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CC-coupling reactions at low-valent molybdenum centers. Selective formation of η^2 -iminoacyl, η^3 -1-azaallyl and η^2 -1,4-diazabutadien-2-yl complexes of molybdenum from ethyl isocyanide complexes *

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Abstract

A stepwise, high-yield synthesis of low-valent molybdenum η^2 -iminoacyl, η^3 -azaallyl and η^2 -1,4-diazabutadien-2-yl complexes is reported starting from readily accessible ethyl isocyanide complexes. Thus reduction of *cis/trans*-Cp*Mo(CO)₂(EtNC)I (Cp* = η^5 -C₅Me₅) (**1a/1b**) with sodium gives the Mo⁰-metallate Na[Cp*Mo(CO)₂(EtNC)] (**2**) in quantitative yield. Reaction of **2** with RI yields (via alkylation of the metal center and insertion of the ethyl isocyanide ligand into the metal-alkyl bond exclusively the Mo^{II}-iminoacyl complexes Cp*(CO)₂Mo[η^2 -C(NEt)R] (**3**: R = Me; **4**: R = Et). Complexes **3** and **4** undergo isomerization in refluxing toluene by H-migration into the 1-azaallyl compounds Cp*(CO)₂Mo(η^3 -CH₂=CH=NEt) (**5**) and Cp*(CO)₂Mo(η^3 -CH(Me)=CH=NEt) (**6**), respectively. Treatment of **3** with RNC (R = Me, Et) results in the quantitative formation of the isocyanide insertion products Cp*(CO)₂Mo[C(NR)C(NEt)Me] (**7**: R = Me; **8**: R = Et). The solid state structure of **8** was established by a single-crystal X-ray crystallographic study. A striking feature of the structure is the planarity of the four-membered metallaheterocycle resulting from (C,N)-coordination of the 1,4-diaza-3-methylbutadien-2-yl ligand to molybdenum.

Introduction

As part of our work on electron-rich isocyanide complexes we have recently described the high yield synthesis of the isocyanide metallates Na[(η^5 -C₅R₅)M(CO)_n(EtNC)_{3-n}] (R = H, Me; n = 1, 2) and the homoleptic isocyanide complexes M(RNC)₆ (R = Et, ^tBu) of Mo⁰ and W⁰ starting from M(CO)₆ [1–4]. The synthetic procedures developed involve a sequence of clean, large scale reactions starting from readily accessible and well-characterized M⁰-, M^{II}- and M^{IV}-isocyanide complexes, thus facilitating considerably exploration of the chemistry of

* Dedicated to Professor P.L. Pauson on the occasion of his retirement.

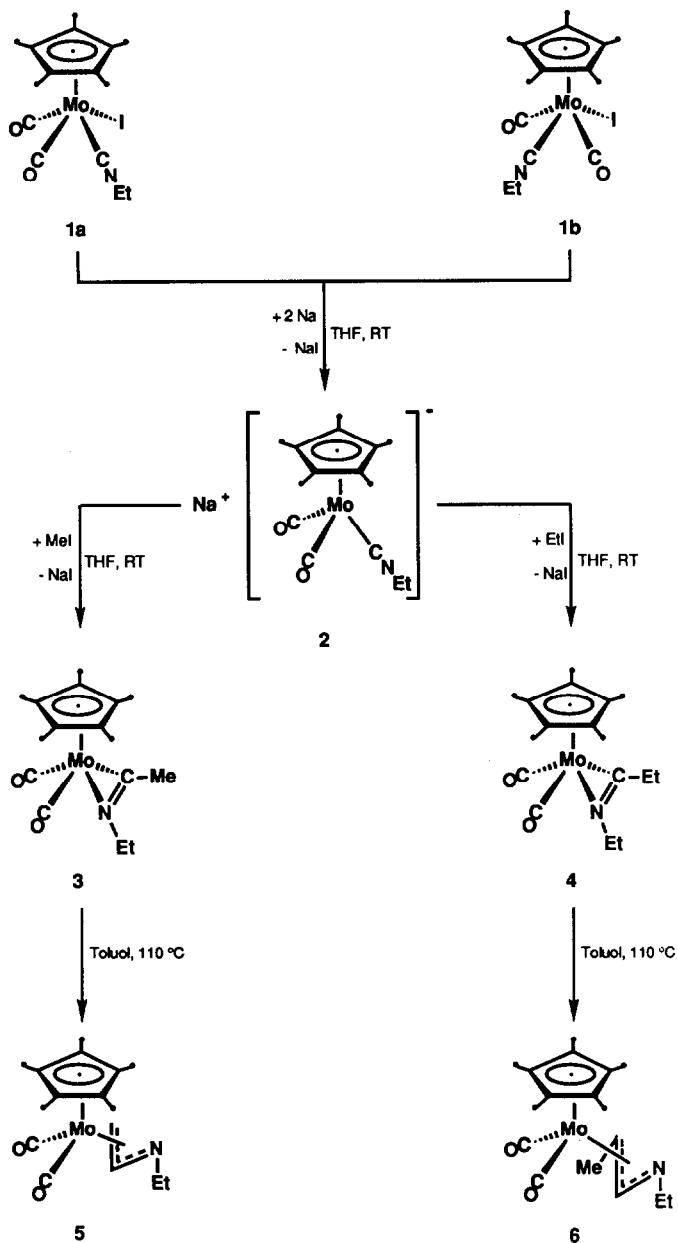
these rare electron-rich compounds. We have studied their reactions with electrophiles and have found these to follow two competitive pathways. The first involves attack of the electrophile at the isocyanide nitrogen and leads to aminocarbyne complexes. Representative examples of this pathway are the ethylations of $\text{Na}[(\eta^5\text{-C}_5\text{R}_5)\text{W}(\text{CO})_n(\text{EtNC})_{3-n}]$ ($\text{R} = \text{H, Me; } n = 1, 2$) and $\text{M}(\text{EtNC})_6$ ($\text{M} = \text{Mo, W}$) with Et_3OBF_4 to give $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_n(\text{EtNC})_{2-n}\text{W}\equiv\text{CNEt}_2$ [1,3] and $[(\text{EtNC})_5\text{M}\equiv\text{CNEt}_2]\text{BF}_4$, respectively [4], and the silylation of $\text{W}(\text{RNC})_6$ with Me_3SiOTf to give $[(\text{RNC})_5\text{W}\equiv\text{CN}(\text{SiMe}_3)\text{R}]\text{OTf}$ ($\text{R} = \text{Et, } ^t\text{Bu}$) [6]. The second pathway involves attack of the electrophile at the metal center and affords alkyl compounds. This is illustrated by the displacement reactions of $\text{Na}[\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})]$ with MeI and EtI to give *cis* / *trans*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{Me})$ and *cis* / *trans*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{Et})$, respectively [5]. Both types of product, i.e. aminocarbyne and alkyl complexes, are of particular interest. The former have been shown (a) to be useful starting materials for the preparation of a new class of high-valent transition-metal carbyne complexes [1–3,7,8]; (b) to undergo a characteristic acid-induced carbyne–isocyanide coupling to give bis(amino)acetylene complexes [6,9,10]; and (c) to be involved as key intermediates in the reductive coupling of two isocyanide ligands in Mo^{II} - and W^{II} -complexes [6,10–13]. By contrast, the alkyl complexes undergo facile insertion rearrangements to give η^2 -iminoacyl and η^3 -1-azaallyl complexes [2,5]. Parameters that influence the course of the reactions of the metallates $\text{Na}[(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2(\text{EtNC})]$ ($\text{R} = \text{H, Me; M} = \text{Mo, W}$) with carbon-electrophiles have been identified, appropriate variations in the parameters used in the case of tungsten to achieve regioselective formation of the aminocarbyne and the alkyl complexes [1–3,5]. In extension of this work we report herein the facile, high yield synthesis of η^2 -iminoacyl and η^3 -1-azaallyl complexes of molybdenum starting from the metallate $\text{Na}[\text{Cp}^*\text{Mo}(\text{CO})_2(\text{EtNC})]$. We also describe a clean isocyanide insertion reaction of the η^2 -iminoacyl products to give η^2 -1,4-diazabutadien-2-yl complexes.

