Molybdenum Amido Complexes with Single Mo–N Bonds: Synthesis, Structure, and Reactivity

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Abstract: Reactions of the complex [MoCl(η^3-C_3H_4-Me-2)$(CO)_2$(phen)] (**1**) (phen = 1,10-phenanthroline) with potassium arylamides were used to synthesize the amido complexes [Mo(N(R)Ar)(η^3-C_3H_4-Me-2)$(CO)_2$(phen)] (R = H, Ar = Ph, **2a**; R = H, Ar = *p*-tolyl, **2b**; R = Me, Ar = Ph; **2c**). For **2b** the Mo–N(amido) bond length (2.105(4) Å) is consistent with it being a single bond, with which the metal attains an 18-electron configuration. The reaction of **2b** with HOTf affords the amino complex [Mo(η^3-C_3H_4-Me-2)(NH_2(*p*-tol))$(CO)_2$(phen)]OTf (**3**-OTf). Treatment of **3**-OTf with *n*BuLi or KN($SiMe_3$)$_2$ regenerates **2b**. The new amido complexes react with CS_2, arylisothiocyanates and maleic anhydride. A single product corresponding to the formal insertion of the electrophile into the Mo–N(amido) bond is obtained in each case. For maleic anhydride, ring opening accompanied the formation of the insertion product. The reaction of **2b** with maleimide affords [Mo(η^3-C_3H_4-Me-2){NC(O)CH=CHC(O)}$(CO)_2$(phen)] (**7**), which results from simple acid–base metathesis. The reaction of **2b** with (*p*-tol)NCO affords [{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}$_2$(η^2-MoO_4)] (**8**), which corresponds to oxidation of one third of the metal atoms to Mo^{VI}. Complex **8** was also obtained in the reactions of **2b** with CO_2 or the lactide 3,6-dimethyl-1,4-dioxane-2,5-dione. The structures of the compounds **2b**, **3**-OTf, [Mo(η^3-C_3H_4-Me-2){SC(S)(N(H)Ph)}$(CO)_2$(phen)] (**4**), [Mo(η^3-C_3H_4-Me-2){SC(N(*p*-tol))(NH(*p*-tol))}$(CO)_2$(phen)] (**5a**), and [Mo(η^3-C_3H_4-Me-2){OC(O)CH=CHC(O)(NH(*p*-tol))}$(CO)_2$(phen)] (**6**), **7**, and **8** (both the free complex and its *N*,*N*′-di(*p*-tolyl)urea adduct) were determined by X-ray diffraction.

Keywords: allyl ligands · amido ligands · carbonyl ligands · insertion · molybdenum

Introduction

Most transition-metal amido complexes feature elements from the left side of the d block in intermediate to high oxidation states.[1, 2] In these compounds, pπ → dπ donation from the amido lone pair to empty metal d orbitals results in a double M–N(amido) bond. Much current interest is attracted by the growing number of low valent, organometallic-type amido complexes of the late transition metals (Groups 8–10) without the possibility of pπ → dπ donation.[3–9] Group 7 is represented within this category by a few rhenium complexes that still possess single Re–N(amido) bonds,[10] and this seems to be the limit toward the left of the periodic system. Thus, a limited number of low-valent molybdenum and tungsten organometallic amido complexes are known, but for all of them a double bond to the amido group must be considered for the metal to attain an 18-electron configuration.[11] Accordingly, short Mo–N bonds have been found for the derivatives whose structures have been crystallographically determined.[12] We have recently found that the reactions of [MoCl(η^3-allyl)$(CO)_2$(N–N)] (N–N = 2,2′-bipyridine or 1,10-phenanthroline) complexes with alkaline alkoxides or hydroxide allow the straightforward preparation of new alkoxo or hydroxo compounds.[13] Here we report the application of a similar method to the synthesis of the first molybdenum amido complexes with single Mo-amido bonds,[14] and a study of their structure and reactivity.

Results and Discussion

The complex [MoCl(η^3-C_3H_4-Me-2)$(CO)_2$(phen)] (**1**)[15] reacts with an equimolar amount of KN(H)Ar (Ar = phenyl or

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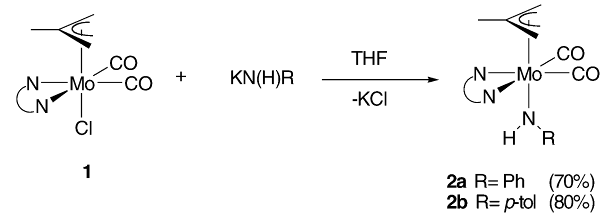
4-methylphenyl (*p*-tolyl)) (generated in situ from the corresponding arylamine and $KN(SiMe_3)_2$) in tetrahydrofuran (THF). The reactions are instantaneous at −78 °C and are accompanied by a change in the color of the solution from garnet to red-brown. The IR spectrum of the product displays two intense ν_{CO} bands at frequencies significantly lower than those of the precursor **1**.[16] This is consistent with a substitution of the Cl ligand by an amido group. Thus, the stronger π-donor character of the latter increases the electron density available for back-donation from the metal center to the CO ligands. The red-brown arylamido complexes **2a** (Ar = Ph) and **2b** (Ar = *p*-tolyl), obtained as single products, could be isolated in good yield after a simple workup procedure (see Experimental Section). The ^1H NMR spectra of **2a**–**b** showed the presence of an intact η^3-methallyl group, confirming that the metal, and neither the allyl ligand nor the carbonyls,[17] has been the site of the amide attack, in line with our recent results employing alkyl,[18] alkoxide,[13b] or hydroxide[13c] nucleophiles toward molybdenum chloro complexes such as **1**. Broad, one-hydrogen singlets at $\delta = 3.88$ (**2a**) and 3.90 ppm (**2b**) in CD_2Cl_2 were assigned to the nitrogen-bonded hydrogen of the amido ligands.[19] The ^1H and ^{13}C NMR spectra indicate, besides of the presence of the N(H)Ar group, the existence of a molecular mirror plane and, therefore, the geometry depicted in Scheme 1 for the amido complexes $[Mo(N(H)Ar)(\eta^3\text{-}C_3H_4\text{-}Me\text{-}2)(CO)_2(phen)]$ (**2a**,**b**). The molecular structure of **2b** in the solid state was determined by single-crystal X-ray diffraction. A thermal ellipsoid plot is displayed in Figure 1, and selected distances and angles are given in Table 1.



Scheme 1. Synthesis of the amido complexes **2a** and **2b** from the chloro precursor **1**.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2b**.

Mo(1)–C(2)	1.962(4)	Mo(1)–N(3)	2.105(4)
Mo(1)–C(1)	1.962(5)	Mo(1)–N(1)	2.266(3)
Mo(1)–C(3)	2.356(4)	Mo(1)–N(2)	2.260(4)
Mo(1)–C(4)	2.280(4)	N(3)–C(31)	1.370(6)
Mo(1)–C(5)	2.354(4)		
C(2)-Mo(1)-C(1)	80.07(18)	C(1)-Mo(1)-N(2)	168.79(16)
C(2)-Mo(1)-N(3)	92.96(17)	N(2)-Mo(1)-N(1)	72.72(12)
C(1)-Mo(1)-N(1)	89.92(16)	C(1)-Mo(1)-N(3)	89.92(16)
C(2)-Mo(1)-N(2)	102.02(16)	C(31)-N(3)-Mo(1)	136.1(3)

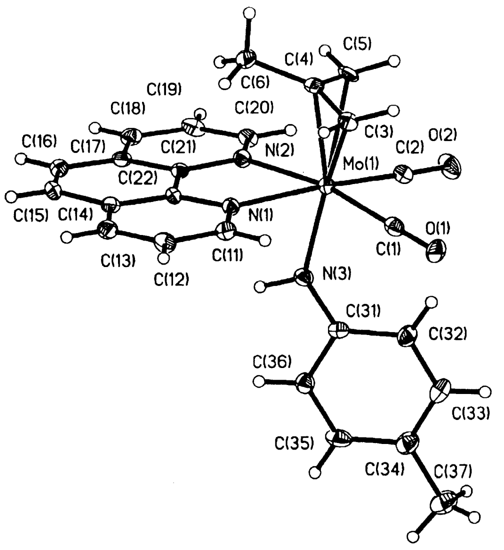
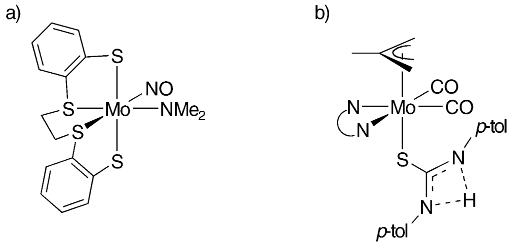


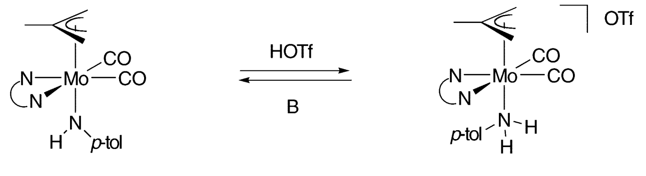
Figure 1. Structure of **2b** (thermal ellipsoid (30 %) plot).



Scheme 2. a) Graphic representation of the compound $[Mo(NO)(NMe_2)(dttd)]$;[20] b) hydrogen exchange between the two nitrogens in **5a** makes the two aryl groups equivalent.

