)
Cl(1)–Mo(1)–O(2)	83.6(1)	Cl(2)–Mo(1)–O(2)	82.5(1)
Cl(3)–Mo(1)–O(2)	89.2(1)	O(1)–Mo(1)–O(2)	79.8(2)
Cl(1)–Mo(1)–N(3)	100.7(2)	Cl(2)–Mo(1)–N(3)	93.1(2)
Cl(3)–Mo(1)–N(3)	94.9(2)	O(1)–Mo(1)–N(3)	96.2(3)
O(2)–Mo(1)–N(3)	174.0(2)		

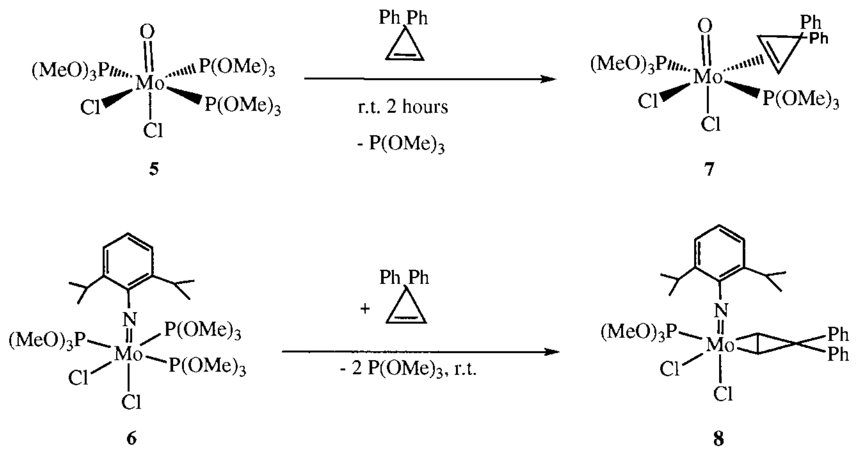
3. Conclusions

The reaction of $MoCl_4(O)$ with ArNCO afforded paramagnetic oxo and amido Mo(V) complexes. The X-ray structure of one of these complexes, $MoCl_3(NAr)L_2$ (L = *N*-2’,6’-diisopropyl phenyl-2,5-dimethyl benzamide) (**3**), supports a pseudo-octahedric arrangement around the molybdenum atom with the imido group occupying one of the axial positions.

Reduction of these Mo(V) complexes with Na amalgam in the presence of three equivalents of $P(OMe)_3$ yielded $MoCl_2(E)[P(OMe)_3]_3$ (E = O (5), NAr (6)). These molybdenum(IV) complexes react with 3,3-diphenylcyclopropene affording olefin complexes Mo(η^2-diphenylcyclopropene)$Cl_2(E)[P(OMe)_3]$ (E = O, NAr) similar to those obtained with analogous tungsten complexes [4]. The thermal stability of the molybdenum derivatives is quite low and they decompose within hours at room temperature to give 1,1,6,6,-tetraphenyl hexatriene.

4. Experimental details

All manipulations were carried out under argon using standard Schlenck techniques or in a nitrogen-filled glove box equipped with a −40°C freezer. Argon was purified by passage through columns Chemalog R3-11 catalyst and Lynde 4-Å molecular sieves. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^{1}H, 22.53 MHz ^{13}C, 36.20 MHz ^{31}P) or a QE-300 Plus (300.10 MHz ^{1}H, 75.49 MHz ^{13}C) spectrometer. All coupling constants are reported in Hz. For the ^{1}H and



Scheme 1.

^{13}C-NMR virtual triplets resonances of the *trans* phosphite ligands, the coupling constant $N = [^2J_{HP} + ^4J_{HP}]$ are given, where N is the separation of the outer lines of the triplet [16].

Toluene, benzene, diethyl ether and tetrahydrofuran were purified by passage through a column of La Roche A-2 alumina and Engelhard Q-5 reactant (supported copper oxide), degassed by freeze-pump-thaw three times. Pentane was stirred over concentrated H_2SO_4, dried over CaH_2 and $MgSO_4$ and vacuum transferred from sodium–benzophenone ketyl. C_6D_6 and THF-d_8 were dried over sodium–benzophenone ketyl and vacuum transferred prior to use. $P(OMe)_3$ was vacuum-transferred from Na and then subjected to several freeze-pump-thaw cycles. $MoCl_4(O)$, ArNCO, $ArNH_2$, 2,6-lutidine and $SiMe_3Cl$ were purchased by commercial sources and purified by distillation prior to use. Finally 3,3-diphenylcyclopropene was prepared following a procedure by Moore [17].

