

Synthesis and Characterization of (2,4,6-Trimethylphenylimido)molybdenum Complexes. X-ray Crystal Structures of (L_{OEt})Mo(Nmes)₂Cl, (L_{OEt})Mo(Nmes)Cl₂, and MoCl₃(Nmes)(depe) (mes = 2,4,6-Trimethylphenyl, L_{OEt} = (η-C₅H₅)Co{P(O)(OEt)₂}₃, depe = Et₂PCH₂CH₂PEt₂)

Agustín Galindo,* Francisco Montilla, Antonio Pastor, and Ernesto Carmona

Departamento de Química Inorgánica, Instituto de Investigaciones Químicas, Universidad de Sevilla-CSIC, Apto 553, 41071 Sevilla, Spain

Enrique Gutiérrez-Puebla, Angeles Monge, and Caridad Ruiz

Instituto de Ciencia de Materiales, CSIC, Serrano 113, 28006 Madrid, Spain

Received September 27, 1996[®]

The bis(imido) complex MoCl₂(Nmes)₂(dme) (**1**) (mes = 2,4,6-trimethylphenyl, dme = 1,2-dimethoxyethane) has been used as the starting material for the preparation of the compounds (L_{OEt})Mo(Nmes)₂Cl (**2**) (L_{OEt} = (η-C₅H₅)Co{P(O)(OEt)₂}₃) and Mo(Nmes)₂(acac)₂ (**5**), as well as for the synthesis of the mixed oxo–imido MoCl₂(Nmes)(O)(dme) (**6**), the latter reaction involving disproportionation of **1** and MoCl₂(O)₂(dme). Similarly, the paramagnetic mono(imido) species Mo(Nmes)Cl₃(dme) (**11**) can also be obtained from **1** by interaction with MoCl₄(THF)₂ (THF = tetrahydrofuran) in refluxing dme. Compounds **6** and **11** are suitable sources for the synthesis of other diamagnetic mixed oxo–imido and paramagnetic mono(imido) compounds, respectively. Three of the newly synthesized complexes, namely, (L_{OEt})Mo(Nmes)₂Cl (**2**), (L_{OEt})Mo(Nmes)Cl₂ (**12**), and MoCl₃(Nmes)(depe) (**14**) (depe = Et₂PCH₂CH₂PEt₂) have been characterized by X-ray crystallography.

Introduction

Oxo and imido ligands form commonly multiple bonds when attached to transition metal centers.¹ The chemistry of the corresponding complexes has experienced a remarkable growth during past 15 years; a large number of compounds of these types are now known for the majority of the transition metals, including the actinides. Both the oxo and the imido groups permit stabilization of high formal oxidation states. In the case of the latter functionality, varying the electronic and steric characteristics of the organic group bonded to nitrogen allows the modification of the properties of the resulting metal complex.

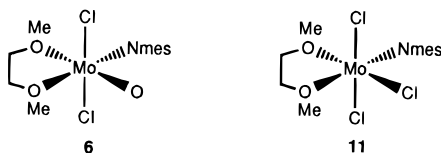
Much of the interest in these compounds is due to the intermediary role they seem to play in many important reactions such as C–H activation,² propylene ammoxidation,³ the oxidation of hydrocarbons,⁴ the polymerization of olefins,⁵ and others. Derivatives of the early transition metals (groups 4–6) are especially relevant in this regard and have therefore been subjected to intense scrutiny, on both experimental and theoretical grounds.^{1,6} An interesting isolobal analogy between the d² M(NR)₂ fragments of group 6 metals and group 4 bent metallocenes has been disclosed recently.⁷

Organoimido complexes of Mo(VI) and Mo(V) can be prepared by a wide range of methods that often make use of organic compounds as the imido transfer reagent.¹ Here we wish to report the synthesis of the mixed oxo–imido compound MoCl₂(Nmes)(O)(dme) (**6**) (mes = 2,4,6-trimethylphenyl, dme = 1,2-dimethoxyethane) by a double transfer reaction that involves the disproportionation of bis(oxo) and bis(imido)

[®] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

- (1) (a) Herrmann, W. A. *Polyhedron* **1987**, 6, 1165. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley Interscience: New York, 1988. (c) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, 28, 339. (d) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, 42, 239.
- (2) For some recent examples see: (a) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 903. (b) Cundari, T. R. *Organometallics* **1993**, 12, 4971. (c) Bennet, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, 116, 2179. (d) Lee, S. V.; Bergman, R. G.; *J. Am. Chem. Soc.* **1995**, 117, 5876. (e) Benson, M. T.; Cundari, T.; Moody, E. W. *J. Organomet. Chem.* **1995**, 504, 1, and references cited therein.
- (3) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, 107, 251.
- (4) (a) Holm, R. H. *Chem. Rev.* **1987**, 87, 1401. (b) Muzart, J. *Chem. Rev.* **1992**, 92, 113. (c) Sundermeyer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1144.

- (5) (a) Schoettel, G.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1062. (b) Schrock, R. R.; Depue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, 9, 2262. (c) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. J. *Am. Chem. Soc.* **1990**, 112, 3875. (d) Fox, H. H.; Schrock, R. R.; O'Dell, R. *Organometallics* **1994**, 13, 635. (e) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1709.
- (6) Selected examples of group 6 imido complexes are in the following: (a) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651. (b) Nielson, A. J.; Ware, D. C. *Polyhedron* **1990**, 9, 603. (c) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1907. (d) Green, M. L. H.; Konidaris, P. C.; Michaelidou, D. M.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1995**, 155. (e) Morrison, D. L.; Rodgers, P. M.; Chao, Y.-W.; Bruck, M. A.; Grittini, C.; Tajima, T. L.; Alexander, S. J.; Rheingold, A. L.; Wigley, D. E. *Organometallics* **1995**, 14, 2435. (f) Morrison, D. L.; Wigley, D. E. *Inorg. Chem.* **1995**, 34, 2610. (g) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 2111. (h) Dyer, P. W.; Gibson, V. C.; Clegg, W. J. *J. Chem. Soc., Dalton Trans.* **1995**, 3313. (i) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 271.
- (7) (a) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, 112, 6728. (b) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1666. (c) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Wilson, C. J. *Organomet. Chem.* **1993**, 462, C15. (d) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, 12, 4560. (e) Sundermeyer, J.; Runge, D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1255. (f) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, 14, 103.



derivatives, as well as that of the Mo(V) organoimido Mo(Nmes)Cl₃(dme) (**11**) by the reaction of MoCl₂(Nmes)₂(dme) (**1**) with MoCl₄(THF)₂ (THF = tetrahydrofuran). Compounds **6** and **11** are useful starting materials for the preparation of several related complexes containing monoanionic, formally tridentate ancillary ligands, such as η -cyclopentadienyls, Kläui's ligand,⁸ L_{OEt} = (η -C₅H₅)Co{P(O)(OEt)₂}₃, and the hydrotris(pyrazolyl)borate, Tp = HB(pz)₃.⁹

Results and Discussion

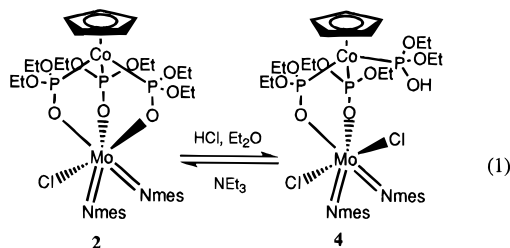
Synthesis and Structural Characterization of d⁰ Bis(imido) Complexes of Molybdenum. Our approach to the chemistry of these compounds makes use of the Mo(VI) derivative MoCl₂(Nmes)₂(dme) (**1**). This is a member of a well-known series of complexes which can be prepared following the method of Schrock and co-workers,¹⁰ namely, by the reaction of (NH₄)₂-Mo₂O₇ with 2,4,6-trimethylphenylamine, H₂Nmes, in the presence of ClSiMe₃ and NEt₃, in refluxing dme. While our work was in progress, the synthesis of **1** by the same procedure, but using Na₂MoO₄ as the Mo source, has been described.^{11a} Hence, NMR data for **1**, which is coincidental with those given in ref 11a, will not be described.