Results and discussion

A mixture of the Mo^{II} -isomers *cis*- and *trans*- $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{EtNC})\text{I}$ (**1a**, **1b**) is readily reduced by an excess of sodium powder in THF to give the yellow, extremely air- and water-sensitive, Mo^0 -metallate $\text{Na}[\text{Cp}^*\text{Mo}(\text{CO})_2(\text{EtNC})]$ (**2**) in quantitative yield [14]. Reductive dehalogenation of isocyanide-substituted M^{II} -halo complexes ($\text{M} = \text{Mo, W}$) has been shown previously to offer a convenient route to electron-rich metallates [1–3,15,16].

Complex **2** is a strong nucleophile and reacts therefore rapidly with RI ($\text{R} = \text{Me, Et}$) in THF to give the iminoacyl complexes $\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{R}]$ (**3**: $\text{R} = \text{Me}$; **4**: $\text{R} = \text{Et}$) (Scheme 1). Compounds **3** and **4** are isolated as red, air-sensitive solids in 88 and 79% yield respectively. They are soluble in all common organic solvents and melt without decomposition at 110 and 111 °C, respectively.

Formation of **3** and **4** can be accounted for in terms of a three-step reaction sequence. The initial step involves exclusive alkylation of **2** at the metal center to give an alkyl complex. This step is followed by a migratory insertion of the ethylisocyanide ligand into the metal–alkyl bond to give the 16e iminoacyl intermediate $\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^1\text{-C}(\text{NEt})\text{R}]$ ($\text{R} = \text{Me, Et}$). Finally the 16e intermediate affords, via coordination of the iminoacyl-nitrogen to the molybdenum center, the



Scheme 1.

products 3 and 4 [5]. Evidence for the intermediate formation of an alkyl complex is provided by the IR spectrum of the solution obtained when a mixture of 2 and MeI in THF is stirred for 1 h at -78°C . This spectrum shows, in addition to the two strong $\nu(\text{C}\equiv\text{O})$ absorptions of 3 at 1912 and 1810 cm^{-1} , three other bands at $2120(\text{w})$, $1940(\text{m})$ and $1870(\text{s})\text{ cm}^{-1}$ that can be tentatively assigned respectively to the isocyanide stretching vibration and the symmetric CO and the antisymmetric

CO stretching modes of the *trans*-isomer $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{EtNC})(\text{Me})$. This assignment is based upon (a) the position and relative intensity of the bands [17,18], and (b) comparison with the positions of the bands for the analogous tungsten compound *trans*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{Me})$ in THF [$\nu(\text{C}\equiv\text{NEt})$ 2104 cm^{-1} , $\nu(\text{C}\equiv\text{O})_s$ 1920 cm^{-1} , $\nu(\text{C}\equiv\text{O})_{as}$ 1861 cm^{-1}] [2,5].

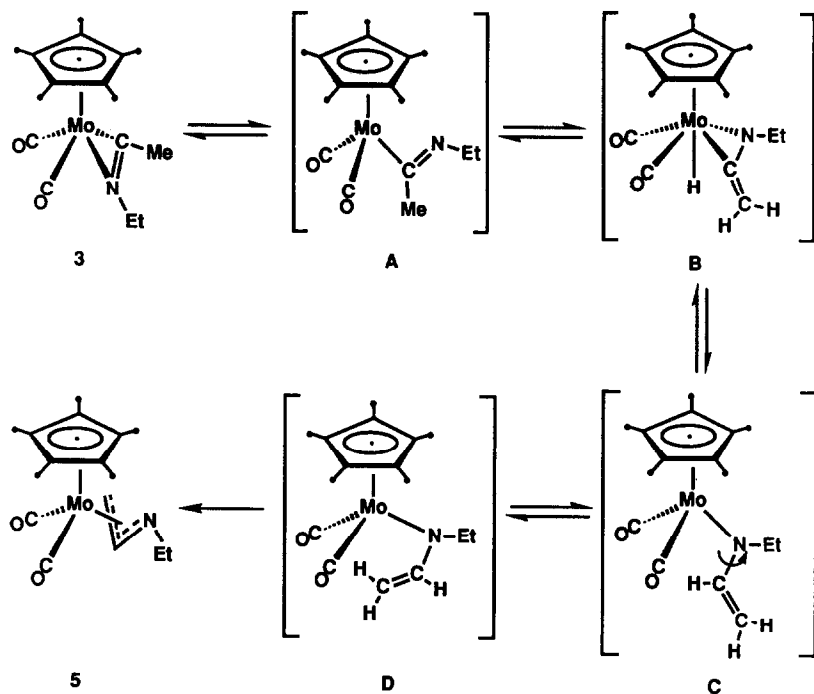
Further support for the suggested three-step sequence to give **3** and **4** is provided by (a) the reaction of the analogous tungsten complex $\text{Na}[\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})]$ with MeI, which leads to a mixture of the W^{II} -methyl isomers *cis*- and *trans*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{Me})$ in high yield, (b) the thermal-induced isocyanide rearrangement of these isomers to give the η^2 -iminoacyl complex $\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{Me}]$ and the η^3 -1-azaallyl complex $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-CH}_2\text{=CH=NEt})$, the tungsten analogues of **3** and **5**, respectively (Scheme 1), and (c) the thermal-induced rearrangement of the W^{II} -ethyl isomers *cis*- and *trans*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{Et})$ to give $\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ and $\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$, the tungsten analogues of **4** and **6**, respectively (Scheme 1). These rearrangements are assumed to proceed via the 16e iminoacyl intermediate $\text{Cp}^*(\text{CO})_2\text{W}[\eta^1\text{-C}(\text{NEt})\text{R}]$ (R = Me, Et), which is formed from *cis*- $\text{Cp}^*\text{W}(\text{CO})_2(\text{EtNC})(\text{R})$ after a migratory insertion of the ethyl isocyanide ligand in the tungsten-alkyl bond [5]. A similar reaction sequence has been proposed previously for the formation of the iminoacyl complexes $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NR})\text{Me}]$ from $\text{Na}[\text{CpMo}(\text{CO})_2(\text{RNC})]$ and MeI (Cp = $\eta^5\text{-C}_5\text{H}_5$; R = Me, C_6H_5) [16].

In contrast to the observed course of the reaction of **2** with EtI, ethylation of **2** with Et_3OBF_4 was shown previously to occur predominantly at the isocyanide nitrogen to give the aminocarbyne complex $\text{Cp}^*(\text{CO})_2\text{Mo}\equiv\text{CNEt}_2$, the η^2 -iminoacyl complex **4** being formed only in low yield [14].

The η^2 -iminoacyl complexes **3** and **4** isomerize in refluxing toluene to the 1-azaallyl complexes $\text{Cp}^*(\text{CO})_2\text{Mo}(\eta^3\text{-CH}_2\text{=CH=NEt})$ (**5**) and $\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$ (**6**), respectively (Scheme 1). The observed rearrangement results in an overall 1,2-hydrogen shift from the carbon-bonded alkyl substituent to the iminoacyl-carbon. Compounds **5** and **6** are isolated after purification by column chromatography as yellow, sparingly air- and water-sensitive, microcrystalline solids in 88 and 91% yield, respectively. They are soluble in all common organic solvents and melt without decomposition at 72 and 84°C. Similar isomerizations have been observed previously for the tungsten analogues of **3** and **4**, leading to the 1-azaallyl complexes $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-CH}_2\text{=CH=NEt})$ and $\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$, respectively [5]. One possible pathway for these transformations has been shown to involve cleavage of the metal-nitrogen bond to give a 16e iminoacyl intermediate [5]. This is illustrated in Scheme 2 for the isomerization of the molybdenum complex **3**.

The 16e iminoacyl intermediate **A** undergoes a β -H elimination reaction to give an 18e hydrido(keteneimine) complex (**B**). Migration of the Mo-bonded hydrogen on the central carbon of the coordinated keteneimine leads subsequently to a 16e vinylamide species (**C**, **D**), which collapses to the isolated η^3 -1-azaallyl complex **5**. This sequence is closely related to that previously reported for the formation of molybdenum π -allyl complexes in the reactions of the alkyne compounds $[\text{CpL}_1\text{L}_2\text{Mo}(\eta^2\text{-MeC}\equiv\text{CR})]\text{BF}_4$ ($\text{L}_1, \text{L}_2 = \text{CO}, \text{P}(\text{OMe})_3, \text{PEt}_3$; R = Et, ^iPr) with hydride transfer reagents [19,20].