The Mo–N(amido) bond length of 2.105(4) Å, is significantly longer than the value of 1.924(8) Å found in the complex $[Mo(NO)(NMe_2)(dttd)]$ (see Scheme 2 a),[20] for which a double Mo–N bond resulting from pπ → dπ donation has been inferred from its high barrier to rotation of the Mo–N bond. This complex seems appropriate for a comparison because it shares with our amido complexes the 18-electron configuration, the lack of bulky substituents, the pseudooctahedral geometry and the presence of strongly π-acceptor coligands (NO, CO). The greater length in **2b** is consistent with a single bond, with which this complex attains an 18-electron configuration. For amido complexes like **2a**,**b**, a repulsive interaction between the amido lone electron pair and filled molybdenum d orbitals can be expected to weaken the Mo–N(amido) bond and to enhance the basicity and nucleophilicity of the amido ligand.[21, 22] However, this can be compensated for, at least in part, by lone pair delocalization into the amido aryl substituent, and by donation of electron density from the amido to the carbonyl ligands using the metal d orbitals (push-pull).[21] The importance of the first factor in the stabilization of the amido complexes is strongly supported by the consistent failure of our attempts to isolate related amido derivatives lacking aryl substituents. In fact, low-valent amido complexes without aryl groups are very rare and, as expected, they are much more reactive than arylamido counterparts.[23] A structural consequence of the lone pair delocalization involving the aryl substituent is the fact that, even for complexes in which amido → metal pπ → dπ donation is forbidden, a planar geometry is often found around the amido nitrogen atom. Thus, for **2b** the N–H hydrogen atom on the amido nitrogen atom was located in the difference maps (H3 and H53 for the two molecules present in the asymmetric unit), given a fixed temperature factor ($U_{\mathrm{iso}} = 0.08$) and its coordinates were freely refined. The sum of angles around the amido nitrogen atoms was found to be 358.4(6) and 358.0(6)° for the two molecules in the asymmetric unit, indicating the planarity of the amido group. With regard to the presence of the CO coligands, their role in accepting, at least in part, the electron density donated by the amido group is indicated by the lowering in the ν_{CO} values mentioned above. However, it must be noticed that none of the carbonyl groups of complexes **2a**,**b** are *trans* to the amido ligand, the geometry that maximizes the mutual stabilization of π-donor/π-acceptor ligands.[24]

The reaction of the amido complex **2b** with an equimolar amount of the acid HOTf (OTf = trifluoromethylsulfonate) affords the salt [Mo(η^3-C_3H_4-Me-2)(NH_2Ar)$(CO)_2$(phen)]-OTf (**3**-OTf, Ar = *p*-tolyl) (Scheme 3), which could be isolated in high yield by crystallization (see Experimental Section).[25]



2b B= BuLi or KN(SiMe$_3$)$_2$ **3** (93%)

Scheme 3. Protonation of the amido complex **2b** to afford the amino complex **3**-OTf. Deprotonation of **3**-OTf regenerates **2b**.

Table 2. Selected bond lengths [Å] and angles [°] for complex **3**-Otf.

Mo(1)–C(2)	1.979(5)	Mo(1)–N(3)	2.303(3)
Mo(1)–C(1)	1.964(5)	Mo(1)–N(1)	2.243(3)
Mo(1)–C(3)	2.256(4)	Mo(1)–N(2)	2.239(3)
Mo(1)–C(4)	2.318(4)	N(3)–C(31)	1.449(5)
Mo(1)–C(5)	2.329(4)		
C(2)-Mo(1)-C(1)	81.6(2)	C(1)-Mo(1)-N(2)	100.98(16)
C(2)-Mo(1)-N(3)	88.19(15)	N(2)-Mo(1)-N(1)	73.72(12)
C(1)-Mo(1)-N(1)	169.71(15)	C(1)-Mo(1)-N(3)	88.55(16)
C(2)-Mo(1)-N(2)	167.61(16)	C(31)-N(3)-Mo(1)	116.9(2)

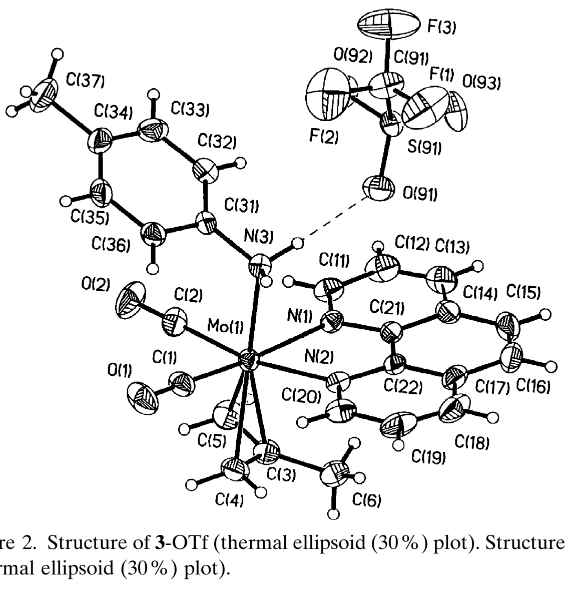
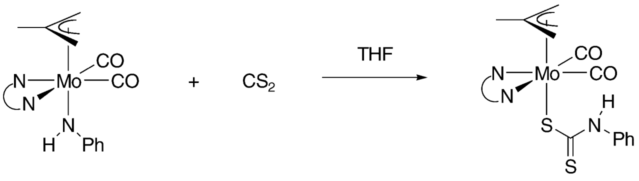


Figure 2. Structure of **3**-OTf (thermal ellipsoid (30%) plot). Structure of **4** (thermal ellipsoid (30%) plot).

The IR spectrum of **3**-OTf showed two strong, similarly intense carbonyl bands at wavenumbers significantly higher than those of **2b**. This is consistent with the formation of a cationic *cis*-dicarbonyl complex. In its ^{1}H NMR spectrum, a single broad signal at $\delta = 5.49$ ppm is assigned to the two N–H amine hydrogens. The structure of **3**-OTf was determined by single-crystal X-ray diffraction (Figure 2 and Table 2). The cation, in regard to the geometry around the metal, is isostructural with the amido precursor; that is consistent with one *p*-tolylamine ligand bound to a {Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)} fragment in the position *trans* to the allyl group.[26] There is a strong hydrogen bond (N(3)···O(91) = 3.050(5) Å) N–H···O interaction (showed as a dashed line in Figure 2) involving one amine N–H bond and one of the oxygen atoms of the triflate anion. The Mo–N(amine) (2.303(3) Å) bond is longer than the corresponding distance in the amido complex **2b** (see above), as expected for a dative bond compared with a covalent one.[28] The distance between the amine nitrogen atom and the *ipso*-carbon atom of the *p*-tolyl group is longer in **3**-OTf (1.449(5) Å) than in **2b** (1.370(6) Å), indicating that significant delocalization of the nitrogen lone pair of the amido ligand takes place involving the aryl group. This feature has been found in other arylamido complexes[29] and explains the planarity of the di-*p*-tolylamido ligand found in the related complex [Mo(η^3-C_3H_4-Me-2)(NAr_2)$(CO)_2$(phen)],[14] a similar 18-electron species for which pπ → dπ to molybdenum would also be forbidden.

The formation of **3**-OTf as the single product in the reaction of **2b** with the very strong acid HOTf shows that the protonation of the amido ligand is strongly favored over that of the allyl group, the latter being a known reaction of some (allyl)molybdenum dicarbonyl complexes.[18] The fact that the product of the reaction is the cationic amino complex, isolated as the triflate salt, stands in contrast to the quantitative formation of the neutral triflato complex in the reaction of the related alkyl or alkoxo complexes with HOTf,[13b, 18a] and reflects the better ligating properties of amines in comparison with alkanes or alcohols. In fact, compound **3**-OTf can be obtained by reaction of the triflato complex [Mo(η^3-C_3H_4-Me-2)(OTf)$(CO)_2$(phen)] with *p*-tolylamine.[25, 30] Deprotonation of the amino complex with strong bases (*n*BuLi, KN(SiMe$_3$)$_2$) cleanly affords **2b**, thus offering an alternative access to the amido complex. Although for the molybdenum compounds reported here both methods are satisfactory, it has been found in some instances that the deprotonation of coordinated amines is a better choice due to the enhancement of the acidity of the amine resulting from its coordination to a cationic metal center.[31] The amido complex **2b** did not react with a weak acid such as phenylacetylene (p$K_a = 23.2$).[32] Thus, the basicity of the amido group is tempered by the presence of the aryl group as an amido substituent and of the π-acceptor carbonyl ligands, as it was suggested above (however, as will be described below, **2b** reacts with the weakly acidic maleimide (p$K_a = 10.8$)[33]).

With a good preparative method at hand, we have explored the reactivity of the new amido complexes. Complex **2a** reacts with carbon disulfide to afford the new complex **4** (Scheme 4), which was characterized by IR and NMR spectroscopy (see Experimental Section) in solution, and by X-ray diffraction in the solid state (see Figure 3 and Table 3). The molecule of **4** consists of a {Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)} fragment bonded to one of the sulfur atoms of a *N*-phenyldithiocarbamate ligand, resulting from the formal insertion of CS_2 into the Mo–N bond,[34] *trans* to the allyl ligand.



2a

4 (86%)

Scheme 4. Insertion of CS_2 into a M–N(amido) bond gives compound **4**, featuring a monodentate dithiocarbamate ligand.