Interaction of **1** with 1 equiv of the monoanionic tripod ligands L_{OEt} and Tp affords the expected compounds (L_{OEt})Mo(Nmes)₂Cl (**2**) and TpMo(Nmes)₂Cl (**3**) in good yields, as shown in Scheme 1 in the case of **2**. Both complexes are crystalline materials, readily soluble in common organic solvents, that exhibit moderate stability to air. The related compound Tp*Mo(N'Bu)₂Cl has been reported recently by Sundermeyer and co-workers.^{11b} The C_s symmetry proposed for these molecules is readily deduced from their NMR data. Thus, the organoimido ligands are equivalent; free rotation around the N–C takes place in solution since only two methyl and one aromatic C–H resonances are observed in each case (2.11, *p*-CH₃; 2.74, *o*-CH₃; 6.70 ppm, *m*-H; intensity ratio 6:12:4; data corresponding to complex **2**). Similarly, an AX₂ spin system appears in the ³¹P{¹H} NMR spectrum of **2** (δ_A = 122.8, δ_X = 109.7 ppm, J_{AX} = 158 Hz).

The crystal structure of (L_{OEt})Mo(Nmes)₂Cl (**2**) has been determined, and the molecular geometry is shown in Figure 1. Table 1 collects selected bond distances and angles. The complex has a distorted octahedral structure with the chelating ligand occupying three facial positions, the other three sites consisting of the N atoms of the imido ligands and of the chloro ligand. Both imido ligands can be considered linear, the Mo–N1–C1 and Mo–N2–C10 angles being respectively 170.4(9) and 164.2(9)°, i.e., well in the 160–180° range expected for such linear linkages.¹ The Mo–O2 bond, *trans* to the chloride ligand, at 2.076(8) Å is somewhat shorter than the others (2.187(8) and 2.236(8) Å, Mo–O1 and Mo–O3, respectively). However, they all appear normal since in the structurally

characterized complexes of Mo and W that contain Kläui's type ligands these distances are in the range 2.12–2.21 Å.¹² It is to be noted, however, that the Mo–O bonds *trans* to the Nmes ligands are elongated by 0.11 and 0.16 Å with respect to the Mo–O bond *trans* to the chloride, in accord with the high *trans* influence expected for the imido ligands in this d⁰ compound.¹³

An interesting reaction ensues when **2** is mixed with an Et₂O solution of HCl (prepared *in situ* from ClSiMe₃ and MeOH). This yields a red crystalline, non-electrolyte solid, **4**, for which analytical data indicate the incorporation of a second chloride into the coordination sphere of the Mo center. The protonation reaction is reversible; complex **2** can be re-formed following treatment of **4** with NEt₃. Although the Cp protons of **4** are slightly shifted to lower field (δ 5.15, *versus* δ 4.88 in **2**), the ³¹P{¹H} NMR spectrum still exhibits an AX₂ spin pattern (δ_A = 125.0, δ_X = 117.1 ppm, J_{AX} = 148 Hz). The most noteworthy NMR feature of **4** is the observation of a low-field ¹H resonance at 14.5 ppm. This rules out the formation of a N–H bond (compare, for example, with the δ 4.10–4.50 value found for the N–H proton in [(Tp*)Mo(N'Bu)(NH'Bu)Cl]BF₄ complex^{11b}) and suggests that protonation occurs at one of the P=O groups of the ligand which, as a result, becomes bidentate (eq 1). A similar proposal has been advanced¹⁴ for the product of the reaction of (L_{OMe})Pt(CH₃)₃ and HCl, the reported ¹H NMR data being very similar to those of **4** (e.g., δ 5.32, Cp; 12.06, P–OH).



Finally, before closing this section it should be mentioned that the reaction of **1** with Tl(acac) is straightforward and provides good yields of complex Mo(Nmes)₂(acac)₂ (**5**) (Scheme 1), directly related to the well-known compounds Mo(NR)₂-(S₂CNEt₂)₂.¹⁵ The proposed C₂ symmetry is based on the observation of two signals for the Me groups of the acac ligands, both in the ¹H and in the ¹³C{¹H} NMR spectra. As in complexes **2** and **3**, there is free rotation around the N–C bonds of the Nmes ligands, only one signal for the *ortho* methyls being observed (see Experimental Section).

d⁰ Mixed Oxo–Imido Complexes of Molybdenum. The conproportion reaction of the bis(imido) MoCl₂(Nmes)₂(dme) (**1**) and the bis(oxo) MoCl₂(O)₂(dme), in refluxing dme, results in high yields of the mixed oxo–imido derivative MoCl₂(Nmes)-(O)(dme) (**6**), as depicted in Scheme 1. Very recently, Gibson and co-workers have reported the synthesis and X-ray crystal characterization of a closely related MoCl₂(N-1-adamantyl)(O)-

(8) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 627.

(9) Trofimenko, S. *Chem. Rev.* **1993**, 93, 943.

(10) (a) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, 31, 2287. (b) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, 459, 185.

(11) (a) Radius, U.; Sundermeyer, J.; Pritzkow, H. *Chem. Ber.* **1994**, 127, 1827. (b) Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, 127, 1201.

(12) (a) Kläui, W.; Müller, A.; Herbst, R.; Egert, E. *Organometallics* **1987**, 6, 1824. (b) Kläui, W.; Hamers, H.; Pfeffer, M.; de Cian, A.; Fischer, J. J. *Organomet. Chem.* **1990**, 394, 213.

(13) See for example: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, 31, 123. (b) Lyne, P. D.; Mingos, D. M. P. *J. Organomet. Chem.* **1994**, 478, 141, and references cited therein.

(14) Nettle, A.; Valderrama, M.; Contreras, R.; Scotti, M.; Peters, K.; Von Schnering, H. G.; Werner, H. *Polyhedron* **1988**, 7, 2101.

(15) See for example: (a) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, 8, 2063. (b) Holm, R. H.; Harlan, E. W. *J. Am. Chem. Soc.* **1990**, 112, 186. (c) Coffey, T. A.; Forster, G. D.; Hogarth, G.; Sella, A. *Polyhedron* **1993**, 12, 2741.