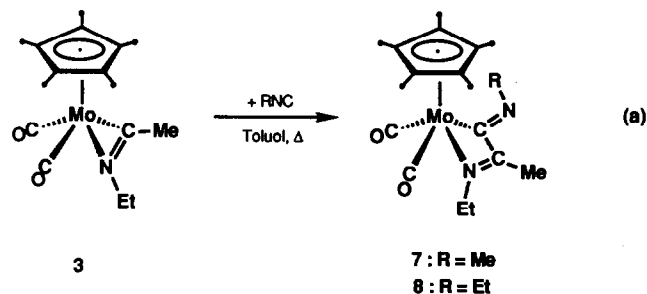
Formation of the η^3 -1-azaallyl complexes can also be accounted for in terms of



Scheme 2. Proposed mechanism for the isomerization of 3 to 5.

an alternative pathway. This involves an intramolecular 1,2-hydrogen migration, and leads directly from 3 to the 16e vinylamide species D (Scheme 2). As mentioned above, the intermediate D collapses subsequently to the η^3 -azaallyl product. However, such 1,2-hydrogen migration reactions have been so far reported only for η^2 -acyl and η^2 -iminoacyl complexes of lanthanides, actinides and early transition metals, and explained in terms of the carbenoid character of the acyl and iminoacyl ligands in these compounds [21–25].

Heating of the η^2 -iminoacyl complex 3 with an excess of RNC (R = Me, Et) leads to the isocyanide insertion products 7 and 8, respectively (equation a).

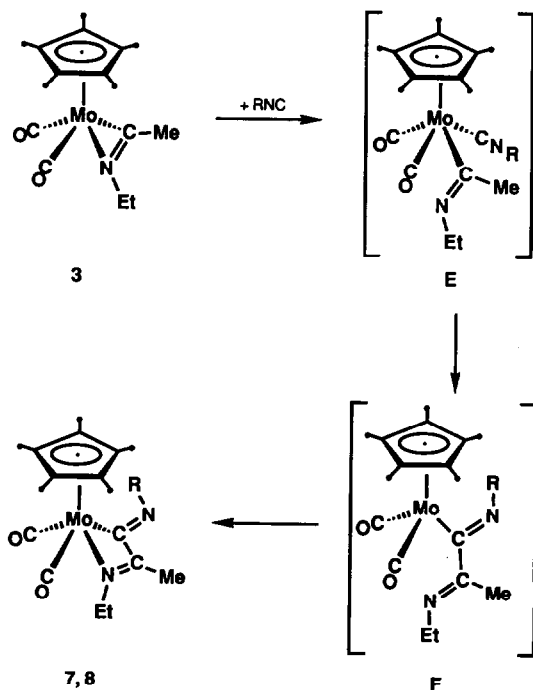


IR spectroscopic investigation of the reaction solutions shows an essentially quantitative conversion of 3 into 7 and 8, respectively. Thus, the two strong $\nu(\text{C}\equiv\text{O})$ absorptions of the starting material in toluene at 1915 and 1813 cm^{-1} are replaced by the two strong $\nu(\text{C}\equiv\text{O})$ absorptions of the insertion products at 1922 and 1831 cm^{-1} (7) and 1921 and 1831 cm^{-1} (8), respectively. Subsequent purification of the

products by column chromatography on alumina slightly lowers the yields to 76 (**7**) and 89% (**8**), apparently due to slow decomposition of the metallacycles **7** and **8** on alumina. The compounds **7** and **8** are isolated as slightly air-sensitive, red, microcrystalline solids, which are very soluble in CH_2Cl_2 , THF, toluene and Et_2O , but moderately soluble in *n*-pentane. They are thermally stable, melting without decomposition at 152 and 97°C, respectively.

By analogy to the manganese ketoacyl complex $\text{Cp}'(\text{CO})(\text{NO})\text{Mn}[\eta^1\text{-C}(\text{O})\text{C}(\text{O})\text{R}]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$; $\text{R} = \text{Ph}$, *p*- $\text{C}_6\text{H}_4\text{Me}$) the metallacycles **7** and **8** can be regarded as complexes containing a dihapto-bonded (α -imino)iminoacyl ligand [26]. An alternative description of the compounds **7** and **8** is that of a 1,4-diaza-3-methylbutadien-2-yl group dihapto bonded to a $\text{Cp}^*\text{Mo}(\text{CO})_2$ -fragment (see *Crystal structure of 8*) [27]. Complexes such as **7** and **8** are rare, and have been so far reported only for Mn and Fe. They were prepared by photo-induced decarbonylation of isocyanide-substituted η^1 -acyl complexes such as $\text{Cp}(\text{CO})(\text{CyNC})\text{Fe}[\text{C}(\text{O})\text{R}]$ [28], photo-induced or PdO-catalyzed carbonyl substitution reaction of alkyl complexes such as $\text{CpFe}(\text{CO})_2\text{Me}$ and $(\text{CO})_5\text{MnCH}_2\text{C}_6\text{H}_4\text{-}p\text{-X}$ ($\text{X} = \text{Cl}$, OMe) with isocyanides [28,29], and oxidative addition of alkyl halides to electron-rich isocyanide complexes such as $\text{Fe}(\text{}^t\text{BuNC})_5$ [30]. However these reactions are accompanied by formation of side products and so after tedious purification procedures the desired metallacycles are isolated in rather low yields [28–30].

In the light of the proposed reaction sequence for the isomerization of the η^2 -iminoacyl complexes **3** and **4** to the 1-azaallyl compounds **5** and **6**, a mechanism can be proposed for the reaction of **3** with RNC to give **7** and **8**, respectively.



Scheme 3. Proposed mechanism for the formation of the metallacycles **7** and **8**.

(Scheme 3). The first step involves displacement of the coordinated iminoacyl-nitrogen in **3** by the entering isocyanide and leads to the 18e η^1 -iminoacyl complex **E** (Scheme 3). This step is followed by a rapid insertion of the isocyanide ligand into the Mo–C bond to give the 16e η^1 -1,4-diaza-3-methylbutadien-2-yl intermediate **F**. The intermediate **F** finally gives, upon coordination of the β -carbon bonded imino-nitrogen to the molybdenum center, the metallacycles **7** and **8**. However an alternative route to **7** and **8** involving direct insertion of the isocyanide in the Mo–C bond of **3** is possible. Reaction sequences involving intermediates such as **E** and **F** have been previously proposed for the formation of multiple isocyanide insertion products in the reactions of transition-metal alkyl complexes with isocyanides [28–32].

Spectroscopic investigations

IR spectra

The IR spectral data are consistent with the structures suggested for **3–8**. All the compounds exhibit in the 2200–1500 cm^{-1} region two bands of almost equal intensity, which are assigned to the $\nu(\text{C}\equiv\text{O})$ stretching vibrations of the mutually *cis*-oriented carbonyl ligands (Table 1). The position of these bands is strongly dependent on the solvent polarity. This is demonstrated by the IR spectra of **3–8** in *n*-pentane and CH_2Cl_2 , which show a shift of the $\nu(\text{C}\equiv\text{O})$ absorptions to lower

Table 1

$\nu(\text{C}\equiv\text{O})$ and $\nu(\text{C}=\text{N})$ absorptions for the molybdenum complexes **3–8** and analogous tungsten compounds in cm^{-1} , solvent *n*-pentane (a), CH_2Cl_2 (b)

