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# Synthesis and Characterization of (2,4,6-Trimethylphenylimido)molybdenum Complexes. X-ray Crystal Structures of ($L_{OEt}$)Mo(Nmes)$_2$Cl, ($L_{OEt}$)Mo(Nmes)Cl$_2$, and MoCl$_3$(Nmes)(depe) (mes = 2,4,6-Trimethylphenyl, $L_{OEt}$ = ($\eta$-C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$, depe = Et$_2$PCH$_2$CH$_2$PEt$_2$)

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The bis(imido) complex MoCl$_2$(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)$_2$Cl (**2**) ($L_{OEt}$ = ($\eta$-C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$) and Mo(Nmes)$_2$(acac)$_2$ (**5**), as well as for the synthesis of the mixed oxo−imido MoCl$_2$(Nmes)(O)(dme) (**6**), the latter reaction involving conproportionation of **1** and MoCl$_2$(O)$_2$(dme). Similarly, the paramagnetic mono(imido) species Mo(Nmes)Cl$_3$(dme) (**11**) can also be obtained from **1** by interaction with MoCl$_4$(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)$_2$Cl (**2**), ($L_{OEt}$)Mo(Nmes)Cl$_2$ (**12**), and MoCl$_3$(Nmes)(depe) (**14**) (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$) 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 d$^2$ 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 MoCl$_2$(Nmes)(O)(dme) (**6**) (mes = 2,4,6-trimethylphenyl, dme = 1,2-dimethoxyethane) by a double transfer reaction that involves the conproportionation of bis(oxo) and bis(imido)

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⊗ 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. *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. 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. 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.

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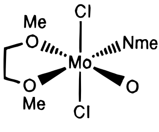
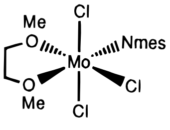


**6**



**11**

derivatives, as well as that of the Mo(V) organoimido Mo(Nmes)$Cl_3$(dme) (**11**) by the reaction of $MoCl_2(Nmes)_2$(dme) (**1**) with $MoCl_4(THF)_2$ (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 $\eta$-cyclopentadienyls, Kläui's ligand,[8] $L_{OEt}$ = ($\eta$-$C_5H_5$)Co{P(O)$(OEt)_2$}$_3$, and the hydrotris(pyrazolyl)borate, Tp = HB$(pz)_3$.[9]

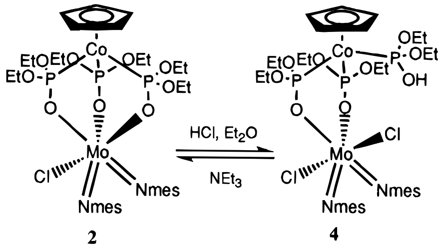
## Results and Discussion

**Synthesis and Structural Characterization of d$^0$ Bis(imido) Complexes of Molybdenum.** Our approach to the chemistry of these compounds makes use of the Mo(VI) derivative $MoCl_2(Nmes)_2$(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 $(NH_4)_2Mo_2O_7$ with 2,4,6-trimethylphenylamine, $H_2$Nmes, in the presence of $ClSiMe_3$ and $NEt_3$, in refluxing dme. While our work was in progress, the synthesis of **1** by the same procedure, but using $Na_2MoO_4$ 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$(Nmes)_2$Cl (**2**) and TpMo$(Nmes)_2$Cl (**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$(N^tBu)_2$Cl 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*-$CH_3$; 2.74, *o*-$CH_3$; 6.70 ppm, *m*-H; intensity ratio 6:12:4; data corresponding to complex **2**). Similarly, an $AX_2$ spin system appears in the $^{31}P\{^1H\}$ NMR spectrum of **2** ($\delta_A$ = 122.8, $\delta_X$ = 109.7 ppm, $J_{AX}$ = 158 Hz).