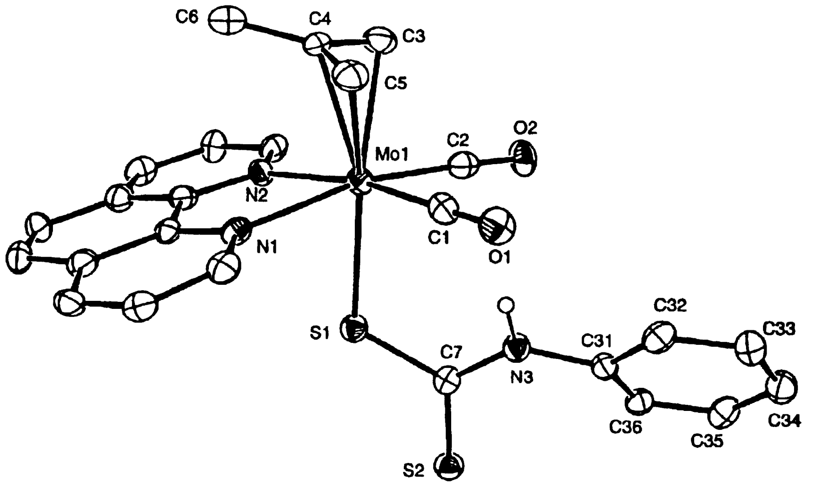


Figure 3.

The Mo–S length in **4** (2.508(3) Å) is very close to that in the complex [Mo{SC(NPh)OCH_3}(η^3-C_3H_4-Me-2)$(CO)_2$(phen)],[13b] obtained by reaction of the corresponding methoxo complex with phenylisothiocyanate (2.493(2) Å); the two C–S bond lengths (1.711(9) Å and 1.689(9) Å) are intermediate between single and double bond values,[35] and similar to those found in [CpM{SC(S)NR_2}$(CO)_3$] complexes (M = Cr, W).[36] The solution spectroscopic data of **4** (see Experimental Section) agree well with the structure found in the solid state.

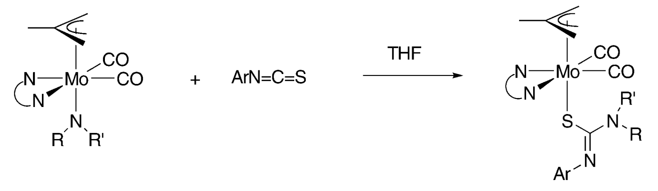
Table 3. Selected bond lengths [Å] and angles [°] for complex **4**.

Mo(1)–C(2)	1.965(8)	Mo(1)–S(1)	2.5114(18)
Mo(1)–C(1)	1.958(8)	S(1)–C(7)	1.718(7)
Mo(1)–C(3)	2.316(7)	S(2)–C(7)	1.695(7)
Mo(1)–C(4)	2.296(7)	C(7)–N(3)	1.351(9)
Mo(1)–C(5)	2.344(7)	N(3)–C(31)	1.413(9)
C(2)-Mo(1)-C(1)	83.9(3)	C(1)-Mo(1)-S(1)	95.2(2)
C(2)-Mo(1)-N(1)	166.3(3)	C(7)-S(1)-Mo(1)	116.9(3)
C(1)-Mo(1)-N(1)	98.7(2)	N(3)-C(7)-S(2)	123.4(5)
C(2)-Mo(1)-N(2)	102.2(2)	N(3)-C(7)-S(1)	117.1(5)
C(1)-Mo(1)-N(2)	170.3(3)	S(2)-C(7)-S(1)	119.5(4)
N(2)-Mo(1)-N(1)	73.68(18)	C(7)-N(3)-C(31)	133.6(6)

It is instructive to compare the reaction of **2a** with CS_2 to yield **4** with the formation of complex [Mo(η^3-C_3H_4-Me-2)(SC(OMe)NPh)$(CO)_2$(phen)][13b] (containing a monodentate xanthate group) by reaction of CS_2 with the methoxo complex [Mo(η^3-C_3H_4-Me-2)(OMe)$(CO)_2$(phen)]. Thus, whereas at room temperature the formation of **4** takes 15 min, the insertion of CS_2 into the Mo–O bond is instantaneous.[13b] The ν_{CO} values of the amido complex **2a** are slightly lower than those of the methoxo derivative (1931 and 1843 cm^{-1} in CH_2Cl_2). This can be taken as an indication of a more electron-rich fragment for the amido complex, which could therefore be expected to be more nucleophilic. The fact that the reaction with CS_2 is faster for the alkoxo complex than for its amido counterpart can thus be attributed to a more difficult approach of the CS_2 molecule to the more sterically congested amido ligand. A similar predominance of steric effects in the reactions with carbon disulfide has been previously found for the series [Re(OR)(bipy)$(CO)_3$] (R = Me, Et, *t*Bu).[13b]

Dithiocarbamate derivatives are known for different oxidation states of virtually every metal.[37] In most of these compounds the dithiocarbamate ligand acts as an *S,S'*-bidentate chelate, and the monodentate coordination mode is rare. In complex **4** this coordination is enforced by the saturated nature of the metal fragment.[36]

Complex **2b** reacted with *p*-tolylisothiocyanate[38] to afford [Mo(η^3-C_3H_4-Me-2){SC(NHAr)-NAr}$(CO)_2$(phen)] (**5a**) (Ar = *p*-tolyl), the product of the formal insertion of the isothiocyanate into the Mo–N(amido) bond (Scheme 5). The IR and ^1H NMR spectra indicated the incorporation of the isothiocyanate and the formation of a single product, but did not allow the proposal of its structure, and low solubility precluded the acquisition of the ^{13}C NMR spectrum. The structure of **5a** was determined by single-crystal X-ray diffraction, and the results are presented in Figure 4 and Table 4. The molecule contains a *N,N'*-di(*p*-tolyl)thioureato ligand bonded through the sulfur atom to a {Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)} fragment. The Mo–S length (2.5081(9) Å) is similar to that found in **4** (see above), and the bond lengths C(10)–N(3) (1.382(4) Å) and C(10)-N(4) (1.273(4) Å) correspond to a single and double bond, respectively. The geometry of the SCN_2 moiety is planar, as indicated by the value of 360° for the sum of angles



	R	R'
2b	H	*p*-tol
2c	Me	Ph

	R	R'	Ar	Yield
5a	H	*p*-tol	*p*-tol	80%
5b	Me	Ph	Ph	57%

Scheme 5. Insertion of isothiocyanates into an M–N(amido) bond is the origin of compounds **5a**–**b**.

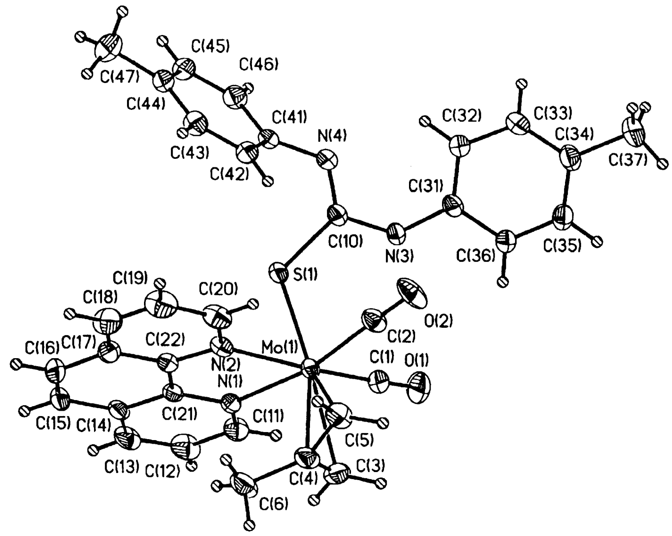


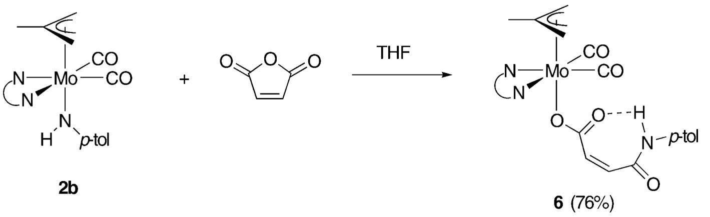
Figure 4. Structure of **5a** (thermal ellipsoid (30%) plot).

Table 4. Selected bond lengths [Å] and angles [°] for complex **5a**.

Mo(1)–C(2)	1.962(3)	S(1)–C(10)	1.780(3)
Mo(1)–C(1)	1.943(4)	N(3)–C(10)	1.382(4)
Mo(1)–C(3)	2.338(3)	N(4)–C(10)	1.273(4)
Mo(1)–C(4)	2.270(3)	N(3)–C(31)	1.413(3)
Mo(1)–C(5)	2.340(3)	N(4)–C(41)	1.411(4)
Mo(1)–S(1)	2.5081(9)		
C(2)-Mo(1)-C(1)	81.78(13)	N(1)-Mo(1)-S(1)	78.52(6)
C(2)-Mo(1)-N(1)	167.03(10)	N(2)-Mo(1)-S(1)	79.78(6)
C(1)-Mo(1)-N(1)	99.68(11)	C(10)-S(1)-Mo(1)	111.96(9)
C(2)-Mo(1)-N(2)	103.86(11)	N(3)-C(10)-S(1)	114.9(2)
C(1)-Mo(1)-N(2)	169.27(11)	C(10)-N(4)-C(41)	123.2(2)
N(2)-Mo(1)-N(1)	72.77(8)	N(4)-C(10)-S(1)	124.6(2)
C(1)-Mo(1)-S(1)	91.36(9)	N(4)-C(10)-N(3)	120.4(2)
C(2)-Mo(1)-S(1)	88.58(9)		

around C(10). In the ^{1}H NMR spectrum the two *p*-tolyl groups are seen as equivalent and no signal is observed for the N(3)-bonded hydrogen. These facts are consistent with a shift of this hydrogen between N(3) and N(4), as represented in Scheme 2b, in solution. To check this, we sought to study the reaction of PhNCS with an amido complex similar to **2b**, but lacking the N–H bond. Thus, the product of the reaction of phenylisothiocyanate with [Mo(N(Me)Ph)(η^3-C_3H_4-Me-2)-$(CO)_2$(phen)] (**2c**) (generated from **1** and potassium *N*-methyl-*N*-phenylamide) displayed spectroscopic and analytical data (see Experimental Section) consistent with a [Mo(η^3-C_3H_4-Me-2){SC(N(Me)Ph)NPh}$(CO)_2$(phen)] (**5b**) formulation, and, in contrast with **5a**, two inequivalent (^{1}H and ^{13}C NMR spectra) phenyl groups, supporting the rationale given above for the NMR equivalence of the two aryl groups of **5a**.