Complex	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{N})$	Solvent
$\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Me}]$ (3)	1927 vs, 1832 vs		a
	1905 vs, 1795 vs	1709 w	b
$\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{Me}]$	1919 vs, 1823 vs	1663 w	a [5]
	1893 vs, 1781 vs	1684 w	b
$\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ (4)	1926 vs, 1831 vs	1681 w	a
	1904 vs, 1795 vs	1702 w	b
$\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{Et}]$	1917 vs, 1822 vs	1654 w	a [5]
	1894 vs, 1782 vs	1676 w	b
$\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^3\text{-CH}_2\text{=CH=NEt}]$ (5)	1947 vs, 1871 vs	–	a
	1934 vs, 1847 vs	–	b
$\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}_2\text{=CH=NEt}]$	1939 vs, 1861 vs	–	a [5]
$\text{Cp}^*(\text{CO})_2\text{Mo}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$ (6)	1942 vs, 1866 vs	–	a
	1929 vs, 1843 vs	–	b
$\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$	1934 vs, 1857 vs	–	a [5]
	1920 vs, 1831 vs	–	b
$\text{Cp}^*(\text{CO})_2\text{Mo}[\overline{\text{C}(\text{NMe})\text{C}(\text{NEt})\text{Me}}]$ (7)	1931 vs, 1846 vs	1634 w, 1593 vw	a
	1917 vs, 1819 vs	1635 w, 1592 vw	b
$\text{Cp}^*(\text{CO})_2\text{W}[\overline{\text{C}(\text{NMe})\text{C}(\text{NEt})\text{Me}}]$	1923 vs, 1832 vs	1634 w, 1589 vw	a [33]
	1906 vs, 1804 vs	1635 w, 1590 vw	b
$\text{Cp}^*(\text{CO})_2\text{Mo}[\overline{\text{C}(\text{NEt})\text{C}(\text{NEt})\text{Me}}]$ (8)	1931 vs, 1844 vs	1635 w, 1588 vw	a
	1917 vs, 1819 vs	1632 w, 1586 vw	b
$\text{Cp}^*(\text{CO})_2\text{W}[\overline{\text{C}(\text{NEt})\text{C}(\text{NEt})\text{Me}}]$	1921 vs, 1831 vs	1631 w, 1585 vw	a [33]
	1905 vs, 1803 vs	1631 w, 1583 vw	b

frequency, when the polarity of the solvent is increased (Table 1). In contrast, a shift of the $\nu(\text{C}=\text{O})$ absorptions to higher frequency is observed in the sequence $3 < 7 < 5$ and $4 < 8 < 6$ as a consequence of the increasing σ -donor/ π -acceptor ratio in the ligand series η^3 -azaallyl $<$ η^2 -1,4-diazabutadien-2-yl $<$ η^2 -iminoacyl. The $\nu(\text{C}=\text{O})$ absorption bands of the molybdenum compounds 3–8 are found at higher frequency than those for analogous tungsten complexes (Table 1).

The presence of only two $\nu(\text{C}=\text{O})$ absorptions in the IR spectra of the η^3 -1-azaallyl complexes 5 and 6 confirms the presence of only one isomer in solution. This isomer is assigned the *endo* conformation on the basis of the ^1H and ^{13}C NMR spectra (Figs. 1 and 3) [5]. In contrast, the IR spectra of the structurally related π -allyl complexes $(\eta^5\text{-C}_3\text{R}_5)(\text{CO})_2\text{M}(\eta^3\text{-CH}_2\text{=CH=CH}_2)$ ($\text{R} = \text{H, Me; M} = \text{Mo, W}$) were shown previously to contain four carbonyl stretching bands, and rationalized in terms of a temperature- and solvent-dependent equilibrium between the *exo* and *endo* conformers [34,35].

The iminoacyl complexes 3 and 4 exhibit, in addition to the two strong $\nu(\text{C}=\text{O})$ absorptions, a weak band at 1709 and 1702 cm^{-1} (CH_2Cl_2), respectively (Table 1). This band is assigned to the $\nu(\text{C}=\text{N})$ stretching vibration of the dihapto-bonded iminoacyl ligand. The position of this band depends on the solvent polarity and the substituents in the iminoacyl moiety (compare for example the $\nu(\text{C}=\text{N})$ absorptions of 4 in *n*-pentane and CH_2Cl_2 , and those of 3 and 4 in CH_2Cl_2 , Table 1). Moreover this band is found at a higher frequency for the molybdenum complexes 3 and 4 than for the analogous tungsten compounds $\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{R}]$ ($\text{R} = \text{Me, Et}$) (Table 1) [5]. Similar absorption bands were previously reported for other low-valent molybdenum η^2 -iminoacyl complexes such as $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ [$\nu(\text{C}=\text{N})$ in CH_2Cl_2 : 1730 cm^{-1}] [2], $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NMe})\text{Me}]$ [$\nu(\text{C}=\text{N})$ in *n*-pentane: 1720 cm^{-1}] [16] or [$(^t\text{BuNC})_3\text{Mo}[\eta^2\text{-C}(\text{N}^t\text{Bu})\text{Me}]\text{I}$] [$\nu(\text{C}=\text{N})$ in Nujol mull: 1758 cm^{-1}] [36]. These bands appear at considerably higher frequency than those for low-valent molybdenum η^1 -iminoacyl complexes: e.g., $\text{Cp}(\text{CO})_2(\text{TCNE})\text{Mo}[\eta^1\text{-C}(\text{NPh})\text{Me}]$ [$\nu(\text{C}=\text{N})$ in MeCN: 1615 cm^{-1}] (TCNE: tetracyanoethylene) [16,37].

In contrast, the isocyanide insertion products 7 and 8 are characterized by two weak absorptions at low frequency resulting from the two $\nu(\text{C}=\text{N})$ stretching vibrations of the dihapto bonded 1,4-diaza-3-methylbutadien-2-yl ligand (e.g. $\nu(\text{C}=\text{N})$ of 7 in *n*-pentane: 1634 and 1593 cm^{-1}) (Table 1). The position of these bands is not influenced by the solvent polarity (Table 1). Similar low frequency absorptions have been previously observed in the IR spectra of analogous manganese- and iron-metallacycles e.g. $(\text{CO})_4\text{Mn}[\text{C}(\text{NR})\text{C}(\text{NR})\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-OMe}]$ ($\text{R} = p\text{-tolyl}$) [$\nu(\text{C}=\text{N})$ in CCl_4 : 1624 and 1615 cm^{-1}] [29], $\text{Cp}(\text{CO})\text{Fe}[\text{C}(\text{N}^t\text{Bu})\text{-C}(\text{N}^t\text{Bu})\text{Me}]$ [$\nu(\text{C}=\text{N})$ in benzene: 1632 and 1587 cm^{-1}] [28] and $\text{I}(^t\text{BuNC})_3\text{-Fe}[\text{C}(\text{N}^t\text{Bu})\text{C}(\text{N}^t\text{Bu})\text{Me}]$ [$\nu(\text{C}=\text{N})$ in Nujol mull: 1631 and 1571 cm^{-1}] [30].

^1H NMR spectra

Further support for the assigned structures to 3–8 is provided by the ^1H NMR spectra (Table 2). All compounds possess C_1 symmetry and are chiral. Therefore the methylene protons of each N-bonded ethyl group are diastereotopic and appear as two separate ABX₃ doublets of quartets with $^2J(\text{H}_\text{A}\text{H}_\text{B}) = 12\text{--}13$ Hz and $^3J(\text{H}_\text{A}\text{H}_\text{X}) = ^3J(\text{H}_\text{B}\text{H}_\text{X}) = 7.3$ Hz. Two doublets of quartets at δ 2.11 and 2.26 with a slightly larger geminal coupling constant [$^2J(\text{H}_\text{A}\text{H}_\text{B}) = 15.3$ Hz] [38] are also observed for the diastereotopic methylene protons of the C-bonded ethyl group in 4 (Table 2).

The methyl protons of the iminoacyl ligand in **4** give rise to two distinct triplets, at δ 0.76 and 1.20. The resonance at higher field (δ 0.76) is assigned to the methyl protons of the N-bonded ethyl group, and that at lower field (δ 1.20) to the methyl protons of the C-bonded ethyl group. This assignment is based on a comparison of the ^1H NMR data for **4** with those for **3**, which contains only a N-bonded ethyl group (Table 2). In contrast, the methylene proton resonances of the N-bonded ethyl group of **4** appear at lower field (δ 2.72 and 3.09) than those of the C-bonded ethyl group (δ 2.11 and 2.26). The same feature was previously observed for the ^1H NMR spectra of the iminoacyl complexes $\text{Cp}(\text{CO})_2\text{M}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ ($\text{M} = \text{Mo}, \text{W}$) [**2**] and $\text{Cp}^*(\text{CO})_2\text{W}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ [**5**].