The crystal structure of ($L_{OEt}$)Mo$(Nmes)_2$Cl (**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 d$^0$ compound.[13]

An interesting reaction ensues when **2** is mixed with an $Et_2O$ solution of HCl (prepared *in situ* from $ClSiMe_3$ 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 $NEt_3$. Although the Cp protons of **4** are slightly shifted to lower field ($\delta$ 5.15, *versus* $\delta$ 4.88 in **2**), the $^{31}P\{^1H\}$ NMR spectrum still exhibits an $AX_2$ spin pattern ($\delta_A$ = 125.0, $\delta_X$ = 117.1 ppm, $^2J_{AX}$ = 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 $\delta$ 4.10−4.50 value found for the N−H proton in [(Tp*)Mo$(N^tBu)(NH^tBu)$Cl]$BF_4$ 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 advanced[14] for the product of the reaction of ($L_{OMe}$)Pt$(CH_3)_3$ and HCl, the reported $^1H$ NMR data being very similar to those of **4** (e.g., $\delta$ 5.32, Cp; 12.06, P−OH).



(1)

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$(NR)_2(S_2CNEt_2)_2$.[15] The proposed $C_2$ symmetry is based on the observation of two signals for the Me groups of the acac ligands, both in the $^1H$ and in the $^{13}C\{^1H\}$ 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).

**d$^0$ Mixed Oxo−Imido Complexes of Molybdenum.** The conproportion reaction of the bis(imido) $MoCl_2(Nmes)_2$(dme) (**1**) and the bis(oxo) $MoCl_2(O)_2$(dme), in refluxing dme, results in high yields of the mixed oxo−imido derivative $MoCl_2$(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 $MoCl_2$(*N*-1-adamantyl)(O)-

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(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.

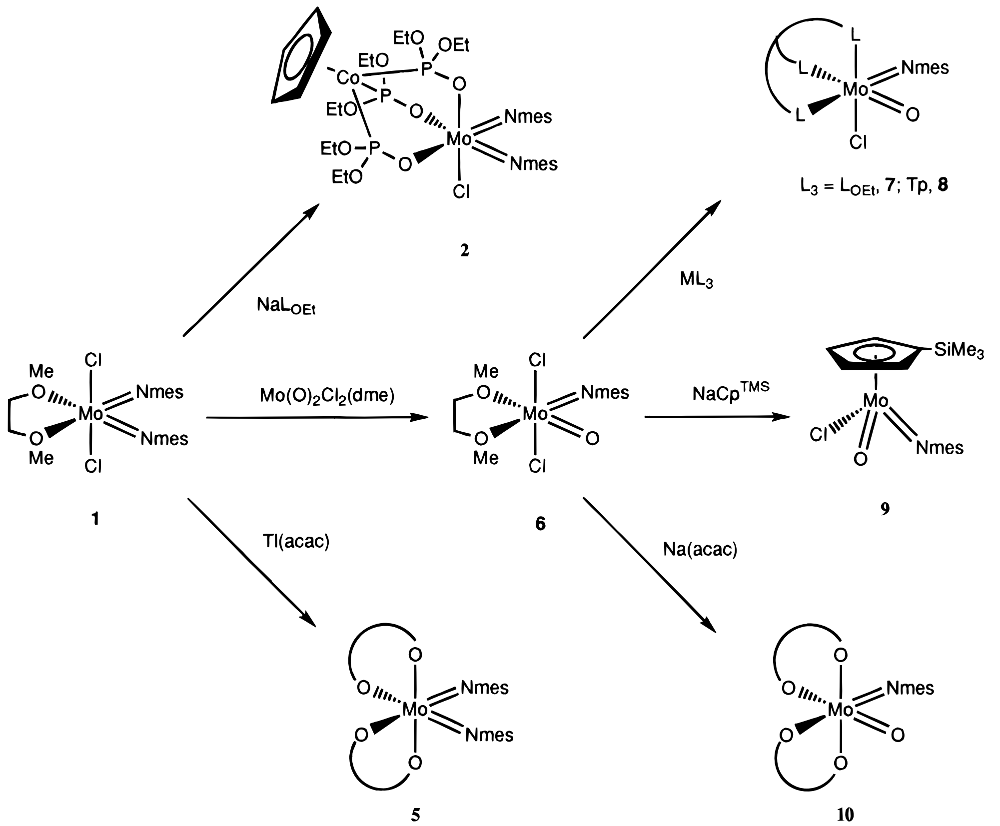
(12) (a) Kläui, W.; Müller, A.; Herbst, R.; Egert, E. *Organometallics* **1987**, *6*, 1824. (b) Kläui, W.; Hamers, H.; Pfeffer, M.; de Cian, A.; Fischer, J. *J. Organomet. Chem.* **1990**, *394*, 213.