The amido complex **2b** reacted with maleic anhydride to afford the ring-opened product **6** showed in Scheme 6.[39] The most relevant spectroscopic data of **6** are the two one-hydrogen singlets at $\delta = 5.45$ and 5.44 ppm, due to the two different olefinic H atoms, and a broad one-hydrogen singlet at $\delta = 12.70$ ppm attributed to an N–H group. The structure of **6** was confirmed by X-ray diffraction, and the result is displayed in Figure 5, with selected distances and angles collected in Table 5. The molecule of **6** features a {Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)} fragment bonded to one of the



Scheme 6. Reaction of **2b** with maleic anhydride affords **6**, resulted from the ring opening and insertion into a M–N(amido) bond.

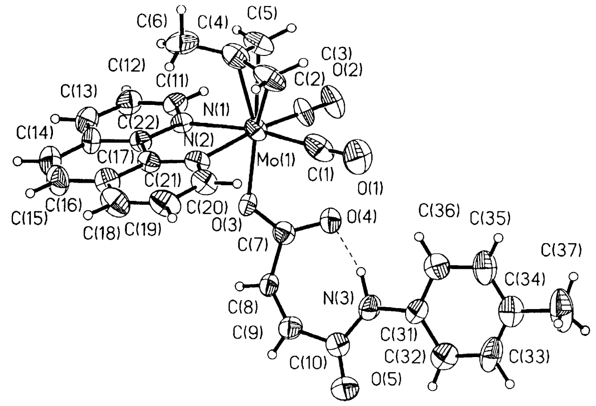


Figure 5. Structure of **6** (thermal ellipsoid (30%) plot).

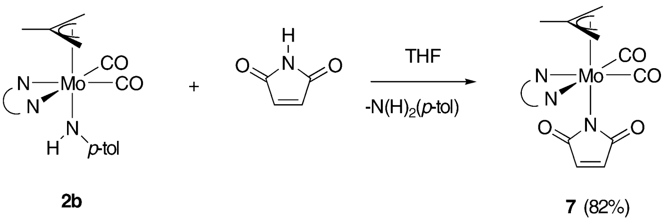
Table 5. Selected bond lengths [Å] and angles [°] for complex **6**.

Mo(1)–C(2)	1.924(7)	O(3)–C(7)	1.252(7)
Mo(1)–C(1)	1.938(7)	O(4)–C(7)	1.243(7)
Mo(1)–C(3)	2.308(6)	O(5)–C(10)	1.206(6)
Mo(1)–C(4)	2.225(8)	C(7)–C(8)	1.515(7)
Mo(1)–C(5)	2.317(6)	C(8)–C(9)	1.293(6)
Mo(1)–O(3)	2.148(4)	C(9)–C(10)	1.501(8)
N(3)–C(10)	1.341(7)	N(3)–C(31)	1.433(7)
C(2)-Mo(1)-C(1)	80.8(3)	C(8)-C(9)-C(10)	134.8(6)
C(2)-Mo(1)-O(3)	91.0(2)	O(5)-C(10)-N(3)	124.7(7)
C(1)-Mo(1)-O(3)	90.9(2)	O(5)-C(10)-C(9)	120.2(7)
C(7)-O(3)-Mo(1)	124.5(4)	N(3)-C(10)-C(9)	115.1(6)
O(4)-C(7)-O(3)	126.7(7)	C(10)-N(3)-C(31)	125.7(6)
O(4)-C(7)-C(8)	118.8(7)	C(9)-C(8)-C(7)	130.4(6)
O(3)-C(7)-C(8)	115.1(7)		

carboxylato oxygens of the carbamoylpropenoato ligand resulting from the coupling between maleic anhydride and the amido group. The localized C(8)=C(9) double bond features a C–C length (1.293(6) Å) clearly shorter than those between the adjacent single C–C bonds (C(7)–C(8) = 1.515(7) Å, C(9)–C(10) = 1.501(8) Å). An intramolecular hydrogen bond between the uncoordinated carboxylato oxygen and the amido N–H hydrogen (N(3)–O(4) = 2.704(9) Å) is shown by means of the dashed line in Figure 5.

The reactions of the amido complexes **2a**, **b** with CS$_2$, *p*-tolylisothiocyanate, and maleic anhydride are a manifestation of the nucleophilicity of the amido ligands. Thus, the amido attack to the electrophilic carbon atom of the substrate would afford a zwitterionic intermediate or transition state. The intramolecular displacement of the resulting nitrogen-bonded ligand by the sulfur or oxygen terminus would be driven by the charges of the atoms involved (cationic nitrogen and anionic sulfur or oxygen), and would afford the observed products. This rationale, shown in Scheme 7, is in line with our proposal for the insertion of organic electrophiles into the metal–OR bonds of low-valent alkoxo complexes of Groups 6–7 metals.[13a,b] A driving force for the overall reactions would be the relief of filled–filled (metal–lone pair) interactions present in the amido reagent, since the lone pairs on the donor atom of the anionic ligand of the products are stabilized by delocalization with the conjugate =S, =NAr or =O group.[21]

In contrast to the reactions described previously, complex **2b** reacts with maleimide to afford the product of the simple acid–base exchange shown in Scheme 8. The product, the amido complex **7**, was characterized by IR and NMR spectroscopy in solution and by single crystal X-ray diffraction (see Figure 6 and Table 6) in the solid state. The IR spectrum of **7** in the ν_{CO} region consists of the two expected



Scheme 8. Compound **7** is obtained by acid–base metathesis between **2b** and maleimide.

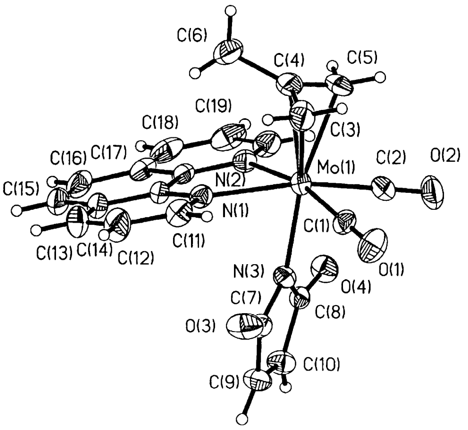
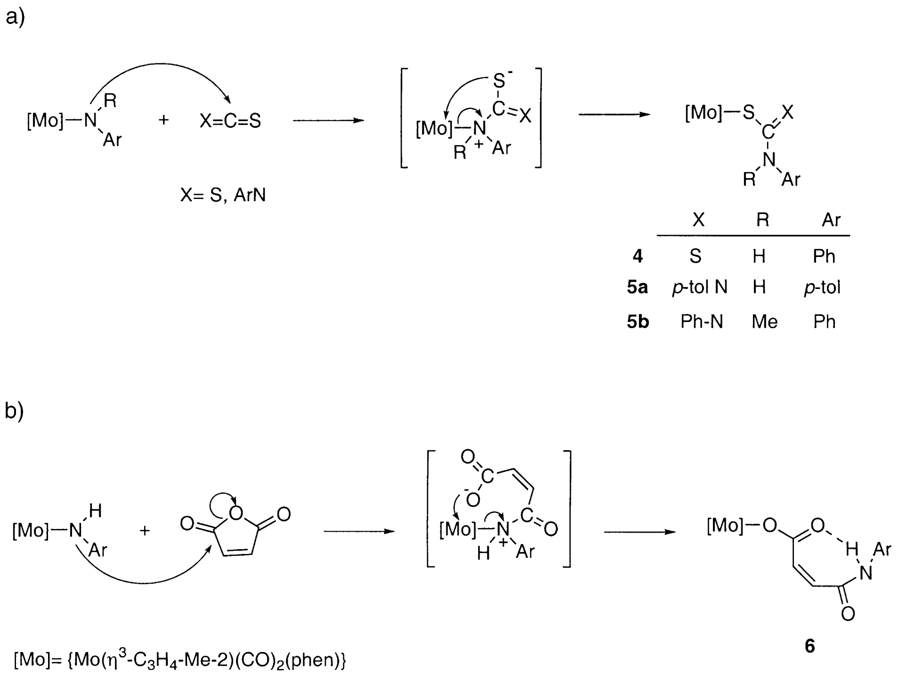


Figure 6. Structure of **7** (thermal ellipsoid (30%) plot). a) Structure of **8** (thermal ellipsoid (30%) plot); b) structure of **8**-urea (thermal ellipsoid (30%) plot).

cis-Mo(CO)$_2$ bands (at frequencies considerably higher than those of the amido precursor **2b**, reflecting the electron-withdrawing ability of the carbonyl groups within the maleimide moiety), and a band at 1728 cm^{-1} due to the "organic" C=O groups. In the ^{1}H NMR spectrum, the two olefinic hydrogen atoms are equivalent, in agreement with the symmetric structure (confirmed by its ^{13}C NMR spectrum, see Experimental Section) represented in Scheme 8, and in contrast with the ring-opened product **6** described above.[40] The Mo–N(amido) bond length in **7** (2.212(3) Å) is somewhat longer than that found in **2b**, reflecting the fact that the maleimidato ligand is a weaker donor than the *p*-tolyl group, as mentioned above with regard to the IR spectra.