Scheme 1

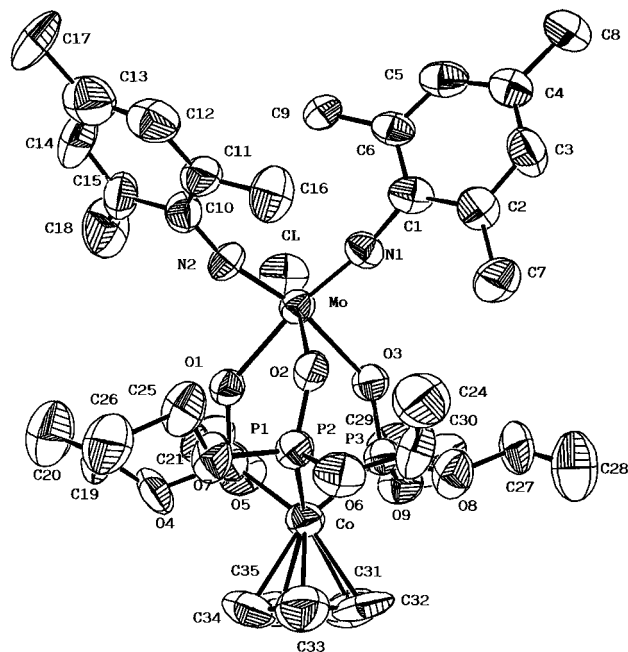
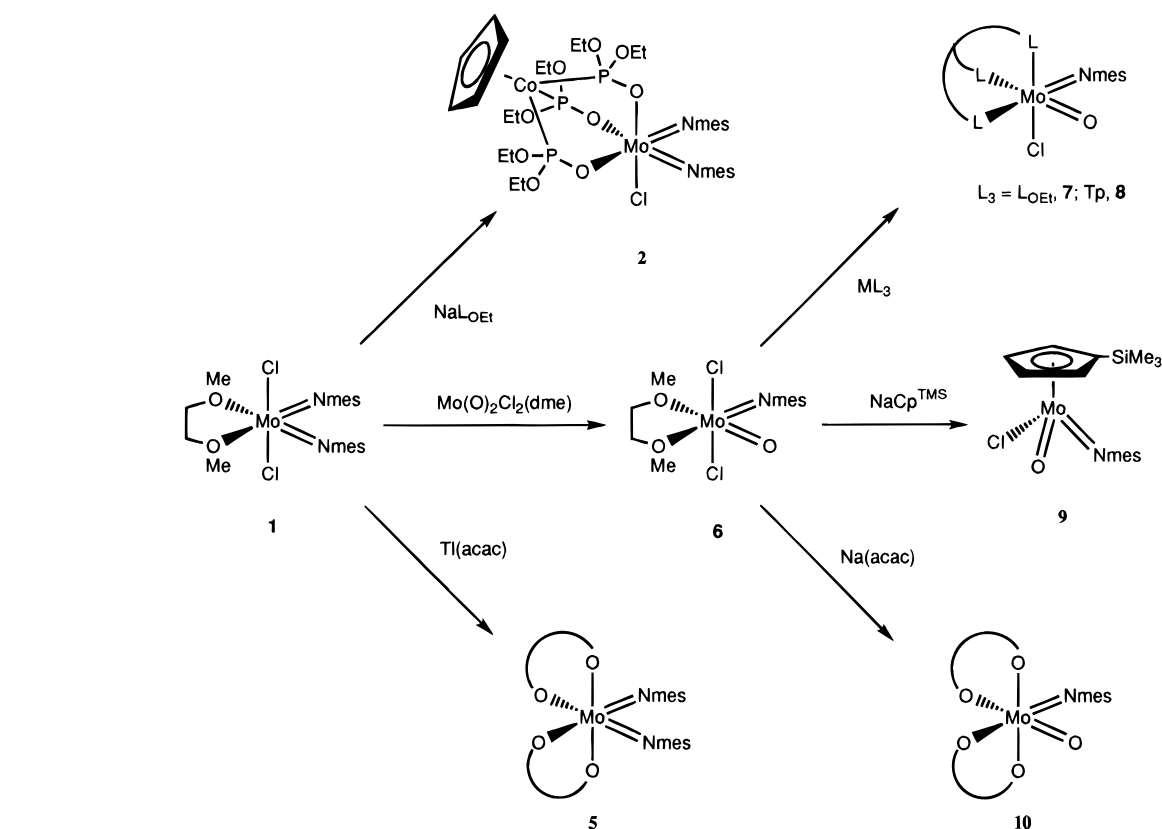


Figure 1. ORTEP view of the molecular structure of $(\text{LOEt})\text{Mo}(\text{Nmes})_2\text{Cl}$ (**2**).

(dme) complex.¹⁶ Compound **6** is a red crystalline solid, which can be conveniently handled and, as described below, used as the starting material for the synthesis of other oxo–imido complexes. Its formation involves likely a concerted oxo and imido transfer reaction, which is doubtless facilitated by the lability of the dme ligands of the formally Mo(VI) compounds. Such a process is uncommon, although some precedent already exists in the literature, e.g., the reactions between OsO_4 and

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for $(\text{LOEt})\text{Mo}(\text{Nmes})_2\text{Cl}$ (**2**)

Mo–Cl	2.385(3)	Mo–O1	2.187(8)
Mo–N1	1.728(9)	Mo–O2	2.076(8)
Mo–N2	1.744(9)	Mo–O3	2.236(8)
O2–Mo–O3	78.7(3)	N1–Mo–O1	169.9(4)
O1–Mo–O3	79.9(3)	N1–Mo–N2	101.2(4)
O1–Mo–O2	82.1(3)	Cl–Mo–O3	86.1(2)
N2–Mo–O3	167.1(4)	Cl–Mo–O2	160.5(2)
N2–Mo–O2	93.6(4)	Cl–Mo–O1	83.3(2)
N2–Mo–O1	88.8(4)	Cl–Mo–N2	98.9(3)
N1–Mo–O3	90.2(4)	Cl–Mo–N1	94.1(4)
N1–Mo–O2	98.0(4)		

$\text{Mo}(\text{NAr})_2(\text{O}^t\text{Bu})_2$ ¹⁷ and between $\text{Mo}(\text{O})_2(\text{O}^t\text{Bu})_2$ and $\text{Mo}(\text{NR})_2(\text{O}^t\text{Bu})_2$.¹⁸ Compounds with two different organoimido ligands have also been prepared similarly, by reacting the corresponding $\text{MoCl}_2(\text{NR}^1)_2(\text{dme})$ and $\text{MoCl}_2(\text{NR}^2)_2(\text{dme})$ derivatives.¹⁹

As represented in Scheme 1, the interaction of **6** with NaLOEt , KTp , NaCp^{TMS} ($\text{Cp}^{\text{TMS}} = \text{C}_5\text{H}_4\text{SiMe}_3$), and $\text{Na}(\text{acac})$ gives the corresponding compounds $(\text{LOEt})\text{Mo}(\text{Nmes})(\text{O})\text{Cl}$ (**7**), $\text{TpMo}(\text{Nmes})(\text{O})\text{Cl}$ (**8**), $(\text{Cp}^{\text{TMS}})\text{Mo}(\text{Nmes})(\text{O})\text{Cl}$ (**9**), and $\text{Mo}(\text{Nmes})(\text{O})_2(\text{acac})_2$ (**10**), whose structures may be readily inferred from their NMR spectra.²⁰ For example, in the ^1H NMR spectrum of **8**, nine well-defined signals are observed for the hydrogen nuclei of the pyrazolyl rings. As for the acac complex **10**, four

(16) Copley, R. C. B.; Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Marshall, E. L.; Wang, W.; Whittle, B. *Polyhedron* **1996**, *15*, 3001.