(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**



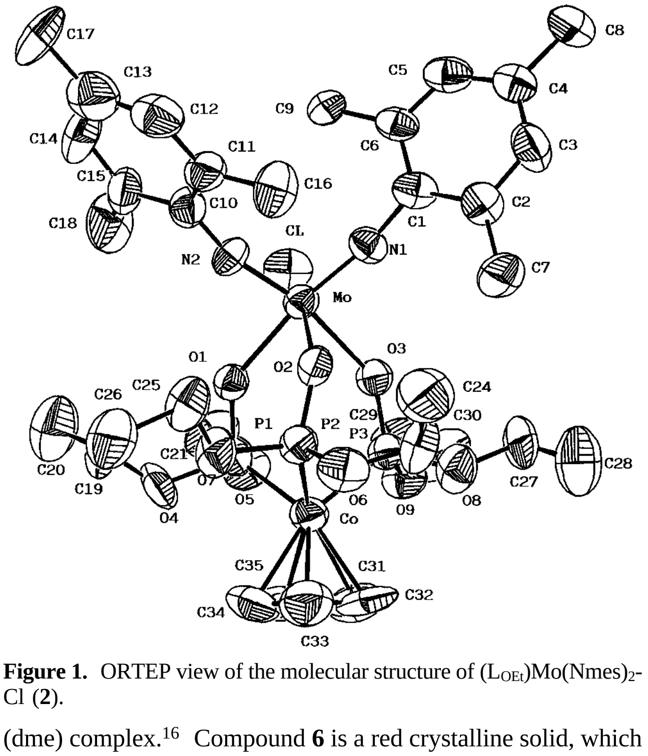


**Figure 1.** ORTEP view of the molecular structure of $(L_{OEt})Mo(Nmes)_2Cl$ (**2**).

(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 exits in the literature, e.g., the reactions between $OsO_4$ and $Mo(NAr)_2(O^tBu)_2$[17] and between $Mo(O)_2(O^tBu)_2$ and $Mo(NR)_2(O^tBu)_2$.[18] Compounds with two different organoimido ligands have also been prepared similarly, by reacting the corresponding $MoCl_2(NR^1)_2(dme)$ and $MoCl_2(NR^2)_2(dme)$ derivatives.[19]

**Table 1.** Selected Bond Lengths (Å) and Bond Angles (deg) for $(L_{OEt})Mo(Nmes)_2Cl$ (**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) | | |

As represented in Scheme 1, the interaction of **6** with $NaL_{OEt}$, KTp, $NaCp^{TMS}$ ($Cp^{TMS} = C_5H_4SiMe_3$), and Na(acac) gives the corresponding compounds $(L_{OEt})Mo(Nmes)(O)Cl$ (**7**), TpMo(Nmes)(O)Cl (**8**), $(Cp^{TMS})Mo(Nmes)(O)Cl$ (**9**), and $Mo(Nmes)(O)(acac)_2$ (**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

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(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.