4.1. Reaction of $MoCl_4(O)$ with ArNCO

4.1.1. Formation of '$MoCl_3(O)$' **1**

A 5 ml benzene solution of 2,6-diisopropyl phenyl isocyanate (0.81 ml, 3.8 mmol) was added to a red suspension of $MoCl_4(O)$ (0.97 g, 3.8 mmol) in benzene, toluene or octane. The resulting mixture was refluxed over 24 h after which the colour of the suspension changed from red to brown–yellow, then the mixture was allowed to settle. Filtration afforded a brown–yellow solution. Solvent was removed under vacuum and the resulting dark yellow residue washed three times with pentane (10 ml) to yield a yellow powder characterised as **1** on the basis of its paramagnetic character and its reactivity (0.5 g, 60%).

4.1.2. Formation of '$MoCl_3(O)$' **1** and '$MoCl_3(NAr)$' **2**

Repetition of the above procedure, employing chlorobenzene as solvent gave a yellow product that was identified as a mixture of **1** and **2** according to the reactivity exhibited by this solid.

4.1.3. Formation of $MoCl_3(NAr)(L_2)$. L = N-2',6'-diisopropylphenyl-2,5-dimethyl benzamide **3**

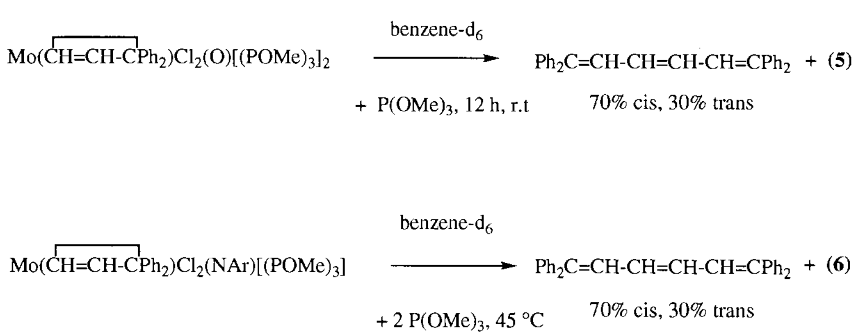
A 10 ml *p*-xylene solution of aryl isocyanate (2.5 ml, 11.7 mmol) was added over a red suspension of $MoCl_4(O)$ (1 g, 3.9 mmol) in *p*-xylene. The resulting mixture was refluxed for over 24 h and then allowed to settle. Filtration afforded a yellow–brown solution. This solution was concentrated under vacuum until only 5 ml were left and then cooled to 0°C for 12 h to give yellow crystals of **3** (1.77 g, 45%). Anal. Calcd. for ($C_{54}H_{71}Cl_3O_2N_3Mo$): C, 65.09; H, 7.18; N, 4.21%; Found: C, 64.89; H, 7.12; N, 4.18%.

4.2. $MoCl_3(NAr)(dme)$ **4**

Over a stirred solution of $MoCl_4(O)$ (0.67 g, 2.6 mmol) in dimethoxyethane (30 ml) cooled to −30°C, the following were added were added in this order: 2,6 lutidine (0.56 ml, 5.2 mmol) in 5 ml of DME, Me_3SiCl (1.42 ml, 13.0 mmol) in 10 ml of DME and $ArNH_2$ (0.46 ml, 2.6 mmol) in 5 ml of DME.

Addition of 2,6 lutidine resulted in a green suspension, and this colour persisted until all chemicals were added. The mixture was allowed to warm to room temperature over a period of 3 h. When the temperature began to increase the solution's colour changed from green to orange and at the same time began the precipitation of a white solid.