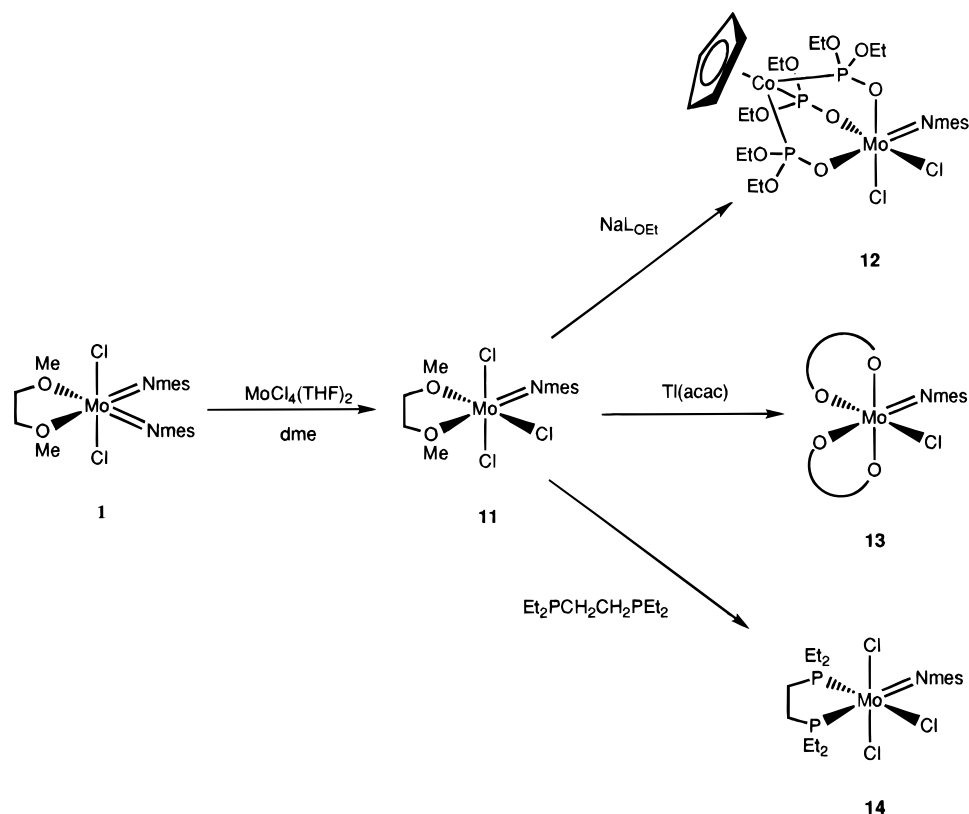
(17) Wolf, J. R.; Bazan, G. C.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 4155.

(18) Jolly, M.; Mitchell, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1331.

(19) Bell, A.; Clegg, W.; Dyer, P. W.; Elsegood, M. R. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2247.

(20) Related complexes have been reported; see for example: (a) Legzdins, P.; Rettig, S. J.; Ross, K. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 5579. (b) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Organomet. Chem.* **1995**, *485*, 37. (c) Köhler, K.; Roesky, H. W.; Herzog, A.; Gornitzka, H.; Steiner, A.; Usón, I. *Inorg. Chem.* **1996**, *35*, 1773.

Scheme 2



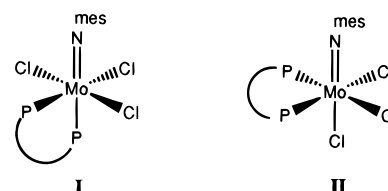
carbonyl and four methyl resonances are detected in the 185–194 and 25–27 ppm ranges, respectively, for the two inequivalent bidentate ligands. Additional spectroscopic data for these complexes are collected in the Experimental Section.

d^1 Imido Complexes of Molybdenum. A convenient entry into the chemistry of the d^1 Mo(Nmes) fragment has been developed. This is based in the comproportion reaction of **1** and $\text{MoCl}_4(\text{THF})_2$ (Scheme 2), which provides high yields of the mono(imido) molybdenum(V) compound $\text{MoCl}_3(\text{Nmes})\text{-(dme)}$ (**11**). This complex has chemical reactivity similar to that already described for **1** and **6**, treatment with NaLOEt and $\text{Ti}(\text{acac})_3$ yielding respectively $(\text{LOEt})\text{Mo}(\text{Nmes})\text{Cl}_2$ (**12**) and $\text{Mo}(\text{Nmes})\text{Cl}(\text{acac})_2$ (**13**). Substitution of the coordinated dme can be achieved readily; addition of equimolar amounts of $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ (depe) to solutions of **11** gives $\text{MoCl}_3(\text{Nmes})\text{-(depe)}$ (**14**), as represented in Scheme 2.

Compounds **11**–**14** are orange or brown crystalline solids, soluble in Et_2O , THF, and other common organic solvents. They are moderately stable to air in the solid state but react rapidly with ambient moisture and air in solution. If the imido ligand is assumed to donate four electrons to the metal center, the complexes can be considered as formally having seventeen valence electrons and therefore are paramagnetic. Their magnetic susceptibilities have been determined in solution using the Evans' method²¹ and in some cases also in the solid state with the aid of a magnetic susceptibility balance. As detailed in the Experimental Section, the measured effective magnetic moments are in the range 1.6–1.7 μ_B , close to the spin-only value of a single unpaired electron and therefore consistent with the proposed d^1 ground-state electronic configuration.

Of the new complexes **11**–**14**, compound **12** containing Kläui's ligand and the depe derivative **14** were considered suitable candidates for solid-state structural determinations by

X-ray methods, because of the relevant information these studies might provide. For the first of these two compounds, comparison of its bonding parameters with those of **2** seemed appropriate. As for **14**, an X-ray analysis would unambiguously differentiate between the two possible isomeric structures, **I** and **II**, that have, respectively, *mer* and *fac* chloride ligands.



Moreover, would structure **I** be adopted by this compound, as it has been found to be the case (see below), two significantly different Mo–P bonds should be expected; measurement of their lengths would give information about the *trans* influence exerted by the imido ligand.

Figure 2 contains an ORTEP drawing representing the structure of the molecules of **12**; important distances and angles for this compound are collected in Table 2. The tridentate nature of Kläui's ligand leaves only one possible distribution for the imido and chloride groups, the overall geometry being that of a distorted octahedron. The Mo–O bonds are not significantly different from those found for the Mo(VI) bis(imido) complex **2**, although the two Mo–O units *trans* to the chlorides (Mo–O1 = 2.084(8); Mo–O2 = 2.09(1) Å) are somewhat shorter than the third Mo–O3 bond, which at 2.160(8) Å, occupies the position *trans* to the imido ligand. As encountered previously in other related series of complexes, the *trans* influence of the imido ligand of a d^1 M(NR) fragment is smaller than that observed in the analogous d^0 M(NR) linkage.^{13,22} The Mo–N–C18 part of the imido functionality is linear (177(1)°), and the Mo–N distance of 1.714(9) Å can be regarded as corre-

(21) (a) Evans, D. *J. Chem. Soc.* **1959**, 2003. (b) Grant, D. H. *J. Chem. Educ.* **1995**, 72, 39.

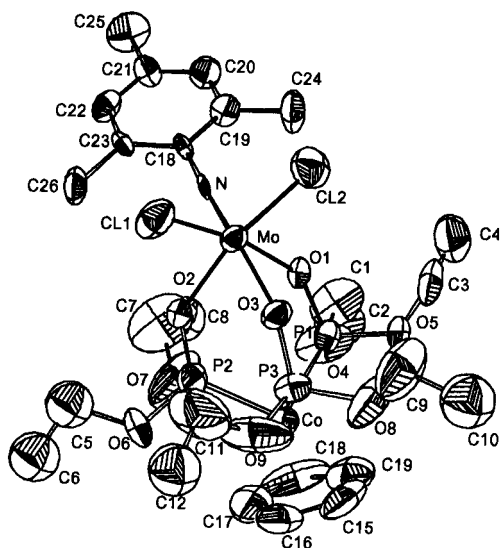


Figure 2. Molecular structure of $(L_{OEt})Mo(Nmes)Cl_2$ (**12**).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $(L_{OEt})Mo(Nmes)Cl_2$ (**12**)

Mo–Cl1	2.355(4)	Mo–O1	2.084(8)
Mo–Cl2	2.295(5)	Mo–O2	2.09(1)
Mo–N	1.714(9)	Mo–O3	2.160(8)
O2–Mo–O3	82.6(3)	N–Mo–O1	92.7(4)
O1–Mo–O3	82.5(3)	N–Mo–Cl2	96.9(3)
O1–Mo–O2	83.4(3)	Cl 1–Mo–O3	86.2(3)
Cl 2–Mo–O3	86.1(2)	Cl 1–Mo–O2	90.0(3)
Cl 2–Mo–O2	168.2(3)	Cl 1–Mo–O1	167.6(3)
Cl 2–Mo–O1	92.0(3)	Cl 1–Mo–Cl2	92.4(2)
N–Mo–O3	174.5(4)	Cl 1–Mo–N	98.3(4)
N–Mo–O2	94.1(4)		

sponding to molybdenum–nitrogen triple bond. For comparative purposes, in the related complex $CpMo(N^tBu)Cl_2$ described recently by Green and co-workers,²³ the Mo–N distance, 1.712(2) Å, is identical within experimental error.