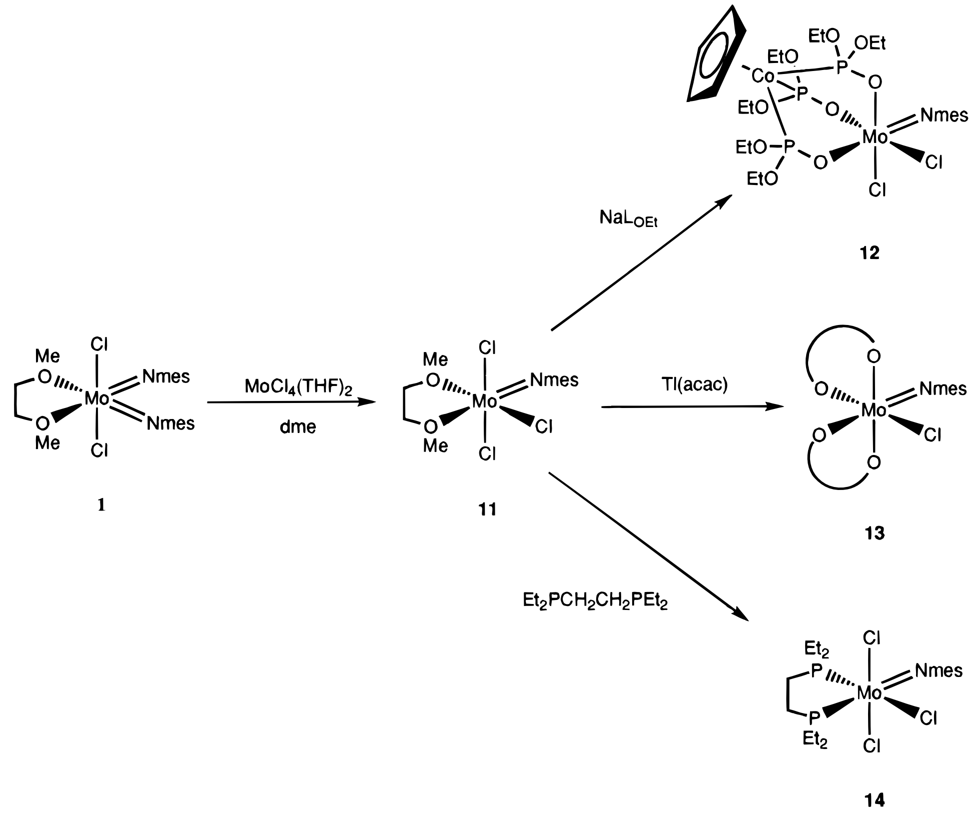
(17) Wolf, J. R.; Bazan, G. C.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 4155.

(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**

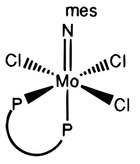


carbonyl and four methyl resonances are detected in the 185−194 and 25−27 ppm ranges, respectively, for the two inequivalent bidentate ligands. Additional spectroscopic data for these complexes are collected in the Experimental Section.

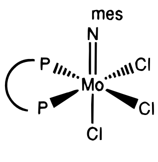
**d$^1$ Imido Complexes of Molybdenum.** A convenient entry into the chemistry of the d$^1$ Mo(Nmes) fragment has been developed. This is based in the conproportion reaction of **1** and $MoCl_4(THF)_2$ (Scheme 2), which provides high yields of the mono(imido) molybdenum(V) compound $MoCl_3$(Nmes)(dme) (**11**). This complex has chemical reactivity similar to that already described for **1** and **6**, treatment with $NaL_{OEt}$ and Tl(acac) yielding respectively ($L_{OEt}$)Mo(Nmes)$Cl_2$ (**12**) and Mo(Nmes)Cl(acac)$_2$ (**13**). Substitution of the coordinated dme can be achieved readily; addition of equimolar amounts of $Et_2PCH_2CH_2PEt_2$ (depe) to solutions of **11** gives $MoCl_3$(Nmes)(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' method[21] 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 $\mu_B$, 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.