When the reaction finished, the precipitate was filtered and the solution concentrated in vacuo until half of its initial volume remained. At this stage, a crystalline yellow solid precipitated from the solution



Scheme 2.

and was recovered by filtration, dried under vacuum and characterised as the paramagnetic complex $MoCl_3(NAr)(dme)$ (0.74 g, 60%). This solid presents few solubility in C_6D_6 and CD_2Cl_2 but is soluble in THF-d_8. The ^1H-NMR spectrum in THF-d_8 shows the paramagnetic character of this solid and also shows two signals corresponding to free DME. Anal. Calcd. for ($C_{16}H_{27}Cl_3O_2NMo$): C, 41.1; H, 5.82; N, 2.99%; Found: C, 41.37; H, 5.74; N, 3.03%.

4.3. $MoCl_2(O)[P(OMe)_3]_3$ **5**

4.3.1. Method A

A toluene solution of $MoCl_4(O)$ (0.86 g, 3.4 mmol) was added over a sodium amalgam (6% Na, 0.16 g of Na, 6.8 mmol), and then $P(OMe)_3$ (1.20 ml, 10.2mmol) was added via syringe.

The original solution turned green as the reaction mixture was stirred for 12 h. This suspension was filtered and the solvent removed under vacuum, the resulting green residue was left under dynamic vacuum for an additional 12 h period and then extracted with diethyl ether (2 × 15 ml). This ether solution was concentrated in vacuo and cooled to − 20°C, leading after 24 h to green crystals of $MoCl_2(O)[P(OMe)_3]_3$ (1.31 g, 70%). ^1H-NMR (C_6D_6): δ 3.77 (t, 18, $N = 10.5$ Hz); 3.64 (d, 9, $J_{HP} = 10.5$ Hz). ^{13}C-NMR (C_6D_6) δ 52.8(t, 2 $P(OMe)_3$); 52.6 (d, $J_{C-P} = 5.36$ Hz). ^{31}P-NMR (C_6D_6) δ 142.8 (t, 1, $J_{PP} = 21$ Hz); 128.5 (d, 2, $J_{PP} = 21$ Hz). Anal. Calcd. for ($C_9H_{27}Cl_2O_{10}P_3Mo$): C, 19.47; H, 4.90%; Found: C, 19.08; H, 4.87%.

4.3.2. Method B

A yellow toluene solution of '$MoCl_3(O)$' (0.4 g, 1.83 mmol) was added over a sodium amalgam (6% Na, 0.042 g of Na, 1.83 mmol) and just prior to stirring, $P(OMe)_3$ (0.65 ml, 5.5 mmol) was added via syringe.

Working up the reaction as in the method A, it was also possible to get green crystals of **5** (0.35 g, 35%).

4.4. $MoCl_2(NAr)[P(OMe)_3]_3$ **6**

4.4.1. Method A

Over a sodium amalgam (6% of Na, 0.04 g of Na, 1.8mmol) a 30-ml toluene solution of **3** (0.9 g, 0.9 mmol) was transferred via canula, next $P(OMe)_3$ (0.32 ml, 2.71 mmol) was added via syringe to the reaction flask. The reaction mixture was stirred for 12 h and then filtered leading to a brown-solution which was evaporated to dryness. In addition to the desired product, the brown residue contained two molecules of *N*-2',6'-diisopropyl phenyl-2,5-dimethyl bezamide whose solubility is quite similar to **6** in the usual solvents. Extracting several times with diethyl ether, it was possible to remove this ligand and isolate the complex $MoCl_2(NAr)[P(OMe)_3]_3$ in low yield. ^1H-NMR (C_6D_6): δ 6.99 (m, 3, $H_{aromatic}$), 4.62 (sp, 2, $J_{HH} = 6.6$ Hz, $-CHMe_2$), 3.69 (t, 18, $N = 10.5$ Hz, $P(OMe)_3$), 3.59 (d, 9, $J_{HP} = 10.5$ Hz, $P(OMe)_3$), 1.32 (d, 12, $J_{HH} = 6.6$ Hz). Anal. Calcd. for ($C_{21}H_{44}Cl_2NO_9P_3Mo$): C, 35.31; H, 6.21; N, 1.96%: Found: C, 35.08; H, 5.87; N, 1.85%.