As already advanced, compound **14** adopts a structure of type **I**, i.e., with a meridional arrangement of the chloride ligands (Figure 3). The X-ray analysis also reveals a pseudo-octahedral geometry, of local C_s symmetry, around the Mo atom. Once again, the Mo–N–C part of the metal–imido moiety is almost linear ($173(1)^\circ$), the Mo–N separation of 1.74(1) Å being identical, within the limits of detection, to that of **12** and in agreement with a molybdenum–nitrogen bond of order 3. The three chlorine atoms of the equatorial plane are pushed away from the imido ligand, deviations of the N–Mo–Cl angles from the ideal 90° value being significant, particularly for N–Mo–Cl2 (104.5°). The P1–Mo–P2 angle is of $75.8(2)^\circ$, and since the Mo–P1 vector is perpendicular to the Mo–N vector (N–Mo–P1 = $91.1(4)^\circ$), the second phosphorus atom, P2, is forced to deviate somewhat from the 180° position *trans* to the imido ligand, the N–Mo–P2 angle being of $166.1(4)^\circ$.

By far the main structural feature of compound **14** is the nonsymmetrical coordination of the diphosphine ligand, which results in what could be regarded as a normal Mo–P1 distance of 2.505(5) Å and a considerably larger Mo–P2 bond of 2.734(5) Å. Most Mo–P bond lengths range from 2.3 to 2.6 Å and usually cluster around 2.45–2.55 Å.²⁴ Furthermore, they

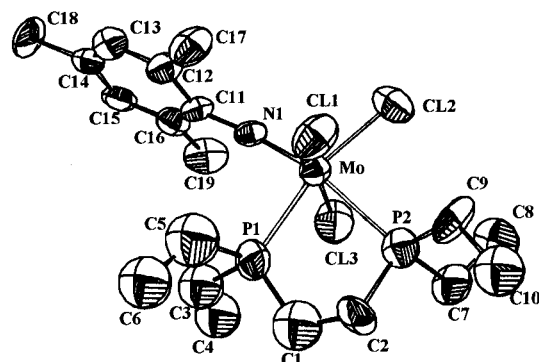


Figure 3. ORTEP drawing of $MoCl_3(Nmes)(depe)$ (**14**).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $MoCl_3(Nmes)(depe)$ (**14**)

Mo–Cl1	2.411(5)	Mo–P1	2.505(5)
Mo–Cl2	2.383(5)	Mo–P2	2.734(5)
Mo–Cl3	2.267(6)	Mo–N	1.74(1)
P2–Mo–N	166.1(4)	Cl3–Mo–P1	87.1(2)
P1–Mo–N	91.1(4)	Cl3–Mo–Cl2	90.9(2)
P1–Mo–P2	75.8(2)	Cl1–Mo–N	97.9(4)
Cl2–Mo–N	104.5(4)	Cl1–Mo–Cl2	90.9(2)
Cl2–Mo–P2	88.5(2)	Cl1–Mo–Cl3	160.6(2)
Cl2–Mo–P1	164.4(2)	Cl1–Mo–P1	86.0(2)
Cl3–Mo–N	100.4(4)	Cl1–Mo–P2	76.9(2)
Cl3–Mo–P2	83.8(2)		

appear not to correlate with the Mo oxidation state.²⁵ Accordingly, the Mo–P2 separation of 2.734(5) Å in **14** can be considered as unusually large, almost in the limits of the Mo–P bonding distances. Nonetheless, other very long M–P bonds (M = Mo or W; recall that both metals have identical atomic radii²⁶) have been reported in the literature, for example, 2.759(3) Å in $MoO_2(OSiPh_3)_2(PPh_3)_2$,²⁵ 2.727(4) Å in $W(NPh)(C\equiv CPh)_2(PhC\equiv CPh)(PMe_3)_2$,^{27a} 2.765(2) Å in $W(N-C_6H_3-Pr^2-2,6)Cl_3(dppe)$,^{27b} or 2.988 Å (av) for the Mo–P *trans* to the Mo–Mo bond of $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$.²⁸

However obvious it might appear, it is worth pointing out that the lengthening of the Mo–P2 bond in **14** is due to the *trans* influence of the imido ligand. It is remarkable that this *trans* influence is so greatly manifested in this complex ($\Delta(Mo-P)$ between Mo–P_{eq} and Mo–P_{ax} is *ca.* 0.23 Å) and in others having also *trans* imido and phosphine groups (e.g., Nielson's $W(N-C_6H_3-Pr^2-2,6)Cl_3(dppe)$,^{27b} $\Delta(Mo-P)$ *ca.* 0.20 Å), much more than in the analogous derivatives that have O- or Cl-functionalities *trans* to the imido group. For comparative purposes, in **12** $\Delta(Mo-O) \approx 0.05$ Å; in $Mo(Ntol)Cl_3(PPh_2-Et)_2$,²² $Mo(Nallyl)Cl_3(PPh_3)_2$,²⁹ and $Mo(o-NC_6H_4NH_2)Cl_3(PMe_2-Ph)_2$,³⁰ the three compounds having a *mer,trans* configuration, $\Delta(Mo-Cl)$ is *ca.* 0.07–0.10 Å; and in the *mer,cis*-[$W(NCy)Cl_2(PMe_3)_3]O_3SCF_3$,³¹ $-W(NCy)Cl_2(PMe_3)_3$,³¹ and $-Mo(Nallyl)Cl_3(OPPh_3)_2$ ³² there is also a very modest, almost insignificant, *trans* influence ($\Delta(Mo-Cl)$ is *ca.* 0.05 Å). Thus, it may appear that the soft P-donors experience a larger *trans* influence from the imido group than the harder O- and Cl- donors.

(22) Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *Inorg. Chem.* **1986**, 25, 822.

(23) Green, M. L. H.; Konidaris, P. C.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2851.

(24) Data from the Cambridge Structural Database. Allen, F.; Kennard, O. *Acc. Chem. Res.* **1983**, 16, 146.

(25) Huang, M.; DeKock, C. W. *Inorg. Chem.* **1993**, 32, 2287.

(26) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

(27) (a) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1157. (b) Clark, G. R.; Glenny, M. W.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1995**, 1147.

(28) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1982**, 21, 1318.

(29) Maatta, E. A.; Du, Y.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1990**, 756.

(30) Redshaw, C.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *Polyhedron* **1993**, 12, 2013.

(31) Danopoulos, A. A.; Redshaw, C.; Vaniche, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, 12, 1061.

(32) Du, Y.; Rheingold, A. L.; Maatta, E. A. *Inorg. Chem.* **1994**, 33, 6415.

Experimental Section

Microanalyses were carried out by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on a Perkin-Elmer Model 684 or 883 spectrophotometer. ^1H , ^{13}C , and ^{31}P NMR spectra were run on Bruker AMX-300 and Bruker 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 . Magnetic moments were measured in solution by the Evans method²¹ or in the solid state with a Sherwood Scientific (Cambridge Research Laboratory) magnetic balance. All preparations and other operations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had bp 40–60 °C. The compounds $\text{MoCl}_4(\text{THF})_2$ ³³ and $\text{MoCl}_2(\text{O})_2(\text{dme})$ ³⁴ were prepared according to the literature procedures. $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ was purchased from commercial sources and used as received.