The compounds **3** and **4** are like other η^2 -iminoacyl complexes, fluxional on the NMR time scale [2,5,38]. This is demonstrated by the variable-temperature 400 MHz ^1H NMR spectra of **3** and **4** in toluene- d_8 . At 293 K two doublets of quartets at δ 2.72 and 3.09 (**3**) and δ 2.75 and 3.13 (**4**) are observed for the diastereotopic methylene protons of the N-bonded ethyl group. However, as the temperature is raised, these resonances broaden and coalesce at 363 (**3**) or 368 K (**4**). At the fast exchange limit (100 MHz ^1H spectra) only one quartet is observed for these protons. A similar temperature dependence is observed for the two doublets of quartets obtained for the methylene protons of the C-bonded ethyl group of **4** at δ 2.12 and 2.29 (toluene- d_8 , 293 K). The dynamic process also leads to exchange of the two different carbonyl environments, which are observed in the 100.5 MHz ^{13}C NMR spectra of **3** and **4** in C_6D_6 at $+20^\circ\text{C}$ (^{13}C NMR spectra, Table 3). This is demonstrated by the 25.2 MHz ^{13}C -NMR spectra of **3** and **4** at the fast exchange limit (toluene- d_8 , 363 K). The free energy of activation for the site exchange of the methylene protons of the N-bonded ethyl group, $\Delta G^\ddagger(T_c)$, can be calculated from the Eyring equation by using the Gutowsky–Holm equation to derive the rate constant for the site exchange, k_{ex} , at the coalescence temperature T_c (**3**: T_c (400 MHz) = 363 K, **4**: T_c (400 MHz) = 368 K) [39,40]. The activation barrier of 17.2 (**3**) and 17.4 kcal/mol (**4**) is slightly larger than that of the analogous Cp-compound $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ ($\Delta G^\ddagger = 15.8$ kcal/mol) [**2**].

Two mechanisms are suggested for the site exchange of the methylene protons and the carbonyl carbons of the η^2 -iminoacyl complexes **3** and **4**. The first one involves a 180° rotation of the dihapto-bonded iminoacyl ligand about an axis connecting the Mo-atom with the midpoint of the C=N bond, and can best be compared with the mechanism suggested for the rotation of coordinated mono-olefins [41]. The second one involves an initial breaking of the Mo–N bond to give the same coordinatively unsaturated 16e η^1 -iminoacyl intermediate, which is assumed to be involved in the isomerization of **3** to **5** or **4** to **6** (Scheme 2). This step is followed by a 180° rotation of the η^1 -iminoacyl ligand about the Mo–C bond and reformation of the Mo–N bond [2,5,38]. Both rearrangement processes result in an interchange of the C and N coordination sites of the iminoacyl ligand. Either could account for the observed site exchange of the methylene protons and carbonyl carbons, because they traverse an intermediate of C_s -symmetry, in which the symmetry plane bisects both the OC–Mo–CO and the H–C–H fragments. In contrast, a rearrangement process, in which the carbonyl ligands interchange their positions while the dihapto-bonded iminoacyl ligand remains rigid relative to the Cp^* -ligand, traverses an intermediate of C_1 -symmetry and cannot account for the temperature dependent ^1H NMR spectra of **3** and **4** [2,5]. It is noteworthy that such

Table 2

¹H NMR data for the complexes 3–8 in C₆D₆ (a) or CD₂Cl₂ (b) at +20 °C; relative intensities and multiplicities in parentheses, coupling constants in Hz

Complex	H _a	CCH ₂ CH ₃ ; NCH ₂ CH ₃	Cp*	CCH ₃	H _s	NCH ₂ CH ₃ ; CCH ₂ CH ₃	H _c ; NCH ₃	Solv.
3	-	0.74 (3:t) ^a ³ J(HH) 7.3	1.79 (15:s)	2.01 (3:s)	-	2.68 (1,dd) ² J(H _B H _A) 12.8 ³ J(H _B H _X) 7.3; 3.05 (1,dd) ² J(H _A H _B) 12.8 ³ J(H _A H _X) 7.3	-	a
	-	0.76 (3:t) ^a ³ J(HH) 7.3; 1.20 (3:t) ³ J(HH) 7.3	1.80 (15:s)	-	-	2.11 (1,dd) ² J(H _B H _A) 15.3 ³ J(H _B H _X) 7.3; 2.26 (1,dd) ² J(H _A H _B) 15.3 ³ J(H _A H _X) 7.3; 2.72 (1,dd) ^a ² J(H _B H _A) 12.2 ³ J(H _B H _X) 7.3; 3.09 (1,dd) ^a ² J(H _A H _B) 12.2 ³ J(H _A H _X) 7.3	-	a
5	0.88 (1,dd) ³ J(H _A H _C) 7.3 ² J(H _A H _B) 1.2	1.13 (3:t) ³ J(HH) 7.3	1.63 (15:s)	-	2.88 (1,dd) ³ J(H _A H _C) 4.3 ² J(H _A H _B) 1.2	2.69 (1,dd) ² J(H _B H _A) 12.2 ³ J(H _B H _X) 7.3; 3.09 (1,dd) ² J(H _A H _B) 12.2 ³ J(H _A H _X) 7.3	4.76 (1,dd) ³ J(H _C H _A) 7.3 ³ J(H _C H _B) 4.3	a

6	1.54 (1,dq) $^2J(\text{H}_a\text{H}_c)$ 6.7 $^3J(\text{H}_a\text{H}_{\text{Me}})$ 6.1	1.17 (3,t) $^3J(\text{HH})$ 7.3	1.62 (15,s)	1.79 (3,d) $^3J(\text{H}_{\text{Me}}\text{H}_a)$ 6.1	-	2.77 (1,dq) $^2J(\text{H}_\text{B}\text{H}_\text{A})$ 12.2 $^3J(\text{H}_\text{B}\text{H}_\text{X})$ 7.3; 3.11 (1,dq) $^2J(\text{H}_\text{A}\text{H}_\text{B})$ 12.2 $^3J(\text{H}_\text{A}\text{H}_\text{X})$ 7.3	4.63 (1,d) $^3J(\text{H}_\text{c}\text{H}_a)$ 6.7	a
7	-	1.11 (3,t) $^3J(\text{HH})$ 7.3	1.88 (15,s)	1.82 (3,s)	-	3.09 (1,dq) $^2J(\text{H}_\text{B}\text{H}_\text{A})$ 12.2 $^3J(\text{H}_\text{B}\text{H}_\text{X})$ 7.3; 3.37 (1,dq) $^2J(\text{H}_\text{A}\text{H}_\text{B})$ 12.2 $^3J(\text{H}_\text{A}\text{H}_\text{X})$ 7.3	3.46 (3,s)	b
8	-	1.11 (3,t) ^b $^3J(\text{HH})$ 7.3; 1.29 (3,t) $^3J(\text{HH})$ 7.3	1.88 (15,s)	1.84 (3,s)	-	3.09 (1,dq) ^b $^2J(\text{H}_\text{B}\text{H}_\text{A})$ 12.2 $^3J(\text{H}_\text{B}\text{H}_\text{X})$ 7.3; 3.37 (1,dq) ^b $^2J(\text{H}_\text{A}\text{H}_\text{B})$ 12.2 $^3J(\text{H}_\text{A}\text{H}_\text{X})$ 7.3; 3.55 (1,dq) $^2J(\text{H}_\text{B}\text{H}_\text{A})$ 12.7 $^3J(\text{H}_\text{B}\text{H}_\text{X})$ 7.3; 3.65 (1,dq) $^2J(\text{H}_\text{A}\text{H}_\text{B})$ 12.7 $^3J(\text{H}_\text{A}\text{H}_\text{X})$ 7.3	-	b

^a Methyl and methylene protons of the N-bonded ethyl group. ^b Methyl and methylene protons of the metal-bonded NCH_2CH_3 -group.

a rearrangement process has been previously suggested for the fluxional triazenido complexes $\text{Cp}(\text{CO})_2\text{M}(\eta^2\text{-RNNR}')$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R}, \text{R}' = \text{aryl}$) [42].