The reaction of the amido complex **2b** with *p*-tolylisocyanate afforded a single molybdenum *cis*-dicarbonyl product **8** (Scheme 9), as judged from the two similar intensity bands in the ν_{CO} region of the IR spectrum. However, the NMR spectra of the product showed a multitude

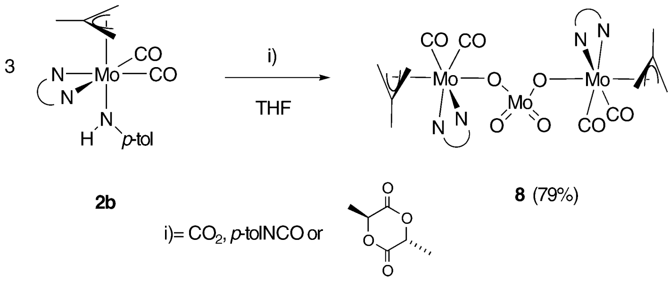


	X	R	Ar
4	S	H	Ph
5a	*p*-tol N	H	*p*-tol
5b	Ph-N	Me	Ph

Scheme 7. Proposed mechanisms for the formation of complexes **4**, **5a**,**b**, and **6**.

Table 6. Selected bond lengths [Å] and angles [°] for complex **7**.

Mo(1)–C(2)	1.956(5)	N(3)–C(7)	1.378(5)
Mo(1)–C(1)	1.945(5)	O(3)–C(7)	1.224(5)
Mo(1)–N(1)	2.232(3)	O(4)–C(8)	1.217(5)
Mo(1)–N(2)	2.238(3)	C(7)–C(9)	1.488(6)
Mo(1)–N(3)	2.212(3)	C(9)–C(10)	1.317(6)
N(3)–C(8)	1.376(5)		
C(2)-Mo(1)-C(1)	81.8(2)	C(8)-N(3)-C(7)	106.7(4)
C(1)-Mo(1)-N(3)	87.17(17)		



Scheme 9. The trinuclear compound **8** was obtained in the reaction of **2b** with *p*-tolNCO, CO_2 or lactide.

of peaks, suggestive of the presence of several organic byproducts. Complex **8** was also obtained in the reactions of **2b** with carbon dioxide and with the lactide 3,6-dimethyl-1,4-dioxane-2,5-dione. From the reaction of **2b** and CO_2, single crystals of **8**, whose IR spectrum matched that of the crude reaction product in the ν_{CO} region, could be obtained by slow diffusion of hexane into a concentrated solution of **8** in CH_2Cl_2. One of them was used for a structural determination by means of X-ray diffraction. The results, which are displayed in Figure 7a and Table 7, indicate that the molecule of **8** consists of a tetraoxomolybdato(VI) group bridging two {Mo(η^3-C_3H_4-Me-2)(CO)$_2$(phen)} fragments. A similar structure was recently found by Limberg et al. in the product of the reaction of [Mo(η^3-C_3H_4-Me-2)(O=CMe$_2$)(CO)$_2$(bipy)]BF_4 with sodium molybdate.[41]

In the reaction between **2b** and (*p*-tolyl)NCO, the product has been found to be a hydrogen-bonded adduct between **8** and *N*,*N*′-di(*p*-tolyl)urea. A view of the results of the X-ray determination is displayed in Figure 7b. Although its accuracy is limited, the connectivity is well established (see Experimental Section), including the interaction between the N–H bonds of the urea and the terminal oxo groups of the tetraoxomolybdato(VI) bridge. Ureas are conventionally synthesized by reactions of amines and isocyanates.[42] McElwee-White found that tungsten carbonyl complexes catalyze the carbonylation of amines to ureas.[43] The mechanism of urea formation in the reaction reported here is not presently clear and remains under study. The reactions of isocyanates,[44] CO_2,[45] and lactides[46] with metal amido complexes have been previously studied. Legzdins et al. found that *p*-tolylisocyanate was polymerized by the amido alkyl complex [WCp*(NO)(CH$_2$CMe$_3$)(NHCMe$_3$)], whereas the reaction with the amido alkoxo complex [WCp*(NO)(OCMe$_3$)(NHCMe$_3$)] affords a mixture of two products resulting from isocyanate insertion into W–O and W–N(amido) bonds.[34a] Boncella and Villanueva found that isocyanates react with [Pd(NHPh)(Ph)(PMe$_3$)$_2$] to yield the products of formal isocyanate insertion into the N–H bond.[39] We recently offered a rationalization for the formation of N–H or M–N insertion products.[47] Magnesium and zinc amides polymerize lactides, and the latter insert carbon dioxide to afford carbamate complexes.[48]

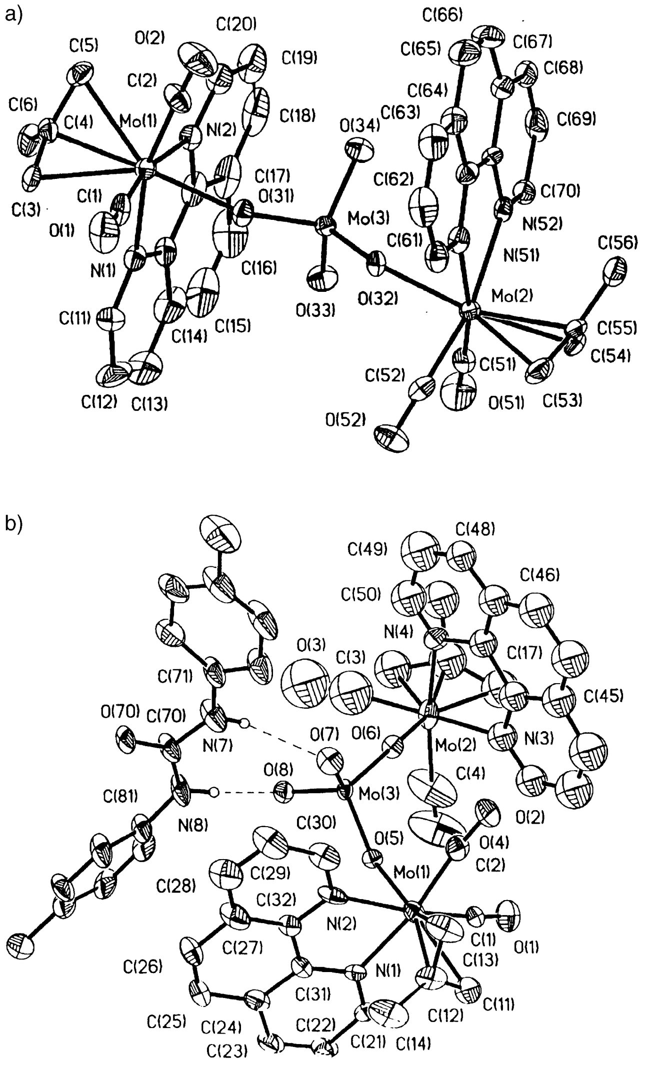
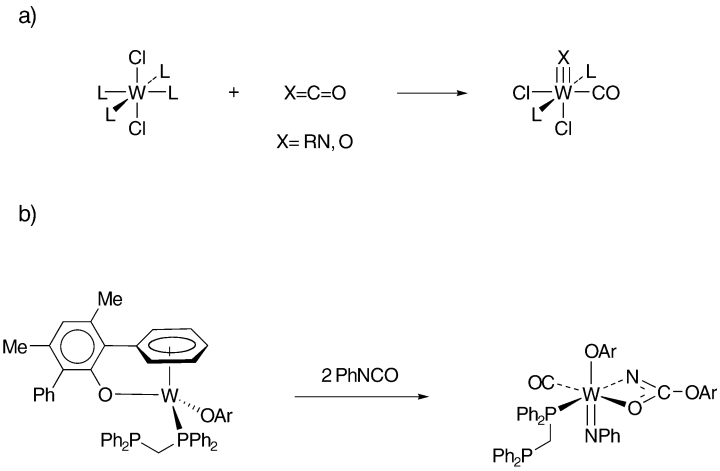


Figure 7.

Table 7. Selected bond lengths [Å] and angles [°] for complex **8**.

Mo(1)–O(31)	2.099(4)	Mo(3)–O(34)	1.719(5)
Mo(2)–O(32)	2.118(3)	Mo(3)–O(32)	1.768(4)
Mo(3)–O(33)	1.706(4)	Mo(3)–O(31)	1.782(4)
C(2)-Mo(1)-O(31)	87.9(2)	O(34)-Mo(3)-O(32)	110.2(2)
C(52)-Mo(2)-O(32)	88.4(3)	O(33)-Mo(3)-O(31)	110.3(2)
O(33)-Mo(3)-O(34)	107.8(2)	O(34)-Mo(3)-O(31)	110.5(2)
O(33)-Mo(3)-O(32)	109.55(19)	Mo(3)-O(31)-Mo(1)	151.3(2)
Mo(3)-O(32)-Mo(2)	144.2(2)		

In contrast with those results, the metal oxidation and scission of the C=O bond of the isocyanate found in the reaction of **2b** with (*p*-tolyl)NCO and CO_2 are reminiscent of the results obtained by Mayer and Bryan[49] in the reaction with the tungsten(II) complex [WCl$_2$(PMePh$_2$)$_4$] (Scheme 10a). Metal oxidation and rupture of the isocyanate



Scheme 10. Results obtained by a) Mayer and b) Rothwell in the reactions of compounds of W^{II} with isocyanates and CO_2.