4.4.2. Method B

A 30-ml toluene solution of $MoCl_3(NAr)(dme)$ and '$MoCl_4(NAr)$' (0.62 g) was added over a sodium amalgam (6% of Na, 0.035 g of Na) and then $P(OMe)_3$ (0.47 ml, 3.97 mmol) was incorporated to the reaction mixture via syringe. This suspension was stirred for 12 h and then filtered and concentrated to dryness, the resulting residue was left under dynamic vacuum for an additional 12 h period in order to remove the excess of phosphite. Next, the brown oily product was washed with pentane (3 × 10 ml) giving rise to a yellow–brown solid that was identified as complex **6** (0.55 g, 58%).

4.5. Observation of Mo(η^2-diphenylcyclopropene)Cl_2-(O)$[P(OMe)_3]_2$ **7**

A 0.5-ml solution of 3,3-diphenylcyclopropene (0.007 g, 0.036 mmol) in deuterated benzene was added over $MoCl_2(O)[P(OMe)_3]_3$ (0.02 g, 0.036 mmol) and the resulting mixture was monitored by ^{1}H-NMR spectroscopy. After 10 min, signals appear which correspond to complex **7**, which keep increasing over a 12 h period. After this time, joined to the signals corresponding to the starting material and complex **7**, it is possible to see the signals corresponding to the dimerization product of 3,3-diphenyl cyclopropene in the spectrum. After 24 h only the signals corresponding to **5** and $Ph_2C{=}CH{-}CH{=}CH{-}CH{=}CPh_2$ are present in the ^{1}H-NMR spectrum. ^{1}H-NMR of **7** (C_6D_6):δ 7.05 (m, 10, $H_{aromatic}$), 5.80 (t, 2, $J_{HH} = 8.1$ Hz, CH=CH), 3.61 (t, 18, $N = 10.8$ Hz).

4.6. *Observation of Mo(η^2-diphenylcyclopropene)Cl_2-(NAr)[P(OMe)$_3$]* **8**

A 0.5-ml solution of 3,3-diphenyl cyclopropene (0.004 g, 0.021 mmol) in deuterated benzene was added over $MoCl_2(NAr)[P(OMe)_3]_3$ (0.015 g, 0.021 mmol) placed in a NMR tube. The reaction was followed by ^{1}H-NMR spectroscopy. The signals corresponding to complex **8** start to grow with the reaction time but the reaction seems to stop after 16 h when the amount of **8** in the mixture is ≈50%. Heating to 40–45°C at this stage leads to the decomposition of the product, with the appearance once again of the dimerization product of 3,3-diphenylcyclopropene. The identification of complex **8** and the assignment of the NMR signals of this complex were made by comparison with the analogous tungsten complex [3]. ^{1}H-NMR of **8** (C_6D_6): δ 7.1 (m, 13, $H_{aromatic}$), 5.35 (dd, 1, $J_{HH} = 4.2$ Hz, $J_{HP} = 0.6$ Hz, C$\underline{H}$–CH), 5.04 (dd, 1, $J_{HH} = 4.2$ Hz, $J_{HP} = 13.8$ Hz), 3.28 (d, 9, $J_{HP} = 10.8$ Hz, P(OMe)$_3$), 1.31 (d, 6, $J_{HH} = 6.6$, CHC$\underline{Me}$Me), 1.30 (d, 6, $J_{HH} = 6.6$, CHCMe$\underline{Me}$).

4.7. *Collection of X-ray diffraction data*

A yellow crystal of approximate dimensions 0.27 × 0.42 × 0.46 mm was oil-mounted [18] on a glass fibber and transferred to the Siemens P3 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out according to procedures similar to those of Churchill [19]. Intensity data were collected at 163 K using a $\theta - 2\theta$ scan technique with Mo–K_α radiation under the conditions described in Table 2. All 4502 data were corrected for Lorentz and polarisation effects and were placed on an approximately absolute scale. The diffraction symmetry was *mmm* with systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$ and $00l$ for $l = 2n + 1$. The non-centrosymmetric orthorhombic space group $P2_12_12_1$ is therefore uniquely defined.