**I**



**II**

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-

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

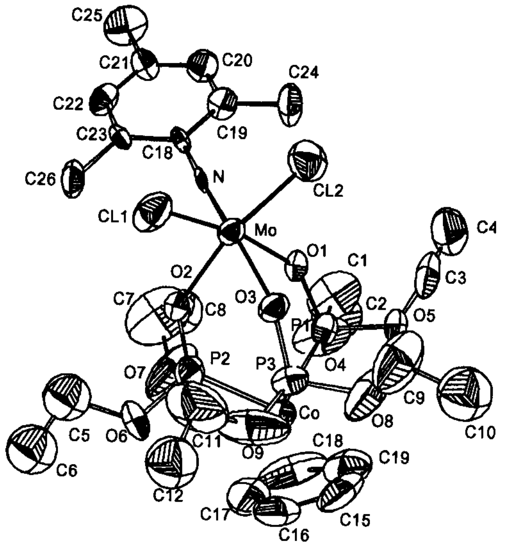

**Figure 2.** Molecular structure of $(L_{OEt})Mo(Nmes)Cl_2$ (**12**).

**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)°), 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)°, and since the Mo−P1 vector is perpendicular to the Mo−N vector (N−Mo−P1 = 91.1(4)°), 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)°.

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 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 radii[26]) have been reported in the literature, for example, 2.759(3) Å in $MoO_2(OSiPh_3)_2(PPh_3)$,[25] 2.727(4) Å in $W(NPh)(C{\equiv}CPh)_2(PhC{\equiv}CPh)(PMe_3)_2$,[27a] 2.765(2) Å in $W(N\text{-}C_6H_3\text{-}Pr^i{}_2\text{-}2,6)Cl_3(dppe)$,[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]

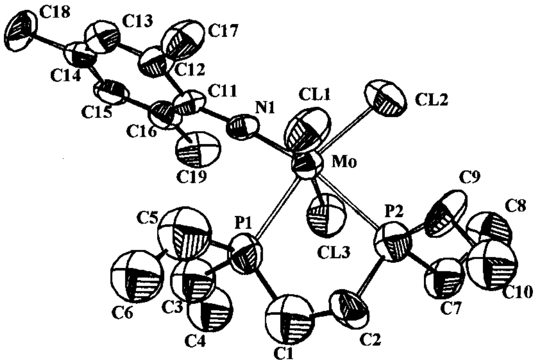

**Figure 3.** ORTEP drawing of $MoCl_3(Nmes)(depe)$ (**14**).

**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) | | |

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 (Δ(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 $W(N\text{-}C_6H_3\text{-}Pr^i{}_2\text{-}2,6)Cl_3(dppe)$,[27b] Δ(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** Δ(Mo−O) ≈ 0.05 Å; in $Mo(Ntol)Cl_3(PPh_2Et)_2$,[22] $Mo(Nallyl)Cl_3(PPh_3)_2$,[29] and $Mo(o\text{-}NC_6H_4NH_2)Cl_3(PMe_2Ph)_2$,[30] the three compounds having a *mer,trans* configuration, Δ(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 (Δ(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.

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## 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. $^1$H, $^{13}$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 method[21] 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 $MoCl_4(THF)_2$[33] and $MoCl_2(O)_2(dme)$[34] were prepared according to the literature procedures. $(NH_4)_2Mo_2O_7$ was purchased from commercial sources and used as received.

**$MoCl_2(Nmes)_2(dme)$ (1).** A solution of $(NH_4)_2Mo_2O_7$ (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%). $^1$H NMR ($C_6D_6$): $\delta$ 6.56 (s, 4, $\mathrm{C}H$, Ph), 3.38 (br, 6, $\mathrm{C}H_3\mathrm{O}$), 3.30 (br, 4, $\mathrm{OC}H_2$), 2.66 (s, 12, $\mathrm{C}H_3$ ortho), 2.02 (s, 6, $\mathrm{C}H_3$ para). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{21}H_{32}N_2Cl_2MoO_2$: C, 50.5; H, 6.1; N, 5.4. Found: C, 50.1; H, 6.5; N, 5.4.