C=N bond was found by Rothwell for the tungsten(II) complex $[W(OC_6HPhMe_2\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)(\eta^1\text{-dppm})]$ (Scheme 10b; dppm = diphenylphosphanylmethane).[50]

The formation of **8** in the reactions reported here implies that one third of the molecules of the molybdenum reagent are oxidized to Mo^{VI}, resulting in the loss of their carbonyl, phenanthroline and allyl ligands. In addition, all amido group are lost. The oxidation of the metal to Mo^{VI} in the reactions of **2b** with mild oxidants such as (*p*-tolyl)NCO, CO_2 or lactide reflects the strong donation of electron density to the metal center from the amido ligand.[21] For the less electron-rich $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})(OMe)(CO)_2(phen)]$,[13b] the reaction with (*p*-tolyl)NCO affords the insertion product.

We have not been able to identify the exact nature of the elimination products. The possibility that the electrons lost by the molybdenum oxidized to Mo^{VI} can be used to create new bonds in the elimination products is attractive, and is currently being explored by us.

To conclude, this work reports the synthesis of the first molybdenum amido complexes without amido → metal π-donation (and, therefore, with a single Mo–N(amido) bond), a feature imposed by their saturated (18-electron) nature. Destabilizing interactions between the amido lone pair and Mo filled d orbitals, partly moderated by delocalization of the amido electron density into (a) the aryl substituent, and (b) strong π-acceptor CO groups (using the metal d orbitals), result in isolable yet highly reactive complexes, which insert CS_2, arylisothiocyanate and maleic anhydride and are oxidized by (*p*-tolyl)NCO, CO_2 and a lactide.

Experimental Section

General conditions are given elsewhere.[13b]

Crystal structure determination for compounds 2b, 3-OTf, 5a, 6, 7, and 8; general description: A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized $Mo_{K\alpha}$ X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[51] program. The structure was solved by direct methods with SHELXTL.[52] A semiempirical absorption correction was applied with the program SADABS.[53] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL. Crystal and refinement data are presented in Tables 8 and 9.

Table 8. Crystal data for **2b**, **3**-OTf, and **4**.

	2b	**3**-OTf	**4**
formula	$C_{29}H_{31}MoN_3O_3$	$C_{52}H_{48}F_6Mo_2N_6O_{10}S_2$	$C_{27}H_{25}Cl_4MoN_3O_4S_2$
fw	565.51	1286.96	725.36
cryst. system	orthorhombic	triclinic	orthorhombic
space group	$P2_12_12_1$	P_1	$P2_12_12_1$
a [Å]	12.1748(8)	11.383(2)	10.9390(4)
b [Å]	17.3496(9)	13.064(3)	11.6011(4)
c [Å]	25.0304(16)	19.602(4)	23.1152(8)
α [°]	90	75.631(4)	90
β [°]	90	79.298(3)	90
γ [°]	90	89.252(4)	90
V [Å^3]	5287.1(6)	2773.0(9)	2933.42(18)
Z	8	4	4
T [K]	293(2)	299(2)	120(2)
ρ_{calcd} [g cm^{-3}]	1.421	3.083	1.642
$F(000)$	2336	2608	1464
$\lambda(Mo_{K\alpha})$ [Å]	1.54184	0.71073	1.54184
crystal size [mm]	0.20 × 0.20 × 0.12	0.11 × 0.23 × 0.27	0.15 × .07 × .07
μ [mm^{-1}]	4.336	1.218	8.600
scan range [°]	$3.10 \leq \theta \leq 70.07$	$1.61 \leq \theta \leq 23.30$	$4.26 \leq \theta \leq 69.38$
no of ref. measured	10736	12436	10094
no of independent ref.	9920	7911	5200
data/restraints/ parameters	9920/0/659	7911/0/723	5200/0/350
goodness-of-fit on F^2	0.672	1.032	1.021
R_1/R_{w2} [$I > 2\theta(I)$]	0.0319/0.0776	0.0378/0.0921	0.0505/0.1158
R_1/R_{w2} (all data)	0.0511/0.0849	0.0519/0.1019	0.0793/0.1285

Regarding the structure of compound **8**-urea, up to four well-shaped prismatic crystals of suitable dimensions were measured. For all of them, after solving the structure, a severe disorder was found, affecting the allyl and two carbonyl groups attached to one Mo atom (Mo(2) in Figure 7b), the corresponding groups of the other Mo atom having normal features. Unfortunately, it was not possible to model the disorder, and the pertaining atoms were constrained to behave as those of the chemically equivalent, non-disordered half. As a consequence of the disorder, the final result is of poor quality. Nevertheless, the connectivity within the coordination sphere around Mo(1), the molybdate group and the molecule of urea can be stablished unambiguously and with enough accuracy.

Crystal structure determination for 4: The crystal structure was solved by Patterson methods, by using the program Dirdif.[54] Anisotropic least-squares refinement was carried out with SHELXL-97.[55] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and refined riding on their parent atoms. An empirical absorption correction was applied by using XABS2.[56] Geometrical calculations were carried out with PARST.[57] The crystallographic plot was made with PLATON.[58] All calculations were done at the University of Oviedo Scientific Computer Center and X-Ray group computers. Crystal and refinement data are presented in Table 8.

CCDC-206831 (**2b**), CCDC-206832 (**3**), CCDC-206833 (**4**), CCDC-206834 (**5a**), CCDC-206835(**6**), CCDC-206836 (**7**), CCDC-206837 (**8**), and CCDC-206838 (**8**-urea) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Table 9. Crystal data for **5a**, **6**, and **7**.

	5a	**6**	**7**	**8**
formula	$C_{33}H_{29}MoN_4O_2S$ 0.5 CH_2Cl_2	$C_{33}H_{33}MoN_3O_6$	$C_{22}H_{17}MoN_3O_4$ 0.25 CH_2Cl_2	$C_{18}H_{15}Mo_{1.5}N_2O_4$
fw	683.06	663.56	504.56	467.23
cryst. system	triclinic	triclinic	tetragonal	monoclinic
space group	P_1	P_1	$I4_{1/a}$	$P2_1$
a [Å]	11.035(3)	11.062(2)	30.926(6)	12.152(2)
b [Å]	11.556(3)	12.598(2)	30.926(6)	10.968(2)
c [Å]	14.163(3)	13.614(2)	9.666(3)	14.208(3)
α [°]	112.792(4)	99.656(4)	90	90
β [°]	105.168(4)	109.673(3)	90	108.275(4)
γ [°]	90.018(4)	110.323(4)	90	90
V [Å^3]	1596.5(6)	1585.7(5)	9245(4)	1798.3(6)
Z	2	2	16	4
T [K]	293(2)	293(2)	299(2)	293(2)
ρ_{calcd} [g cm^{-3}]	1.421	1.390	1.450	1.726
F(000)	698	684	4072	928
$\lambda(Mo_{K\alpha})$ [Å]	1.54180	0.71073	0.71073	0.71073
crystal size [mm]	0.12 × 0.20 × 0.32	0.06 × 0.11 × 0.12	0.05 × 0.06 × 0.30	0.05 × 0.08 × 0.22
μ [mm^{-1}]	0.596	0.461	0.657	1.087
scan range [°]	$1.63 \leq \theta \leq 23.40$	$1.68 \leq \theta \leq 23.31$	$1.32 \leq \theta \leq 23.32$	$1.51 = \theta = 23.29$
no of ref. measured	7105	7201	20203	8162
no of independent ref.	4559	4544	3331	4884
data/restraints/ parameters	4559/0/398	4544/0/390	3331/0/290	4884/1/462
goodness-of-fit on F^2	1.003	0.946	1.023	0.986
R_1/R_{w2} [$I > 2\theta(I)$]	0.0305/0.0840	0.0526/0.0640	0.0374/0.0588	0.0328/0.0491
R_1/R_{w2} (all data)	0.0336/0.0863	0.1191/0.0717	0.0782/0.0654	0.0398/0.0503

[Mo(NHPh)(η^3-C_3H_4-Me-2)(CO)$_2$(phen)] (2a): $KN(SiMe_3)_2$ (1 mL of a 0.5 M solution in toluene, 0.50 mmol) was added to THF (10 mL) and the solution was cooled to −78 °C. Aniline (0.046 mL, 0.50 mmol) was added, the mixture was allowed to reach room temperature, and then added to a solution of **1** (0.200 g, 0.473 mmol) in THF (10 mL) with a cannula. The mixture was stirred for 30 min. The solvent was evaporated under vacuum, the residue was extracted with CH_2Cl_2 (20 mL) and the solution filtered through a short column of diatomaceous earth. In vacuo concentration and addition of hexanes (20 mL) caused the precipitation of a purple microcrystalline solid, which was washed with hexanes and dried under vacuum (0.160 g, 70 %). Elemental analysis calcd (%) for $C_{24}H_{21}MoN_3O_2$: C 60.13, H 4.41, N 8.76; found: C 60.35, H 4.65, N 8.49; IR (CH_2Cl_2): $\tilde{\nu} = 1928$, 1841 (ν_{CO}) cm^{-1} (s); ^{1}H NMR (CD_2Cl_2): $\delta = 8.96$ (dd, $J_{H2,3} = J_{H9,8} = 5.1$ Hz, $J_{H2,4} = J_{H7,9} = 1.4$ Hz, 2H; $H_{2,9}$), 8.46 (dd, 2H, $J_{H4,3} = J_{H7,8} = 7.9$ Hz; $H_{4,7}$), 7.99 (s, 2H; $H_{5,6}$), 7.77 (dd, 2H; $H_{3,8}$), 6.84, 6.66, and 6.21 (m, 5H; Ph), 3.88 (br s, 1H; N−*H*), 3.00 (s, 2H; H_s), 1.49 (s, 2H; H_a), 0.63 ppm (s, 3H, η^3-C_3H_4(*CH$_3$*)-2); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 231.0$ (CO), 161.2, 151.8, 144.6, 137.5, 130.6, 128.9, 127.7, 125.3, 116.1, and 112.8 (phen and Ph), 87.6 (C^2, η^3-$C_3H_4(CH_3)$), 55.6 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 20.0 ppm (η^3-C_3H_4(*CH$_3$*)-2).