4.8. *Solution and refinement of the crystal structure*

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package [20] or the SHELXTL PLUS program set [21]. The analytical scattering factors for neutral atoms were used throughout the analysis [22]; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimised during least-squares analysis was $\Sigma w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0010^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C{-}H) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. There is a molecule of C_8H_{10} present per formula unit. Refinement of positional and thermal parameters led to convergence with $R_F = 5.4\%$; $R_{wF} = 6.5\%$ and GOF = 1.52 for 597 variables refined against those 2231 data with $F > 2.0\sigma(F)$. A final difference-Fourier synthesis yielded $\rho(\max) = 0.60$ e Å^{-3}. The absolute structure was determined by refinement of the Rogers' η-parameter [23] ($\eta = 0.93(15)$).

5. Supplementary material

A complete description of the X-ray experiment for **3**, and tables of crystal data, atomic coordinates, thermal parameters, distances and angles (17 pages), torsion angles (2 pages), and structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Table 2
Experimental data for the X-ray diffraction study of **3**

Formula	$C_{54}H_{69}N_3O_2Cl_3Mo{-}C_8H_{10}$
FW	1100.6
Temperature (K)	163
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	10.8194(8)
b, Å	23.528(2)
c, Å	23.914(2)
V, Å^3	6087.4(9)
Z	4
D_{calcd}, g cm^{-3}	1.201
Diffractometer	Siemens P3
Radiation	Mo–K_α ($\lambda = 0.710730$ Å)
Monochromator	Highly oriented graphite
Data collected	$+h$, $+k$, $+l$
Scan type	$\theta - 2\theta$
Scan width	1.2° plus K_α-separation
Scan speed	3.0° min^{-1} (in ω)
2θ range, °	4.0–45.0
μ(Mo–K_α), mm^{-1}	0.389
Reflections collected	4502
Reflections with $F > 2.0\sigma(F)$	4147
No. of variables	597
R_F	5.4%
R_{wF}	6.5%
Goodness of fit	1.52

Acknowledgements

We gratefully acknowledge Prof. R.H. Grubbs for his support and valuable help, and F.J.M. thanks the Ministerio de Educacion y Ciencia of Spain for a postdoctoral fellowship.

References

[1] (a) K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983. (b) R.H. Grubbs, In: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon, New York, 1982. (c) V. Dragutan, A.T. Balaban, M. Dimonie, Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins, 2nd ed., Wiley-Interscience, New York, 1985. (d) M. Leconte, J.M. Basset, F. Quignard, C. Larroche, In: P.R. Braterman, (Ed.), Reactions of Coordinated Ligands, Plenum, New York, 1986.

[2] (a) R.R. Schrock, R. DePue, J. Feldman, C.J. Schaverien, J.C. Dewan, A.H.J. Liu, Am. Chem. Soc. 110 (1988) 1423. (b) J.S. Murdzek, R.R. Schrock, Organometallics 6 (1987) 1373. (c) R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M.J. O'Regan, Am. Chem. Soc. 112 (1990) 3875.

[3] L.K. Johnson, R.H. Grubbs, J.W.J. Ziller, Am. Chem. Soc. 115 (1993) 8130.

[4] F.J. De la Mata, R.H. Grubbs, Organometallics 15 (1996) 577.

[5] (a) A.V. Butcher, J. Chatt, G.J. Leigh, P.L.J. Richards, Chem. Soc. Dalton Trans. (1972) 1064. (b) E. Carmona, L. Sánchez, M.L. Poveda, Polyhedron 2 (1983) 797.

[6] (a) D.C. Bradley, M.B. Hursthouse, K.M.A. Molik. A.J. Nielson, R.L.J. Short, Chem. Soc. Dalton. Trans. (1983) 2651–2656. (b) A.J. Nielson, R.E. McCarley, S.L. Laughlin, C.D. Carlson, In: J.M. Schreeve, (Ed.), Inorg. Syntheses, vol. 24, Wiley, New York, 1986, pp. 194–200. (c) Reference 3.