$\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (1). A solution of $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ (4.9 g, 14.5 mmol) in 80 mL of dimethoxyethane (dme) was reacted with 8 equiv of NEt_3 dissolved in dme (10 mL), ClSiMe_3 (17 equiv) also in 10 mL of dme, and a solution of 2,4,6-trimethylphenylamine (58 mmol) in dme (10 mL). A condenser was attached to the reaction vessel, and the orange suspension was heated at reflux for 8 h, during which time the reaction mixture turned red. The ammonium salts were eliminated by filtration, the volatiles were pumped off under vacuum, and the residue was washed with petroleum ether and dried in vacuo. The resulting red solid was extracted with Et_2O . Cooling to -30 °C afforded red crystals of **1** (7.5 g, 50%). ^1H NMR (C_6D_6): δ 6.56 (s, 4, CH, Ph), 3.38 (br, 6, CH_3O), 3.30 (br, 4, OCH_2), 2.66 (s, 12, CH_3 ortho), 2.02 (s, 6, CH_3 para). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 154.9 (C ipso), 137.0 (C para), 134.3 (C ortho), 129.4 (C meta), 71.9 (OCH_2), 62.0 (CH_3O), 21.1 (CH_3 para), 18.5 (CH_3 ortho). Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{Cl}_2\text{MoO}_2$: C, 50.5; H, 6.1; N, 5.4. Found: C, 50.1; H, 6.5; N, 5.4.

$(\text{LOEt})\text{Mo}(\text{Nmes})_2\text{Cl}$ (2). A reaction flask was charged with $\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (0.6 g, 1.1 mmol) and NaLOEt (0.58 g, 1.1 mmol). A 50 mL volume of THF was added, and the red solution was stirred at ambient temperature overnight. Volatiles were removed; the residue was extracted with Et_2O (20 mL), and filtered to remove NaCl. Concentration of the solution, addition of 10 mL of petroleum ether, and cooling to -20 °C afforded red crystals of compound **2** (0.67 g, 60%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): AX_2 spin system, δ 109.7 (d, $^2J_{\text{PP}} = 158$ Hz), 122.8 (t). ^1H NMR (C_6D_6): δ 6.70 (s, 4, CH, Ph), 4.88 (s, 5, Cp), 4.51, 4.18, 4.00 (m, 4, CH_2), 2.74 (s, 12, CH_3 ortho), 2.11 (s, 6, CH_3 para), 1.30, 1.15, 1.07 (t, $^3J_{\text{HH}} = 7$ Hz, 6, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 155.8 (C ipso), 133.0 (C para), 131.7 (C ortho), 128.1 (C meta), 89.1 (Cp), 62.2 (m, CH_2), 61.0 (br d, CH_2), 60.8 (br d, CH_2), 20.7 (CH_3 para), 18.8 (CH_3 ortho), 16.6, 16.4, 16.3, 16.2 (CH_3). Anal. Calcd for $\text{C}_{35}\text{H}_{57}\text{N}_2\text{ClCoMoO}_9\text{P}_3$: C, 45.0; H, 6.1; N, 3.0. Found: C, 44.6; H, 6.2; N, 3.0.

$\text{TpMo}(\text{Nmes})_2\text{Cl}$ (3). To a mixture of $\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (0.3 g, 0.57 mmol) and KTp (0.14 g, 0.57 mmol) was added THF (35 mL). The brown solution was stirred at room temperature for 1 day, and the volatiles were removed under reduced pressure. The brown residue was extracted with Et_2O and filtered to remove KCl. The filtrate was concentrated and cooled to -20 °C. Green crystals of **3** were obtained in 55% yield. ^1H NMR (C_6D_6): δ 8.23 (d, $^3J_{\text{HH}} = 1.9$ Hz, 2, CH, pz), 7.34 (d, $^3J_{\text{HH}} = 2.2$ Hz, 1, CH, pz), 7.25 (t, $^3J_{\text{HH}} = 2.2$ Hz, 3, CH, pz), 6.62 (s, 4, CH, Ph), 5.75 (t, $^3J_{\text{HH}} = 1.9$ Hz, 2, CH, pz), 5.58 (t, $^3J_{\text{HH}} = 2.2$ Hz, 1, CH, pz), 2.30 (s, 12, CH_3 ortho), 2.08 (s, 6, CH_3 para). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 154.3 (C ipso), 144.4, 143.9, 136.0 (C, pz), 135.3 (C para), 133.6 (C, pz), 133.3 (C ortho), 128.6 (C meta), 105.6, 105.1 (C, pz), 20.6 (CH_3 para), 18.7 (CH_3 ortho). Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_6\text{ClBMo}$: C, 53.1; H, 5.2; N, 18.4. Found: C, 53.5; H, 5.5; N, 18.0.

$(\eta^2\text{-HL}_{\text{OEt}})\text{Mo}(\text{Nmes})_2\text{Cl}_2$ (4). A solution of HCl in Et_2O (10 mL), prepared *in situ* from ClSiMe_3 (0.2 mL, excess) and MeOH (1 mL), was added to a solution of $(\text{LOEt})\text{Mo}(\text{Nmes})_2\text{Cl}$ (0.10 g, 0.1 mmol) in

Et_2O (20 mL). The solution was stirred for 10 min. The solvent was removed in vacuo and the red oil obtained was extracted with Et_2O and concentrated in vacuo. Cooling the solution at -20 °C afforded compound **4** as a crystalline red solid. The reaction was quantitative by NMR. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): AX_2 spin system, δ 125.0 (t, $^2J_{\text{AX}} = 148$ Hz), 117.1 (d). ^1H NMR (C_6D_6): δ 14.5 (br, 1, OH), 6.55 (s, 4, CH, Ph), 5.15 (s, 5, Cp), 4.35, 4.23 (br, 6, CH_2), 2.60 (s, 12, CH_3 ortho), 2.05 (s, 6, CH_3 para), 1.2 (br m, 18, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 153.0 (C ipso), 138.7 (C para), 135.7 (C ortho), 128.6 (C meta), 90.2 (Cp), 62.8 (br m, CH_2), 20.7 (CH_3 para), 18.5 (CH_3 ortho), 16.5 (br, CH_3). Anal. Calcd for $\text{C}_{35}\text{H}_{58}\text{N}_2\text{Cl}_2\text{CoMoO}_9\text{P}_3$: C, 43.3; H, 6.0; N, 2.9. Found: C, 42.8; H, 6.3; N, 2.5.

$\text{Mo}(\text{Nmes})_2(\text{acac})_2$ (5). A mixture of $\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (0.52 g, 1 mmol) and $\text{Ti}(\text{acac})_3$ (0.61 g, 2 mmol) in THF (50 mL) was stirred at ambient temperature for 6 h. After removal of the solvent under vacuum the resulting residue was dissolved in petroleum ether (60 mL) and filtered to separate the TiCl_4 . The filtrate was concentrated and cooled to -20 °C. Compound **5** was obtained as a brown solid (0.36 g, 66%). ^1H NMR (C_6D_6): δ 6.68 (s, 4, CH, Ph), 5.28 (s, 2, CH, acac), 2.51 (s, 12, CH_3 ortho), 2.10 (s, 6, CH_3 para), 1.82, 1.74 (s, 6, CH_3 , acac). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 191.6, 185.6 (CO, acac), 156.1 (C ipso), 133.2 (C para), 129.8 (C ortho), 128.0 (C meta), 101.8 (CH, acac), 27.2, 26.2 (CH_3 , acac), 20.7 (CH_3 para), 18.5 (CH_3 ortho). Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{MoO}_4$: C, 60.0; H, 6.4; N, 5.0. Found: C, 60.0; H, 6.8; N, 4.5.