[Mo{NH(*p*-tol)}(η^3-C_3H_4-Me-2)(CO)$_2$(phen)] (2b): a) KN(H)(*p*-tol) (0.26 mmol, prepared from (*p*-tolyl)NH_2 and $KN(SiMe_3)_2$ as described for **2a**) in THF (10 mL) was added to a solution of **1** (0.100 g, 0.236 mmol) in THF (10 mL) at −78 °C. After the mixture had been stirred for 10 min, the solvent was evaporated to dryness, the residue was extracted with CH_2Cl_2 (2 × 5 mL), filtered (Celite), and evaporated. The solid was dissolved in THF (10 mL), layered with hexane (20 mL) and, after standing at −20 °C for two days, red crystals were obtained (0.107 g, 80 %). Elemental analysis calcd (%) for $C_{25}H_{23}MoN_3O_2 \cdot$ THF: C 61.59, H 5.52, N 7.43; found: C 61.71, H 5.71, N 7.65; IR (CH_2Cl_2): $\tilde{\nu} = 1926$, 1839 (ν_{CO}) cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 8.94$ (dd, $J_{H2,3} = J_{H9,8} = 5.0$ Hz, $J_{H2,4} = J_{H7,9} = 1.3$ Hz, 2H; $H_{2,9}$), 8.45 (dd, $J_{H4,3} = J_{H7,8} = 8.6$ Hz, 2H; $H_{4,7}$), 7.99 (s, 2H; $H_{5,6}$), 7.76 (dd, 2H; $H_{3,8}$), 6.69, 6.66, 6.60, and 6.57 (AA′BB′, 4H; C_6*H$_4$*), 3.90 (br s, 1H; N−*H*), 3.00 (s, 2H; H_s), 2.08 (s, 3H; C_6H_4−C*H$_3$*), 1.48 (s, 2H; H_a), 0.64 ppm (s, 3H; η^3-C_3H_4(*CH$_3$*)-2); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 231.4$ (CO), 158.8, 151.7, 144.5, 137.4, 130.6, 129.4, 127.7, 125.3, 121.7, and 115.8 (phen and C_6H_4), 87.8 (C^2, η^3-$C_3H_4(CH_3)$), 68.1 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 26.0 (C_6H_4−*C*H_3), 20.1 ppm (η^3-C_3H_4(*CH$_3$*)-2).

b) $KN(SiMe_3)_2$ (154 μL of a 0.5 M solution in toluene, 0.077 mmol) was added to a solution of **3**-OTf (see below) (0.050 g, 0.077 mmol) in THF (10 mL) at −78 °C. The color of the solution immediately changed from orange to deep red. After the mixture had been stirred for 15 min, the solvent was evaporated, the residue was dissolved in CH_2Cl_2 and filtered through diatomaceous earth. In vacuo concentration and precipitation with hexanes afforded a red microcrystalline solid (0.035 g, 92 %) whose spectroscopic data matched those given above for **2b**.

[Mo{NH$_2$(*p*-tol)}(η^3-C_3H_4-Me-2)(CO)$_2$(phen)]OTf (3-OTf): HOTf (triflic acid) (9 μL, 0.100 mmol) was added to a cooled (−78 °C) solution of **2b** (0.050 g, 0.101 mmol) in THF (10 mL). The solution immediately turned orange and two new bands appeared in the CO region of the IR spectrum in solution. The solvent was evaporated under vacuum, the residue was dissolved in CH_2Cl_2, filtered through diatomaceous earth, concentrated and layered with hexanes. After 12 h at room temperature orange crystals of **3**-OTf were obtained (0.060 g, 93 %). Elemental analysis calcd (%) for $C_{26}H_{24}F_3MoN_3O_5S$: C 48.53, H 3.75, N 6.53; found: C 48.91, H 3.97, N 6.55; IR (CH_2Cl_2): $\tilde{\nu} = 1958$, 1876 (ν_{CO}) cm^{-1}; ^{1}H NMR (CD_2Cl_2): $\delta = 9.20$ (dd, $J_{H2,3} = J_{H9,8} = 4.9$ Hz, $J_{H2,4} = J_{H7,9} = 1.3$ Hz, 2H; $H_{2,9}$), 8.61 (dd, $J_{H4,,3} = J_{H7,8} = 8.1$ Hz, $J_{H4,5} = J_{H7,6} = 1.1$ Hz, 2H; $H_{4,7}$), 8.00 (s, 2H; $H_{5,6}$), 7.92 (dd, 2H; $H_{3,8}$), 6.57, 6.54, 6.03, and 6.00 (AA′BB′, 4H; C_6*H$_4$*), 5.49 (br s, 2H; *NH$_2$*), 3.13 (s, 2H; H_s), 2.09 (s, 3H; C_6H_4−C*H$_3$*), 1.56 (s, 2H; H_a), 0.60 ppm (s, 3H; η^3-C_3H_4(*CH$_3$*)-2); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 224.5$ (CO), 154.0, 145.3, 139.7, 139.4, 134.3, 131.2, 130.5, 128.2, 129.6, 128.3, 126.5, 120.1 (phen and C_6H_4), 82.5 (C^2, η^3-$C_3H_4(CH_3)$-2), 56.2 (C^1 and C^3, η^3-$C_3H_4(CH_3)$-2), 20.8 (C_6H_4−*C*H_3), 18.9 ppm (η^3-C_3H_4(*CH$_3$*)-2); ^{19}F NMR (CD_2Cl_2): $\delta = -78.9$ ppm.

[Mo(η^3-C_3H_4-Me-2){SC(S)(N(H)Ph)}(CO)$_2$(phen)] (4): CS_2 (7 μL, 0.110 mmol) was added to a solution of **2a** (0.050 g, 0.104 mmol) in THF (20 mL) and the solution was stirred for 15 min. The solvent was evaporated to dryness and the red solid was dissolved in CH_2Cl_2 (10 mL). Slow diffusion of hexane (25 mL) into a solution of **4** at room temperature afforded red crystals (0.065 g, 86 %), one of which was used for X-ray diffraction. Elemental analysis calcd (%) for $C_{25}H_{21}MoN_3O_2S_2 \cdot 2\,CH_2Cl_2$: C 44.70, H 3.47, N 5.79; found: C 44.25, H 3.64, N 5.91; IR (CH_2Cl_2): $\tilde{\nu} = 1940$, 1854 (ν_{CO}), 1512 cm^{-1} ($\nu_{C=S}$); ^{1}H NMR (CD_2Cl_2): $\delta = 10.59$ (s; N−*H*), 9.00 (dd, $J_{H2,3} = 5.01$ Hz, $J_{H2,4} = 1.4$ Hz, 2H; $H_{2,9}$), 8.49 (dd, $J_{H4,3} = 8.2$ Hz, $J_{H4,5} = 1.2$ Hz, 2H; $H_{4,7}$), 7.96 (s, 2H; $H_{5,6}$), 7.82 (dd, 2H; $H_{3,8}$), 7.71 and 7.17 (m, 5H; Ph), 3.15 (s, 2H; H_s), 1.78 (s, 2H; H_a), 0.62 ppm (s, 3H, η^3-C_3H_4(C*H$_3$*)-2); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 228.36$ (CO), 205.48 (C=S), 152.18, 144.70, 138.67, 138.02, 135.60, 130.82, 129.39, 127.85, 125.60, and 123.52 (phen and

Ph), 87.85 (C^2, η^3-$C_3H_4(CH_3)$), 56.69 (C^1 and C^3, η^3-$C_3H_4(CH_3)$), 18.86 ppm (η^3-$C_3H_4(\mathit{CH_3})$).

[Mo(η^3-C_3H_4-Me-2){SC(N(*p*-tol))(NH(*p*-tol))}$(CO)_2$(phen)] (5a): *p*-Tolylisothiocyanate (0.018 g, 0.128 mmol) was added to a solution of **2b** (0.050 g, 0.101 mmol) in THF (15 mL) and stirred for 30 min. The solvent was evaporated in vacuo, the red residue was dissolved in CH_2Cl_2 (10 mL), layered with hexane (20 mL), and placed at −30 °C, affording red needles of **5a** (0.056 g, 80 %), one of which was used for the structure determination by X-ray diffraction. Elemental analysis calcd (%) for $C_{33}H_{30}MoN_4O_2S \cdot 5CH_2Cl_2$: C 58.73, H 4.56, N 8.17; found: C 59.05, H 4.32, N 8.41; IR (CH_2Cl_2): $\tilde{\nu} = 1941, 1857$ (ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 8.84$ (dd, $J_{H2,3} = J_{H9,8} = 5.0$ Hz, $J_{H2,4} = J_{H7,9} = 1.3$ Hz, 2H; $H_{2,9}$), 8.32 (dd, $J_{H4,3} = J_{H7,8} = 8.3$ Hz, 2H; $H_{4,7}$), 7.79 (s, 2H; $H_{5,6}$), 7.65 (dd, 2H; $H_{3,8}$), 7.21, 7.03, 6.77, 6.57(br s, 8H; 2 × qAB), 2.90 (s, 2H; H_s), 2.24 (br s, 6H; C_6H_4−$\mathit{CH_3}$), 1.55 (s, 2H; H_a), 0.53 ppm (s, 3H, η^3-$C_3H_4(\mathit{CH_3})$-2).