[7] (a) F.-M. Su, C. Cooper, S.J. Geib, A.L. Rheingold, J.M.J. Mayer, Am. Chem. Soc. 108 (1986) 3545–3547. (b) F.-M. Su, J.C. Bryan, S. Jang, J.M. Mayer, Polyhedron 8 (1989) 1261–1277. (c) A.J. Nielson, D.C. Ware, Polyhedron 9 (1990) 603–610. (d) G.R. Clark, A.J. Nielson, C.E.F. Rickard, D.C.J. Ware, Chem. Soc. Chem. Commun. (1989) 343–345. (e) G.R. Clark, A.J. Nielson, C.E.F.J. Rickard, Chem. Soc. Chem. Commun. (1989) 1157–1159. (f) G.R. Clark, A.J. Nielson, C.E.F. Rickard, D.C.J. Ware, Chem. Soc. Dalton Trans (1990) 1173–1178.

[8] C.Y. Chou, J.C. Huffman, E.A.J. Maata, Chem. Soc. Chem. Commun. (1984) 1184.

[9] R.R. Schrock, S.A. Krause, K. Knoll, J. Feldman, J.S. Murdzek, D.C.J. Yang, Mol. Catal. 46 (1988) 243.

[10] ^{1}H-NMR data of *N*-2',6'-diisopropyl phenyl-2,5-dimethyl bezamide: ^{1}H-NMR (THF-d_8): δ 8.65 (s br, 1, $-N\underline{H}-$), 7.13 (m, 6, $H_{aromatic}$), 3.3 (sp, 2, $J_{HH} = 6.9$ Hz, $-C\underline{H}CMe_2$), 2.46 (s, 3, CH_3), 2.35 (s, 3, CH_3), 1.23 (d, 12, $J_{HH} = 6.9$ Hz, $-CHC\underline{Me_2}$). ^{13}C-NMR ((THF-d_8): δ 169.2 (s, O=C–), 147.4, 138.0, 135.8, 134.2, 133.7, 131.5, 130.7, 128.3, 128.2 and 123.6 (10 aromatic carbons), 29.5 (s, $-CHCMe_2$), 24.0 (s, $-CHCMe_2$), 21.0 (s, CH_3), 19.7 (s, CH_3).

[11] See for example: (a) H. Lam, G. Wilkinson, B. Hussain-Bates, M.B.J. Hursthouse, Chem. Soc. Dalton Trans (1993) 781. (b) Reference 2c.

[12] W.A. Nugent, J.M. Mayer, Metal–Ligand Multiple Bonds, Wiley, New York, 1988 and references cited therein.

[13] This new complex of Mo(VI) is quite unstable and decomposes easily in the presence of traces of moisture. The ^{1}H-NMR (C_6D_6): δ 7.02 (t, $J_{H-H} = 8.04$ Hz, 1H), 6.90 (d, $J_{H-H} = 8.04$ Hz, 2H), 4.62 (sp, $J_{H-H} = 6.90$ Hz, 1H), 1.37 (d, $J_{H-H} = 6.90$ Hz, 2H).

[14] Complex **5** can be prepared also by reduction of '$MoCl_3(O)$' in the presence of trimethyl phosphite but always in lower yields.

[15] The reduction of $MoCl_3(NAr)L_2$ (**3**) with Na/Hg in the presence of three equivalents of phosphite leads the formation of **6** liberating two molecules of *N*-2',6'-diisopropyl phenyl-2,5-dimethyl benzamide, in low to moderate yields.

[16] R.K. Harris, Can. J. Chem. 42 (1964) 2275.

[17] J.S. Moore, S.T. Nguyen, R.H. Grubbs, unpublished results.

[18] The crystal was immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fibre (the oil acts as the adhesive) which is attached to an elongated brass mounting-pin. Further details appear in H. Hope, In: A.L. Wayda, M.Y. Darensbourg (Eds.), Experimental Organometallic Chemistry: A Practicum in synthesis and Characterization, ACS Symposium Series No. 357, 1987.

[19] M.R. Churchill, R.A. Lashewycz, F.J. Rotella, Inorg. Chem. 16 (1977) 265–271.

[20] C. Strouse, UCLA Crystallographic Computing Package, University of California Los Angeles, 1981, personal communication.

[21] G.M. Sheldrick, Siemens Analytical X-Ray Instruments, SHELXTL Program, Madison, WI, 1990.

[22] International Tables for X-Ray Crystallography, Vol. C, Dordrecht: Kluwer Academic Publishers, 1992.

[23] D. Rogers, Acta. Cryst. A37 (1981) 734–741.