The ^1H NMR spectrum of the 1-azaallyl complex **5** confirms, in accordance with the IR data, the presence of only one of the four possible isomers in solution. This isomer is assigned the *endo* conformation, with the N-bonded ethyl group occupying a *syn* position on the 1-azaallyl fragment (Fig. 1, isomer a). The assignment is based on the comparison of the ^1H NMR data for **5** with those for the analogous tungsten complex $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-CH}_2\text{-CH-NEt})$, for which structure a with a " π -allyl" bonding of the 1-azaallyl ligand to tungsten was confirmed by an X-ray crystallographic study [5]. This comparison shows (a) similar chemical shifts for the *anti*, *syn*- and *central* protons H_a , H_s and H_c of the 1-azaallyl ligand (Fig. 2), and (b) almost equal values for the geminal [$^2J(\text{H}_a\text{H}_s)$] and vicinal coupling constants [$^3J(\text{H}_a\text{H}_c)$, $^3J(\text{H}_s\text{H}_c)$] between these protons in the two compounds [5].

Similar conclusions are drawn from comparison of the ^1H NMR data for **6** and the analogous tungsten compound $\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}(\text{Me})\text{-CH-NEt}]$, and allow an unequivocal assignment of structure e to **6** (Fig. 3) [5]. Thereafter complex **6** adopts an *endo*-conformation with both ethyl and methyl substituents occupying *syn*-positions on the 1-azaallyl fragment.

The ^1H NMR spectra of **5** and **6** (toluene- d_6) are not temperature dependent in the range -80 to $+20^\circ\text{C}$. In contrast, the ^1H NMR spectra of the analogous π -allyl complexes $\text{Cp}(\text{CO})_2\text{M}[\eta^3\text{-CH}_2\text{-CH-CH}_2]$ ($\text{M} = \text{Mo}, \text{W}$) were shown previously to be temperature dependent due to an interconversion of *exo* and *endo* conformers [34,41]. The ^1H NMR spectrum of **8** shows two triplets, at δ 1.11 and 1.29, for the methyl protons and four doublets of quartets, at δ 3.09, 3.37, 3.55 and 3.65, for the diastereotopic methylene protons of the two different nitrogen-bonded ethyl groups. The resonances at δ 1.11, 3.09 and 3.37 are unequivocally assigned to the methyl and methylene protons of the molybdenum-bonded NCH_2CH_3 -group. This assignment is based on the comparison of the ^1H NMR spectrum of **8** with that of **7** (Table 2).

^{13}C NMR spectra

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3-8** provide further support for the proposed structures (Table 3). Thus, two different environments are observed for the mutually

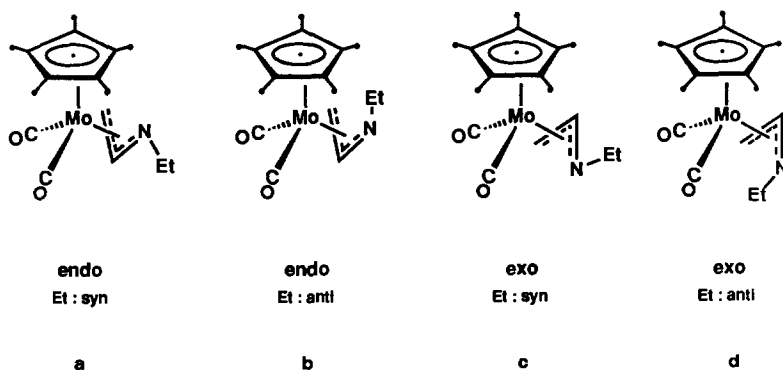


Fig. 1. Possible isomers for the 1-azaallyl complex **5**.

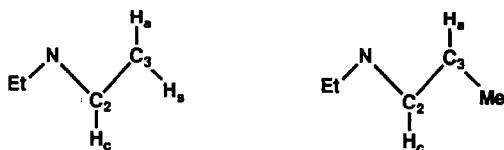


Fig. 2. Notation for the hydrogen and carbon atoms in the 1-azaallyl ligand of **5** and **6**.

cis-oriented carbonyl ligands in **3–8**. As discussed above, an exchange of the two carbonyl environments is observed in the ^{13}C NMR spectra of the η^2 -iminoacyl complexes **3** and **4** at higher temperature (^1H NMR spectra).

The η^2 -iminoacyl complexes **3** and **4** are characterized by a resonance for the imino-carbon at low field (δ 200.6 and 206.0). Comparable chemical shifts have been found for the imino-carbons of other low-valent molybdenum η^2 -iminoacyl complexes such as $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Et}]$ (δ_{C} 197.8, C_6D_6 , $+20^\circ\text{C}$) [2], $[(^t\text{BuNC})_5\text{Mo}[\eta^2\text{-C}(\text{N}^t\text{Bu})\text{Me}]]\text{I}$ (δ_{C} 196.3, acetone- d_6) [36] and $\text{Cp}(\text{CO})_2\text{Mo}[\eta^2\text{-C}(\text{NMe})\text{Me}]$ (δ_{C} 195.2, toluene- d_8 , -10°C) [37]. The ^{13}C NMR spectra of the 1-azaallyl complexes display two characteristic resonances at δ 39.9 and 119.3 (**5**) and 55.9 and 120.6 (**6**), which are assigned to the C_3 and C_2 carbon atoms of the 1-azaallyl ligand, respectively (Table 3, Fig. 2). This is supported by comparison with the C_3 and C_2 resonances of the analogous tungsten complexes $\text{Cp}^*(\text{CO})_2\text{W}(\eta^3\text{-CH}_2\text{=CH=NEt})$ [$\delta(\text{C}_3)$ 32.1, $\delta(\text{C}_2)$ 115.9; C_6D_6 , $+20^\circ\text{C}$] and $\text{Cp}^*(\text{CO})_2\text{W}[\eta^3\text{-CH}(\text{Me})\text{=CH=NEt}]$ [$\delta(\text{C}_3)$ 47.0, $\delta(\text{C}_2)$ 118.1; C_6D_6 , $+20^\circ\text{C}$], for which an unequivocal assignment was made on the basis of the ^1H coupled ^{13}C spectra [5]. The four-membered metallacycles **7** and **8** are characterized by two low-field resonances for the imino-carbons at δ 183.9 and 189.4 (**7**) and 183.4 and 186.9 (**8**) (Table 3). An unambiguous assignment of these resonances becomes possible after comparison with those of the analogous tungsten compounds $\text{Cp}^*(\text{CO})_2\text{W}[\text{C}(\text{NMe})\text{C}(\text{NEt})\text{Me}]$ (**9**) (δ_{C} 179.3 and 190.6; CD_2Cl_2 , $+20^\circ\text{C}$) and $\text{Cp}^*(\text{CO})_2\text{W}[\text{C}(\text{NEt})\text{C}(\text{NEt})\text{Me}]$ (**10**) (δ_{C} 176.7 and 190.7; CD_2Cl_2 , $+20^\circ\text{C}$) [33]. The resonances at δ 179.3 and 176.7 are accompanied by satellites due to the ^{13}C - ^{183}W coupling (**9**: $^1J(\text{CW}) = 61.0$ Hz; **10**: $^1J(\text{CW}) = 60.5$ Hz), and are therefore assigned to the tungsten bonded imino-carbon of **9** and **10**, respectively. A small upfield shift (~ 3 ppm) of this resonance is observed, when the substituents at the imino-nitrogen are changed from Me to Et, i.e. on going from **9** to **10**. The same effect is observed for the resonances of the molybdenum complexes **7** and **8** at δ 189.4 and 186.9, respectively. These resonances are therefore assigned to the

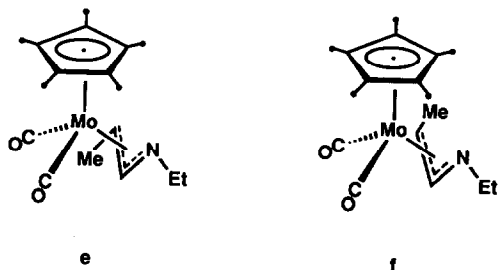


Fig. 3. Two possible *endo*-conformers for **6** with a *syn*-orientation of the N-bonded ethyl group.