$\text{MoCl}_2(\text{Nmes})(\text{O})(\text{dme})$ (6). A suspension of $\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (0.79 g, 1.5 mmol) and $\text{MoCl}_2(\text{O})_2(\text{dme})$ (0.44 g, 1.5 mmol) in dme (35 mL) was heated at reflux, under nitrogen, for 6 h. The solution was cooled to ambient temperature and then evaporated to dryness. The residue was dissolved in Et_2O (120 mL), filtered, concentrated under reduced pressure, and cooled at -20 °C. Compound **6** was obtained as a microcrystalline red solid (0.72 g, 59%). ^1H NMR (C_6D_6): δ 6.51 (s, 2, CH, Ph), 3.44 (br, 6, CH_3O), 3.12 (br, 4, OCH_2), 2.86 (s, 6, CH_3 ortho), 2.04 (s, 3, CH_3 para). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 153.2 (C ipso), 139.5 (C para), 138.3 (C ortho), 128.4 (C meta), 70.7 (br, OCH_2), 63.0 (br, CH_3O), 20.7 (CH_3 ortho), 18.4 (CH_3 para). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NCl}_2\text{MoO}_3$: C, 38.4; H, 5.2; N, 3.5. Found: C, 38.4; H, 5.2; N, 3.1.

$(\text{LOEt})\text{Mo}(\text{Nmes})(\text{O})\text{Cl}$ (7). To a mixture of $\text{MoCl}_2(\text{Nmes})(\text{O})(\text{dme})$ (0.10 g, 0.25 mmol) and NaLOEt (0.14 g, 0.25 mmol) was added THF (25 mL). The resulting orange solution was stirred at ambient temperature overnight. The solvent was pumped off and Et_2O (50 mL) was added to dissolve the orange residue. Following filtration, the resulting solution was concentrated and cooled at -20 °C, giving **7** as a red crystalline solid (0.12 g, 60%). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 124.1 (br t, $J_{\text{PP}} = 156$ Hz), 112.8 (br t, $J_{\text{PP}} = 156$ Hz), 111.1 (br t, $J_{\text{PP}} = 156$ Hz). ^1H NMR (C_6D_6): δ 6.66 (s, 2, CH, Ph), 4.83 (s, 5, Cp), 4.44 (m, 6, CH_2), 4.10 (m, 4, CH_2), 3.89 (m, 2, CH_2), 3.06 (s, 6, CH_3 ortho), 2.12 (s, 3, CH_3 para), 1.25, 1.22, 1.21, 1.12, 1.07, 0.91 (t, $^3J_{\text{HH}} = 7$ Hz, 3, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 153.6 (C ipso), 138.4 (C para), 136.9 (C ortho), 128.0 (C meta), 89.0 (Cp), 62.2, 61.8, 61.8, 61.4, 60.6 (d, $J_{\text{CP}} = 9$ Hz, CH_2), 20.8 (CH_3 para), 18.4 (CH_3 ortho), 16.6, 16.4, 16.3, 16.1 (d, $J_{\text{CP}} = 6$ Hz, CH_3). Anal. Calcd for $\text{C}_{26}\text{H}_{46}\text{NClCoMoO}_{10}\text{P}_3$: C, 38.3; H, 5.6; N, 1.7. Found: C, 38.1; H, 5.7; N, 1.7.

$\text{TpMo}(\text{Nmes})(\text{O})\text{Cl}$ (8). A solution of $\text{MoCl}_2(\text{Nmes})(\text{O})(\text{dme})$ (0.16 g, 0.39 mmol) and KTp (0.10 g, 0.6 mmol) in THF (25 mL) was stirred at room temperature for 1 day. After the volatiles were removed, an orange solid was obtained. Dissolution in Et_2O , filtration, and cooling at -20 °C afforded orange crystals of **8** (0.09 g, 47%). ^1H NMR (C_6D_6): δ 8.42, 8.00, 7.77, 7.67, 7.64, 7.54 (d, $^3J_{\text{HH}} = 2$ Hz, 1, CH, pz), 6.86 (s, 2, Ph), 6.31, 6.19, 6.18 (t, $^3J_{\text{HH}} = 2$ Hz, 1, CH, pz), 2.48 (s, 6, CH_3 ortho), 2.40 (s, 3, CH_3 para). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 152.6 (C ipso), 144.1, 143.6, 143.0, 141.5 (C, pz), 141.4 (C para), 136.7 (C ortho), 134.7, 134.3 (C, pz), 128.5 (C meta), 106.5, 105.7, 105.2 (C, pz), 21.4 (CH_3 para), 18.4 (CH_3 ortho). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_7\text{ClBMoO}$: C, 43.8; H, 4.3; N, 19.9. Found: C, 43.5; H, 4.5; N, 19.6.

$(\text{Cp}^{\text{TMS}})\text{Mo}(\text{Nmes})(\text{O})\text{Cl}$ (9). To a solution of $\text{MoCl}_2(\text{Nmes})(\text{O})(\text{dme})$ (0.43 g, 1.06 mmol) in THF (35 mL) was added a 0.31 M THF solution of NaCp^{TMS} (3.42 mL, 1.06 mmol). The color of the suspension changed from red to brown, and the reaction mixture was

(33) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, 20, 119.

(34) This complex was prepared by a modification of the experimental procedure reported in: Kamenar, B.; Penavic, M.; Korpar-Colig, B.; Markovic, B. *Inorg. Chim. Acta* **1982**, 65, L245.

stirred at room temperature overnight. The volatiles were removed, the brown residue was extracted with petroleum ether and filtered to remove NaCl, and the solution was then concentrated. Cooling at -20°C gave orange crystals of **9** (0.21 g, 48%). ^1H NMR (C_6D_6): δ 6.57 (s, 2, CH, Ph), 6.44, 6.17, 6.03, 5.94 (s, 1, CH, Cp), 2.52 (s, 6, CH_3 ortho), 2.08 (s, 3, CH_3 para), 0.22 (s, 9, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 154.6 (C ipso, Ph), 139.3 (C para), 138.5 (C ortho), 128.5 (C meta), 124.8 (C ipso, Cp), 118.7, 116.7, 114.3, 111.1 (C, Cp), 21.4 (CH_3 para), 18.8 (CH_3 ortho), -0.89 ($\text{Si}(\text{CH}_3)_3$). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{NClMoOSi}$: C, 48.9; H, 5.8; N, 3.4. Found: C, 48.6; H, 5.8; N, 3.1.

Mo(Nmes)(O)(acac)₂ (10). A reaction flask was charged with $\text{MoCl}_2(\text{Nmes})(\text{O})(\text{dme})$ (0.31 g, 0.76 mmol) and $\text{Na}(\text{acac})$ (0.19 g, 1.53 mmol). THF was added (40 mL), and the suspension was stirred at ambient temperature for 5 h. The solvent was removed in vacuo. The crude product was extracted with ether (70 mL), and the NaCl was filtered off. The filtrate was concentrated; cooling the solution to -20°C afforded orange crystals of **10** (0.21 g, 62%). ^1H NMR (C_6D_6): δ 6.63 (s, 2, CH, Ph), 5.29, 5.23 (s, 1, CH, acac), 2.83 (s, 6, CH_3 ortho), 2.09 (s, 3, CH_3 para), 1.74, 1.73, 1.69, 1.67 (s, 3, CH_3 , acac). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 193.4, 192.2, 186.9, 185.1 (CO, acac), 154.1 (C ipso), 138.1 (C para), 128.1 (C ortho), 127.9 (C meta), 103.0, 102.0 (CH, acac), 27.2, 27.1, 25.7, 25.6 (CH_3 , acac), 20.8 (CH_3 para), 18.5 (CH_3 ortho). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NMoO}_5$: C, 51.5; H, 5.6; N, 3.2. Found: C, 51.5; H, 5.7; N, 2.9.