**$(L_{OEt})Mo(Nmes)_2Cl$ (2).** A reaction flask was charged with $MoCl_2(Nmes)_2(dme)$ (0.6 g, 1.1 mmol) and $NaL_{OEt}$ (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%). $^{31}$P{$^1$H} NMR ($C_6D_6$): $AX_2$ spin system, $\delta$ 109.7 (d, $^2J_{PP}$ = 158 Hz), 122.8 (t). $^1$H NMR ($C_6D_6$): $\delta$ 6.70 (s, 4, $\mathrm{C}H$, Ph), 4.88 (s, 5, Cp), 4.51, 4.18, 4.00 (m, 4, $\mathrm{C}H_2$), 2.74 (s, 12, $\mathrm{C}H_3$ ortho), 2.11 (s, 6, $\mathrm{C}H_3$ para), 1.30, 1.15, 1.07 (t, $^3J_{HH}$ = 7 Hz, 6, $\mathrm{C}H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{35}H_{57}N_2ClCoMoO_9P_3$: C, 45.0; H, 6.1; N, 3.0. Found: C, 44.6; H, 6.2; N, 3.0.

**$TpMo(Nmes)_2Cl$ (3).** To a mixture of $MoCl_2(Nmes)_2(dme)$ (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. $^1$H NMR ($C_6D_6$): $\delta$ 8.23 (d, $^3J_{HH}$ = 1.9 Hz, 2, $\mathrm{C}H$, pz), 7.34 (d, $^3J_{HH}$ = 2.2 Hz, 1, $\mathrm{C}H$, pz), 7.25 (t, $^3J_{HH}$ = 2.2 Hz, 3, $\mathrm{C}H$, pz), 6.62 (s, 4, $\mathrm{C}H$, Ph), 5.75 (t, $^3J_{HH}$ = 1.9 Hz, 2, $\mathrm{C}H$, pz), 5.58 (t, $^3J_{HH}$ = 2.2 Hz, 1, $\mathrm{C}H$, pz), 2.30 (s, 12, $\mathrm{C}H_3$ ortho), 2.08 (s, 6, $\mathrm{C}H_3$ para). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{27}H_{32}N_8ClBMo$: C, 53.1; H, 5.2; N, 18.4. Found: C, 53.5; H, 5.5; N, 18.0.

**$(\eta^2\text{-}HL_{OEt})Mo(Nmes)_2Cl_2$ (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 $(L_{OEt})Mo(Nmes)_2Cl$ (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. $^{31}$P{$^1$H} NMR ($C_6D_6$): $AX_2$ spin system, $\delta$ 125.0 (t, $^2J_{AX}$ = 148 Hz), 117.1 (d). $^1$H NMR ($C_6D_6$): $\delta$ 14.5 (br, 1, $\mathrm{O}H$), 6.55 (s, 4, $\mathrm{C}H$, Ph), 5.15 (s, 5, Cp), 4.35, 4.23 (br, 6, $\mathrm{C}H_2$), 2.60 (s, 12, $\mathrm{C}H_3$ ortho), 2.05 (s, 6, $\mathrm{C}H_3$ para), 1.2 (br m, 18, $\mathrm{C}H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{35}H_{58}N_2Cl_2CoMoO_9P_3$: C, 43.3; H, 6.0; N, 2.9. Found: C, 42.8; H, 6.3; N, 2.5.

**$Mo(Nmes)_2(acac)_2$ (5).** A mixture of $MoCl_2(Nmes)_2(dme)$ (0.52 g, 1 mmol) and Tl(acac) (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 TlCl. The filtrate was concentrated and cooled to −20 °C. Compound **5** was obtained as a brown solid (0.36 g, 66%). $^1$H NMR ($C_6D_6$): $\delta$ 6.68 (s, 4, $\mathrm{C}H$, Ph), 5.28 (s, 2, $\mathrm{C}H$, acac), 2.51 (s, 12, $\mathrm{C}H_3$ ortho), 2.10 (s, 6, $\mathrm{C}H_3$ para), 1.82, 1.74 (s, 6, $\mathrm{C}H_3$, acac). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{28}H_{36}N_2MoO_4$: C, 60.0; H, 6.4; N, 5.0. Found: C, 60.0; H, 6.8; N, 4.5.