Table 3

¹³C NMR data of the complexes 3–8 in C₆D₆ (a) or CD₂Cl₂ (b) at +20 °C

Complex	C ₅ (CH ₃) ₅	CCH ₂ CH ₃ ; NCH ₂ CH ₃	CCH ₃ ; CCH ₂ CH ₃ ; C ₃	NCH ₂ CH ₃ ; NCH ₃	C ₅ (CH ₃) ₅	C ₂	C=N	CO	Solv.
3	11.3	14.1	17.9	41.2	106.0	–	200.6	252.9; 255.8	a
4	11.4 ^a	11.4 ^a ; 14.2	25.4	41.9	106.1	–	206.0	253.4; 255.7	a
5	10.6	21.2	39.9	57.9	105.1	119.3	–	247.1; 249.5	a
6	10.5	21.3	17.3; 55.9 ^b	58.0	104.9	120.6	–	247.5; 250.6	a
7	11.2	14.3	11.1	47.1; 47.3	106.0	–	183.9; 189.4 ^d	255.9; 261.7	b
8	11.2	14.3 ^c ; 16.3	11.1	47.2 ^c ; 54.9	106.1	–	183.4; 186.9 ^d	256.1; 261.8	b

^a The methyl-carbon resonances of the η⁵-C₅Me₅ ligand and the C-bonded ethyl group are fortuitously coincident. ^b C₃-carbon resonance. ^c Methyl- and methylene-carbon resonance of the metal-bonded NCH₂CH₃-group. ^d Signal for the molybdenum-bonded imino-carbon.

molybdenum-bonded imino-carbons (Table 3). In contrast, the imino-carbons, which are not bonded to the metal, have nearly the same chemical shift in 7 and 8 as well as in 9 and 10 (7: δ 183.9; 8: δ 183.4; 9: δ 190.6; 10: δ 190.7).

It is noteworthy that all metal-bonded carbon resonances for the molybdenum complexes 3–8 appear at lower field than those for the analogous tungsten compounds [5,33]. This is consistent with the trends in ¹³C shielding previously observed for the Group VI metal triad [43].

Mass spectra

Fragmentations of the complexes 3 and 8 under EI conditions follow a common path, via the ion [Cp*(CO)Mo[C(NEt)Me]]⁺ (*m/z* = 331) (Table 4). This ion is

Table 4

Mass spectra of the complexes 3 and 8; the *m/z* values refer to the ⁹⁸Mo isotope

Complex	<i>m/z</i>	Tentative assignment
3	359	<i>M</i> ⁺
	331	[<i>M</i> – CO] ⁺
	301	[<i>M</i> – CO – C ₂ H ₆] ⁺
	273	[<i>M</i> – 2CO – C ₂ H ₆] ⁺
	258	[<i>M</i> – 2CO – C ₂ H ₆ – CH ₃] ⁺ (basis peak)
8	414	<i>M</i> ⁺
	386	[<i>M</i> – CO] ⁺
	358	[<i>M</i> – 2CO] ⁺
	331	[<i>M</i> – CO – EtNC] ⁺
	301	[<i>M</i> – CO – EtNC – C ₂ H ₆] ⁺ (basis peak)
	273	[<i>M</i> – 2CO – EtNC – C ₂ H ₆] ⁺
	258	[<i>M</i> – 2CO – EtNC – C ₂ H ₆ – CH ₃] ⁺

formed from the parent molecule ion M^+ (**3**: $m/z = 359$; **8**: $m/z = 414$) after loss of one CO ligand (**3**) followed by elimination of the inserted ethyl isocyanide molecule (**8**). Further fragmentation of this ion occurs via elimination of ethane ($m/z = 301$), followed by loss of the second CO ligand ($m/z = 273$) and then loss of one methyl group ($m/z = 258$).

Crystal structure of **8**

The molecular structure of **8** was determined by a single-crystal X-ray diffraction study. Two views of a single molecule, with the atomic numbering scheme used, are given in Figs. 4 and 5. Selected internuclear bond distances and interbond angles are listed in Table 5, and fractional atomic coordinates in Table 6.

The complex contains a 1,4-diaza-3-methylbutadien-2-yl (or (α -imino)iminoacyl) ligand that is dihapto-bonded through the imino-nitrogen and carbon atoms N(1) and C(5) to a $Cp^*(CO)_2Mo$ -fragment (Figs. 4 and 5). The bite of the organic ligand is small, the N(1)–Mo–C(5) angle being only $59.47(4)^\circ$. The Mo–N(1) bond length of $222.5(1)$ pm falls within the range observed for Mo–N(imine) bonds in low-valent molybdenum complexes [44–46], but it is slightly shorter than the length of a Mo–N(sp^2) single bond (231.8 pm) estimated from the sum of covalent radii of a single-bonded molybdenum and sp^2 -hybridized nitrogen atom [$r_{Mo} = (1/2)a(Mo-Mo)$ in $[CpMo(CO)_3]_2 = 161.7$ pm; $r_N = (1/2)a(N-N)$ in $N_2(CF_3)_4 = 70.1$ pm] [47,48].

The Mo–C(5) bond distance of $222.2(1)$ pm is quite close to the Mo–C(sp^2) bond distances reported for η^1 -vinyl and η^1 -iminoacyl complexes of Mo^{II} such as $Cp[P(OMe)_3]_3Mo[\sigma-(E)-CH=CH^tBu]$ [19] and $Cp(CO)_2[P(OMe)_3]Mo[C(NPh)Me]$ [37]. By contrast, the Mo–C(3) distance of 276 pm rules out any bonding interaction between the molybdenum center and the imino-carbon C(3). In the light of these results, the bidentate 1,4-diaza-3-methylbutadien-2-yl ligand can be viewed in **8** as a

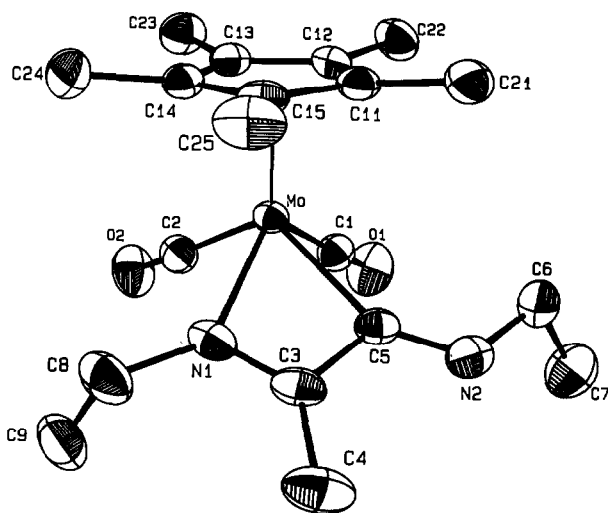


Fig. 4. ORTEP drawing of the molecular structure of $Cp^*(CO)_2Mo[C(NEt)C(NEt)Me]$ (**8**) with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity reasons.

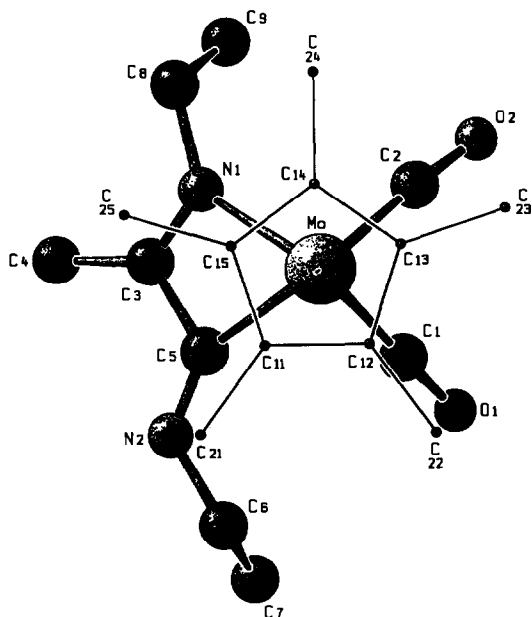


Fig. 5. SCHAKAL plot of the molecular structure of **8** (top view).

three-electron donor; the molybdenum atom thus achieved an 18-electron configuration.