MoCl₃(Nmes)(dme) (11). A mixture of $\text{MoCl}_4(\text{THF})_2$ (0.52 g, 1.6 mmol) and $\text{MoCl}_2(\text{Nmes})_2(\text{dme})$ (0.85 g, 1.63 mmol) was refluxed in 35 mL of dme, under nitrogen. After 3 h, the suspension was filtered and the orange filtrate was taken to almost dryness in vacuo. Addition of Et_2O , in order to precipitate the product, afforded **11** as an orange solid (1.09 g, 79%). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NCl}_3\text{MoO}_2$: C, 36.7; H, 4.9; N, 3.3. Found: C, 33.3; H, 4.7; N, 3.4. No satisfactory analytical data (C percentage) could be obtained for this compound.

(LOEt)Mo(Nmes)Cl₂ (12). A reaction flask was charged with $\text{Mo}(\text{Nmes})\text{Cl}_3(\text{dme})$ (0.17 g, 0.40 mmol), and NaLOEt (0.22 g, 0.40 mmol) and THF (25 mL) were added. The orange solution was stirred at room temperature for 6 h. No change in color was observed. Volatiles were removed, and the orange residue was extracted with ether. NaCl was removed by filtration, and the solution was concentrated and cooled to -20°C to give an orange crystalline solid (0.23 g, 69%). $\mu_{\text{eff}}(\text{acetone}-d_6/\text{BuOH}, 9:1) = 1.67 \mu_{\text{B}}$. $\mu_{\text{eff}}(\text{solid state}) = 1.65 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{26}\text{H}_{46}\text{NCl}_2\text{CoMoO}_3\text{P}_3$: C, 37.4; H, 5.5; N, 1.7. Found: C, 37.5; H, 5.7; N, 1.7.

Mo(Nmes)Cl(acac)₂ (13). To a mixture of $\text{Mo}(\text{Nmes})\text{Cl}_3(\text{dme})$ (0.23 g, 0.54 mmol) and $\text{Ti}(\text{acac})$ (0.33 g, 1.08 mmol) was added THF (35 mL). The suspension was stirred at room temperature for 2 days. The solvent was then removed in vacuo, and the residue, extracted with Et_2O , filtered, and concentrated. Cooling the solution at -20°C afforded compound **13** as a brown crystalline solid (0.16 g, 65%). $\mu_{\text{eff}}(\text{Cl}_3\text{CD}/\text{BuOH}, 9:1) = 1.75 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NClMoO}_4$: C, 49.3; H, 5.4; N, 3.0. Found: C, 49.0; H, 5.7; N, 3.2.

Mo(Nmes)Cl₃(depe) (14). A solution of $\text{Mo}(\text{Nmes})\text{Cl}_3(\text{dme})$ (0.33 g, 0.8 mmol) in THF (40 mL) was treated with a 0.5 M solution of depe (1.6 mL, 0.8 mmol) in THF. Upon addition of depe, a color change from light orange to dark orange occurred. The solution was stirred for 2 days and then evaporated to dryness. The residue was extracted with CH_2Cl_2 and recrystallized from a mixture of CH_2Cl_2 /ether. Cooling at -20°C gave brown crystals of **14** (0.22 g, 52%). Anal. Calcd for $\text{C}_{19}\text{H}_{35}\text{NCl}_3\text{MoP}_2$: C, 42.1; H, 6.5; N, 2.6. Found: C, 42.2; H, 6.5; N, 2.6.

X-ray Diffraction Studies of Complexes 2, 12, and 14. A summary of the fundamental crystal data is given in Table 4. The crystals were coated with an epoxy resin and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo, Co, Cl, and P were taken from the *International Tables for X-Ray Crystallography*.³⁵ The structures were

Table 4. Crystallographic Data for **2**, **12**, and **14**

	2	12	14
formula	$\text{C}_{35}\text{H}_{57}\text{N}_2\text{O}_9\text{P}_3\text{-ClCoMo}$	$\text{C}_{26}\text{H}_{46}\text{NO}_9\text{P}_3\text{-Cl}_2\text{CoMo}$	$\text{C}_{19}\text{H}_{35}\text{NP}_2\text{-Cl}_3\text{Mo}$
fw	933.1	835.3	541.7
space group	$Pna2_1$	$P2_1/n$	$P2_1/n$
<i>a</i> , Å	25.075(4)	18.713(6)	10.911(3)
<i>b</i> , Å	12.293(6)	11.243(4)	16.348(9)
<i>c</i> , Å	14.203(2)	19.021(5)	13.752(8)
β , deg		94.04(2)	94.14(1)
<i>V</i> , Å ³	4378(2)	3607(2)	2447(2)
<i>Z</i>	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.4	1.54	1.47
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	8.74	11.2	9.9
temp, K	295	250	250
$\lambda(\text{Mo K}\alpha)$, Å (graphite monochromated)	0.710 69	0.710 69	0.710 69
<i>R</i> ^a	0.047	0.080	0.083
<i>R</i> _w ^b	0.048	0.095	0.089

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. Weighting scheme, see text.

solved by Patterson and Fourier methods. Empirical absorption corrections³⁶ were applied at the end of the isotropic refinements.

For complex **2**, a final refinement was undertaken with fixed isotropic factors and coordinates for all H atoms and unit weights. No trend in ΔF vs F_o or $(\sin \theta)/\lambda$ was observed.

Because of the crystal decomposition of **12** and the nonresolvable thermal and positional disorder, concerning the LOEt ligand, in spite of the low-temperature data collection, some C atoms have been refined only isotropically, leading to *R* values higher than usual. A mixed refinement was undertaken. Hydrogen atoms were included with fixed isotropic contributions at their calculated positions. In order to prevent bias on ΔF vs F_o or $(\sin \theta)/\lambda$, the last steps of the refinement were carried out with weights $w = w_1w_2$, where $w_1 = 1/(a + b|F_o|)^2$ and $w_2 = 1/(c + d(\sin \theta)/\lambda)$ with the following coefficients calculated by PESOS:³⁷ for $|F_o| < 36$, $a = 7.28$, $b = -0.11$ and for $550 > |F_o| > 36$, $a = 1.87$, $b = 0.03$; when $(\sin \theta)/\lambda < 0.5$, $c = 1.47$, $d = -1.53$ and for $0.7 > (\sin \theta)/\lambda > 0.5$, $c = 0.85$, $d = 0.29$.

In the case of complex **14**, in order to prevent bias on ΔF vs F_o or $(\sin \theta)/\lambda$, the last steps of the refinement were calculated by PESOS³⁷ with weights $w = w_1w_2$, where $w_1 = 1/(a + b|F_o|)^2$ and $w_2 = 1/(c + d(\sin \theta)/\lambda)$ with the following coefficients: for $|F_o| < 20$, $a = 5.67$, $b = -0.13$ and for $360 > |F_o| > 20$, $a = 1.55$, $b = 0.04$. Because of the crystal decomposition and the nonresolvable thermal disorder, in spite of the low-temperature data collection, the *R* values are higher than usual.

Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the *X-Ray 80 System*.³⁸

Acknowledgment. We thank the Spanish Ministry of Education (A.P.) and the Junta de Andalucía (F.M.) for research studentships. We gratefully acknowledge financial support from the DIGICYT and Junta de Andalucía. Thanks are also due to the University of Sevilla for the use of analytical and NMR facilities.

Supporting Information Available: Tables of crystal and refinement data, bond lengths and angles, fractional atomic coordinates and thermal parameters for **2**, **12**, and **14** (26 pages). Ordering information is given on any current masthead page.

IC961190A

(35) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4 pp 72–98.

(36) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

(37) Martínez-Ripoll, M.; Cano, F. H. *PESOS program*; Instituto Rocasolano, CSIC: Serrano, Madrid, Spain, 1975.

(38) Stewart, J. M. *XRAY80 System*; Computer Science Center, University of Maryland: College Park, MD, 1985.