**$MoCl_2(Nmes)(O)(dme)$ (6).** A suspension of $MoCl_2(Nmes)_2(dme)$ (0.79 g, 1.5 mmol) and $MoCl_2(O)_2(dme)$ (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%). $^1$H NMR ($C_6D_6$): $\delta$ 6.51 (s, 2, $\mathrm{C}H$, Ph), 3.44 (br, 6, $\mathrm{C}H_3\mathrm{O}$), 3.12 (br, 4, $\mathrm{OC}H_2$), 2.86 (s, 6, $\mathrm{C}H_3$ ortho), 2.04 (s, 3, $\mathrm{C}H_3$ para). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{13}H_{21}NCl_2MoO_3$: C, 38.4; H, 5.2; N, 3.5. Found: C, 38.4; H, 5.2; N, 3.1.

**$(L_{OEt})Mo(Nmes)(O)Cl$ (7).** To a mixture of $MoCl_2(Nmes)(O)(dme)$ (0.10 g, 0.25 mmol) and $NaL_{OEt}$ (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%). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 124.1 (br t, $J_{PP}$ = 156 Hz), 112.8 (br t, $J_{PP}$ = 156 Hz), 111.1 (br t, $J_{PP}$ = 156 Hz). $^1$H NMR ($C_6D_6$): $\delta$ 6.66 (s, 2, $\mathrm{C}H$, Ph), 4.83 (s, 5, Cp), 4.44 (m, 6, $\mathrm{C}H_2$), 4.10 (m, 4, $\mathrm{C}H_2$), 3.89 (m, 2, $\mathrm{C}H_2$), 3.06 (s, 6, $\mathrm{C}H_3$ ortho), 2.12 (s, 3, $\mathrm{C}H_3$ para), 1.25, 1.22, 1.21, 1.12, 1.07, 0.91 (t, $^3J_{HH}$ = 7 Hz, 3, $\mathrm{C}H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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, $J_{CP}$ = 9 Hz, $CH_2$), 20.8 ($CH_3$ para), 18.4 ($CH_3$ ortho), 16.6, 16.4, 16.3, 16.1 (d, $J_{CP}$ = 6 Hz, $CH_3$). Anal. Calcd for $C_{26}H_{46}NClCoMoO_{10}P_3$: C, 38.3; H, 5.6; N, 1.7. Found: C, 38.1; H, 5.7; N, 1.7.

**$TpMo(Nmes)(O)Cl$ (8).** A solution of $MoCl_2(Nmes)(O)(dme)$ (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%). $^1$H NMR ($C_6D_6$): $\delta$ 8.42, 8.00, 7.77, 7.67, 7.64, 7.54 (d, $^3J_{HH}$ = 2 Hz, 1, $\mathrm{C}H$, pz), 6.86 (s, 2, Ph), 6.31, 6.19, 6.18 (t, $^3J_{HH}$ = 2 Hz, 1, $\mathrm{C}H$, pz), 2.48 (s, 6, $\mathrm{C}H_3$ ortho), 2.40 (s, 3, $\mathrm{C}H_3$ para). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 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 $C_{18}H_{21}N_7ClBMoO$: C, 43.8; H, 4.3; N, 19.9. Found: C, 43.5; H, 4.5; N, 19.6.

**$(Cp^{TMS})Mo(Nmes)(O)Cl$ (9).** To a solution of $MoCl_2(Nmes)(O)(dme)$ (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