[Mo(η^3-C_3H_4-Me-2){SC(NPh)(NMe(*Ph*)}$(CO)_2$(phen)] (5b): A solution of KN(Me)Ph (prepared in situ from HN(Me)Ph (0.032 mL, 0.300 mmol) and $KN(SiMe_3)_2$ (0.600 mL of a 0.5 M solution in toluene, 0.300 mmol) in THF (10 mL) was added to a solution of **1** (0.100 g, 0.236 mmol) in THF (10 mL) cooled to −78°C. The brown solution was stirred for 30 min [IR (THF): $\tilde{\nu} = 1927, 1843$ cm^{-1} (s)) and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, filtered through diatomaceous earth, evaporated to dryness and washed with hexanes (3 × 10ml). The amido complex [Mo(η^3-C_3H_4-Me-2)(N(Me)Ph)$(CO)_2$(phen)) was redissolved in THF (20 mL), PhNCS (0.028 mL, 0.240 mmol) was added and the brown solution was stirred for 8 h. After evaporation, the residue was extracted with CH_2Cl_2, filtered through diatomaceous earth and layered with hexanes. After 12 h at room temperature, brown crystals were obtained (0.085 g, 57 %). Elemental analysis calcd (%) for $C_{32}H_{28}MoN_4O_2S$: C 61.14, H 4.49, N 8.91; found: C 60.97, H 4.65, N 9.23; IR (CH_2Cl_2): $\tilde{\nu} = 1943, 1866$ (ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 8.56$ (dd, $J_{H2,3} = 5.01$ Hz, $J_{H2,4} = 1.4$ Hz, 2H; $H_{2,9}$), 8.34 (dd, $J_{H4,3} = 8.2$ Hz, $J_{H4,5} = 1.2$ Hz, 2H; $H_{4,7}$), 7.89 (s, 2H; $H_{5,6}$), 7.60 (dd, 2H; $H_{3,8}$), 7.43 (m, 2H; Ph), 7.24 (m, 3H; Ph), 6.99 (m, 3H; Ph), 6.71 (m, 2H; Ph), 3.66 (s, 3H; N$\mathit{CH_3}$), 2.85 (s, 2H; H_s), 1.42 (s, 2H; H_a), 0.48 ppm (s, 3H; η^3-$C_3H_4(\mathit{CH_3})$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 228.96$ (CO), 167.04 (C=S), 153.25, 151.98, 149.10, 144.36, 136.77, 130.18, 128.76, 128.24, 127.61, 127.41, 126.25, 126.00, 124.95, 123.63, 123.29, 120.85 (phen and 2 × Ph), 85.35 (C^2, η^3-$C_3H_4(CH_3)$), 53.14 (C^1 and C^3, η^3-$C_3H_4(CH_3)$), 41.21 (N$\mathit{C}H_3$), 18.84 ppm (η^3-$C_3H_4(\mathit{CH_3})$).

[Mo(η^3-C_3H_4-Me-2){OC(O)CH = CHC(O)(NH(*p*-tol))}$(CO)_2$(phen)](6): Maleic anhydride (0.010 g, 0.101 mmol) was added to a solution of **2b** (0.050 g, 0.101 mmol) in THF (10 mL) and the solution was stirred for 1 h. After evaporation to dryness the residue was dissolved in CH_2Cl_2, filtered through diatomaceous earth, and evaporated. The solid was dissolved in THF and layered with hexanes (10 mL) to afford red crystals of **6** (0.051 g, 76 %). Elemental analysis calcd (%) for $C_{29}H_{25}MoN_3O_5 \cdot$THF: C 59.73, H 5.01, N 6.33; found: C 59.91, H 4.80, N 6.54; IR (CH_2Cl_2): $\tilde{\nu} = 1955, 1874, 1781$ (ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 12.70$ (br s; N−*H*), 9.27 (dd, $J_{H2,3} = 5.01$ Hz, $J_{H2,4} = 1.4$ Hz, 2H; $H_{2,9}$), 8.43 (dd, $J_{H4,3} = 8.2$ Hz, $J_{H4,5} = 1.2$ Hz, 2H; $H_{4,7}$), 7.91 (s, 2H; $H_{5,6}$), 7.74 (dd, 2H; $H_{3,8}$), 7.49 and 7.13 (qAB, $J_{HA,B} = 8.2$, 4H; *p*-tol), 5.45 (s, 1H; =CH), 5.44 (s, 1H; =CH), 3.68 (s, 2H; H_s), 2.33 (s, 3H; C_6H_4−$\mathit{CH_3}$), 1.39 (s, 2H; H_a), 0.81 ppm (s, 3H; η^3-$C_3H_4(\mathit{CH_3})$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 226.95$ (CO), 171.95 (OC=O), 163.22 (OC=O), 152.59, 138.39, 133.29, 133.00, 132.83, 130.50, 129.54, 127.63, 124.94, and 120.12 (phen and C_6H_4), 145.21 (C=C), 137.16 (C=C), 87.85 (C^2, η^3-$C_3H_4(CH_3)$), 68.15 (C^1 and C^3, η^3-$C_3H_4(CH_3)$), 21.02 (C_6H_4-$\mathit{C}H_3$), 19.35 ppm (η^3-$C_3H_4(\mathit{CH_3})$).

[Mo(η^3-C_3H_4-Me-2){NC(O)CH=CHC(O)}$(CO)_2$(phen)] (7): Maleimide (0.010 g, 0.110 mmol) was added to a solution of **2b** (0.050 g, 0.101 mmol) in THF (10 mL) and the mixture was stirred for 2 h. The solvent was removed under vacuum, the solid residue was extracted with CH_2Cl_2, filtered through diatomaceous earth and precipitated again with hexanes affording a red microcrystalline solid. By slow diffusion of hexanes into a concentrated solution of **7** in CH_2Cl_2, red crystals were obtained (0.042 g, 82 %) one of which was used for X-ray analysis. Elemental analysis calcd (%) for $C_{22}H_{17}MoN_3O_4 \cdot 0.25CH_2Cl_2$: C 52.96, H 3.49, N 8.32; found: C 52.74, H 3.25, N 8.54; IR (CH_2Cl_2): $\tilde{\nu} = 1948, 1863, 1728$ (ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 9.44$ (dd, $J_{H2,3} = 5.01$ Hz, $J_{H2,4} = 1.4$ Hz, 2H; $H_{2,9}$), 8.43 (dd, $J_{H4,3} = 8.2$ Hz, $J_{H4,5} = 1.2$ Hz, 2H; $H_{4,7}$), 7.88 (s, 2H; $H_{5,6}$), 7.78 (dd, 2H; $H_{3,8}$), 6.01 (s, 2H; =CH), 3.06 (s, 2H; H_s), 1.46 (s, 2H; H_a), 0.62 ppm (s, 3H; η^3-$C_3H_4(\mathit{CH_3})$-2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 226.87$ (CO), 183.09 (OC=O), 154.81, 145.31, 137.70, 135.80, 127.18, 123.90 (phen), 129.80 (C=C), 80.53 (C^2, η^3-$C_3H_4(CH_3)$), 54.65 (C^1 and C^3, η^3-$C_3H_4(CH_3)$), 18.22 ppm (η^3-$C_3H_4(\mathit{CH_3})$).

[{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}$_2$(η^2-MoO_4)] (8): a) CO_2 was bubbled through a solution of **2b** (0.050 g, 0.101 mmol) in THF (10 mL) for 1 h. The color of the solution changed from deep red to purple. The solution was filtered through diatomaceous earth, concentrated and layered with hexane, affording purple crystals of **8**, one of which was employed in an X-ray study. b) Lactide 3,6-dimethyl-1,4-dioxane-2,5-dione (0.015 g, 0.101 mmol) was added to a solution of **2b** (0.050 g, 0.101 mmol) in THF (10 mL) and the solution was stirred for 7 h. After this time the purple solution was worked up as described above.

[{Mo(η^3-C_3H_4-Me-2)$(CO)_2$(phen)}$_2$(η^2-MoO_4)] · N,N′-di(*p*-tolyl)urea (8-urea): *p*-tolylNCO (29 µL, 0.230 mmol) was added to a solution of **2b** (0.113 g, 0.229 mmol) in THF (20 mL). Immediately, the color of the solution changed from deep red to purple. After the mixture had been stirred for 30 min, the solvent was evaporated under vacuum. The residue was dissolved in CH_2Cl_2, filtered through diatomaceous earth, and precipitated again with hexanes. By slow diffusion of hexanes into a concentrated solution of **8** in THF, purple crystals were obtained, one of which was used for X-ray diffraction (0.070 g, 79 %). The results showed the compound to consist of an adduct **8** · *N,N′*-di(*p*-tolyl)urea. Elemental analysis calcd (%) for $C_{51}H_{46}Mo_3N_6O_9$: C 52.14, H 3.94, N 7.15; found: C 51.82, H 3.70, N 7.45; IR (THF): $\tilde{\nu} = 1950$, 1876 (sh), 1864 (ν_{CO}) cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 8.83$ (dd, $J_{H2,3} = 4.69$ Hz, $J_{H2,4} = 1.4$ Hz, 4H; $H_{2,9}$), 7.87 (dd, $J_{H4,3} = 8.22$ Hz, $J_{H4,5} = 1.57$ Hz, 4H; $H_{4,7}$), 7.27 (s, 2H; $H_{5,6}$), 7.18 (dd, 4H; $H_{3,8}$), 2.72 (s, 4H; H_s), 1.08 (s, 4H; H_a), 0.42 (s, 6H; η^3-$C_3H_4(\mathit{CH_3})$-2); N,N′-di(*p*-tolyl)urea: 6.78, 6.74, 6.35, 6.30 (AA′BB′, 8H; $C_6\mathit{H_4}$), 2.31 ppm (s, 6H; C_6H_4-$\mathit{CH_3}$).

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