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(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%). $^1$H NMR ($C_6D_6$): $\delta$ 6.57 (s, 2, C*H*, Ph), 6.44, 6.17, 6.03, 5.94 (s, 1, C*H*, Cp), 2.52 (s, 6, C$H_3$ ortho), 2.08 (s, 3, C$H_3$ para), 0.22 (s, 9, Si*Me*$_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 ($Si(CH_3)_3$). Anal. Calcd for $C_{17}H_{24}NClMoOSi$: 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 $MoCl_2$(Nmes)(O)(dme) (0.31 g, 0.76 mmol) and Na(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%). $^1$H NMR ($C_6D_6$): $\delta$ 6.63 (s, 2, C*H*, Ph), 5.29, 5.23 (s, 1, C*H*, acac), 2.83 (s, 6, C$H_3$ ortho), 2.09 (s, 3, C$H_3$ para), 1.74, 1.73, 1.69, 1.67 (s, 3, C$H_3$, acac). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 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 $C_{19}H_{25}NMoO_5$: C, 51.5; H, 5.6; N, 3.2. Found: C, 51.5; H, 5.7; N, 2.9.

**MoCl$_3$(Nmes)(dme) (11).** A mixture of $MoCl_4(THF)_2$ (0.52 g, 1.6 mmol) and $MoCl_2(Nmes)_2$(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 $C_{13}H_{21}NCl_3MoO_2$: 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.

**(L$_{OEt}$)Mo(Nmes)Cl$_2$ (12).** A reaction flask was charged with Mo(Nmes)$Cl_3$(dme) (0.17 g, 0.40 mmol), and Na$L_{OEt}$ (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%). $\mu_{eff}$(acetone-$d_6$/$^t$BuOH, 9:1) = 1.67 $\mu_B$. $\mu_{eff}$(solid state) = 1.65 $\mu_B$. Anal. Calcd for $C_{26}H_{46}NCl_2CoMoO_9P_3$: 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 Mo(Nmes)$Cl_3$(dme) (0.23 g, 0.54 mmol) and Tl(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%). $\mu_{eff}$($Cl_3CD$/$^t$BuOH, 9:1) = 1.75 $\mu_B$. Anal. Calcd for $C_{19}H_{25}NClMoO_4$: C, 49.3; H, 5.4; N, 3.0. Found: C, 49.0; H, 5.7; N, 3.2.

**Mo(Nmes)Cl$_3$(depe) (14).** A solution of Mo(Nmes)$Cl_3$(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 $C_{19}H_{35}NCl_3MoP_2$: 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 $\kappa$ diffractometer. The cell dimensions were refined by least-squares fitting of the $\theta$ 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 solved by Patterson and Fourier methods. Empirical absorption corrections[36] were applied at the end of the isotropic refinements.

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

| | **2** | **12** | **14** |
|---|---|---|---|
| formula | $C_{35}H_{57}N_2O_9P_3ClCoMo$ | $C_{26}H_{46}NO_9P_3Cl_2CoMo$ | $C_{19}H_{35}NP_2Cl_3Mo$ |
| fw | 933.1 | 835.3 | 541.7 |
| space group | *Pna*2$_1$ | *P*2$_1$/*n* | *P*2$_1$/*n* |
| *a*, Å | 25.075(4) | 18.713(6) | 10.911(3) |
| *b*, Å | 12.293(6) | 11.243(4) | 16.348(9) |
| *c*, Å | 14.203(2) | 19.021(5) | 13.752(8) |
| $\beta$, deg | | 94.04(2) | 94.14(1) |
| *V*, Å$^3$ | 4378(2) | 3607(2) | 2447(2) |
| *Z* | 4 | 4 | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.4 | 1.54 | 1.47 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 8.74 | 11.2 | 9.9 |
| temp, K | 295 | 250 | 250 |
| $\lambda$(Mo K$\alpha$), Å (graphite monochromated) | 0.710 69 | 0.710 69 | 0.710 69 |
| $R^a$ | 0.047 | 0.080 | 0.083 |
| $R_w{}^b$ | 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.

For complex **2**, a final refinement was undertaken with fixed isotropic factors and coordinates for all H atoms and unit weights. No trend in $\Delta F$ 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 $L_{OEt}$ 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 $\Delta F$ 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 $\Delta F$ vs $F_o$ or (sin $\theta$)/$\lambda$, the last steps of the refinement were calculated by PESOS[37] 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]

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**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.

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