Chelation of the 1,4-diaza-3-methylbutadien-2-yl ligand through the atoms N(1) and C(5) leads to a four-membered metallacyclic ring. This ring is planar, deviations from the least squares plane being less than 3 pm. The planarity of the four-mem-

Table 5

Selected bond distances (pm) and bond angles ($^{\circ}$) with estimated standard deviations for **8**^a

Mo–N1	222.5 (<1)	N1–Mo–C1	117.92(4)
Mo–C1	194.2(2)	N1–Mo–C2	87.85(4)
Mo–C2	195.8(1)	N1–Mo–C5	59.47(4)
Mo–C5	222.2(1)	C1–Mo–C2	74.46(4)
Mo–C11	239.1 (<1)	C1–Mo–C5	80.59(4)
Mo–C12	233.9 (<1)	C2–Mo–C5	121.74(4)
Mo–C13	231.4 (<1)	Cp*–Mo–C1	122.1
Mo–C14	232.3 (<1)	Cp*–Mo–C2	120.5
Mo–C15	236.5 (<1)	Cp*–Mo–N1	118.2
Mo–Cp*	200.4	Cp*–Mo–C5	117.5
C1–O1	115.9(1)	Mo–C1–O1	178.07(9)
C2–O2	115.9(1)	Mo–C2–O2	175.07(9)
N1–C3	128.0(1)	N1–C3–C4	128.6(1)
N1–C8	146.8(1)	N1–C3–C5	105.83(9)
N2–C5	126.6(1)	N2–C5–C3	118.47(9)
N2–C6	145.6(1)	C3–N1–C8	123.7(2)
C3–C4	149.7(2)	C4–C3–C5	125.6(1)
C3–C5	148.0(1)	C5–N2–C6	119.72(9)

^a Cp* denotes the center of the pentamethylcyclopentadienyl ring.

Table 6

Fractional atomic coordinates and their estimated standard deviations for non-hydrogen atoms in **8**^a

Atom	x	y	z	B_{eq} (Å ²)
Mo	0.14653(2)	0.19712(1)	0.20809(1)	1.844(3)
O1	0.4870(2)	0.2379(1)	0.1464(1)	4.34(3)
O2	0.2621(2)	0.1404(1)	-0.0500(1)	4.16(3)
N1	-0.0923(2)	0.3695(1)	0.1737(1)	2.64(3)
N2	0.0964(2)	0.4851(1)	0.3484(1)	2.97(3)
C1	0.3581(2)	0.2252(2)	0.1696(2)	2.66(4)
C2	0.2117(2)	0.1650(2)	0.0450(2)	2.72(4)
C3	-0.0938(2)	0.4671(2)	0.2351(2)	2.74(4)
C4	-0.2254(3)	0.6126(2)	0.2545(2)	4.44(6)
C5	0.0652(2)	0.4077(2)	0.2849(1)	2.31(4)
C6	0.2540(2)	0.4309(2)	0.3961(2)	3.32(4)
C7	0.3598(3)	0.5158(2)	0.3532(2)	4.52(5)
C8	-0.2251(2)	0.3864(2)	0.1053(2)	3.95(5)
C9	-0.1804(3)	0.4255(2)	-0.0139(2)	4.75(5)
C11	0.1204(2)	0.1073(2)	0.3940(1)	2.37(4)
C12	0.2713(2)	0.0137(2)	0.3271(1)	2.29(3)
C13	0.2222(2)	-0.0397(2)	0.2379(1)	2.35(4)
C14	0.0409(2)	0.0233(2)	0.2480(1)	2.39(3)
C15	-0.0213(2)	0.1143(2)	0.3443(1)	2.43(4)
C21	0.1097(3)	0.1742(2)	0.5039(2)	3.45(5)
C22	0.4495(2)	-0.0321(2)	0.3522(2)	3.38(4)
C23	0.3387(2)	-0.1523(2)	0.1540(2)	3.45(5)
C24	-0.0649(2)	-0.0168(2)	0.1801(2)	3.63(4)
C25	-0.2047(2)	0.1963(2)	0.3916(2)	3.79(5)
Cp*	0.1270	0.0440	0.3100	

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta_{11} + \dots + ab(\cos \gamma)\beta_{12} + \dots]$.

bered metallacycle is further reflected in the sum of 359.9° for the sum of the four bond angles within the cycle. The atoms N(2), C(4), C(6) and C(8) also lie in this plane (the maximum deviation from the least-squares plane defined by Mo, N(1), N(2), C(3), C(4), C(5), C(6) and C(8) is 8 pm).

As illustrated in Fig. 6, the dihapto-bonded 1,4-diaza-3-methylbutadien-2-yl ligand adopts an *s-trans* conformation, with the N-ethyl substituents in *anti* positions. An alternation of single and double bonds is observed in the planar C(6)-N(2)=C(5)-C(3)=N(1)-C(8) skeleton of the ligand. Thus the bond distances

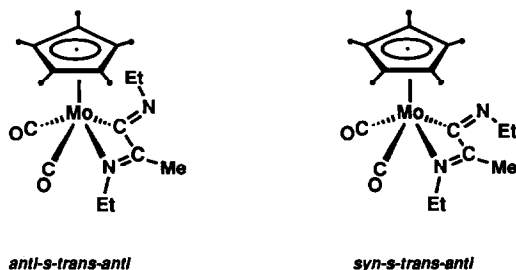


Fig. 6. The two possible conformations of the bidentate 1,4-diaza-3-methylbutadien-2-yl ligand in **8**.

N(1)–C(8) and N(2)–C(6) [146.8(1) and 145.6(1) pm, respectively] are those expected for a C(sp^3)–N(sp^2) single bond (147 pm), while the bond distances N(1)–C(3) and N(2)–C(5) [128.0(1) and 126.6(1), respectively] are very near to the C(sp^2)=N(sp^2) standard double bond length (127 pm) [27,49–52]. The two C=N groups are joined by a C(sp^2)–C(sp^2) single bond [C(3)–C(5) = 148.0(1)] [27,49,53,54]. It is noteworthy that the same *anti-s-trans-anti* conformation with an alternation of single and double bonds was observed previously for free and σ -N monodentate coordinated 1,4-diaza-1,3-butadiene ligands [49] as well as for monohapto bonded (1e) 1,4-diazabutadien-2-yl ligands in the solid state [27].

The ligated atoms of the organic moiety N(1) and C(5) and the carbonyl carbons C(1) and C(2) are coplanar (maximal deviation from the least squares plane is less than 2 pm). This plane is parallel to the Cp* ring plane (dihedral angle between the two planes = 2.6°). On the assumption that the Cp* ligand occupies only one coordination site, the geometry around the Mo atom can be described as square pyramidal, with the Cp* ligand at the apex of the pyramid (Fig. 4). Distortions from this geometry are due to the small bite of the ligand and the differences in length between the longer Mo–N(1) and Mo–C(5) bonds [222.5(< 1) and 222.2(1) pm, respectively] and the shorter Mo–CO bonds [194.2(2) and 195.8(1), respectively] (Fig. 5). The orthogonal distance of the Mo-atom from the basal plane of the distorted square pyramid is 102.4 pm, and that from the Cp* ring 200.7 pm. Bond distances and bond angles within the Cp*Mo(CO)₂-fragment are very close to those in other four-legged piano-stool complexes of the type *cis*-(η^5 -C₅R₅)Mo(CO)₂LL' (R = H, Me), and are therefore only briefly discussed [55–58]. The Mo–CO bond distances [194.2(2) and 195.8(1), respectively] are considerably shorter than those in Mo(CO)₆ [206.3(3)] [59] supporting along with the relatively low ν (C=O) frequencies (*IR-spectra*, Table 1) the argument for an extensive π -back-donation to the carbonyls in **8**. The Cp* ligand is slightly tilted, probably owing to the *trans* effect of the carbonyl ligands. This is indicated by the elongated Mo–ring-carbon distances *trans* to the carbonyls [Mo–C(11), Mo–C(15)] (Fig. 5). Such ring-slip distortions have been previously reported for other Cp*-complexes, and explained theoretically [5,60–62].

Conclusion

Reactions of the electron-rich isocyanide complex Na[Cp*Mo(CO)₂(EtNC)] with carbon-electrophiles such as MeI and EtI have been studied. These reactions proceed via exclusive alkylation of the metal center to give reactive isocyanide-substituted alkyl intermediates. The intermediates subsequently undergo a clean isocyanide migratory insertion reaction leading to the η^2 -iminoacyl complexes Cp*(CO)₂Mo[η^2 -C(NEt)R] (R = Me, Et). Comparison of the reactions of Na[Cp*Mo(CO)₂(EtNC)] with that of the analogous tungsten complex Na[Cp*W(CO)₂(EtNC)] leads to following preliminary conclusions; (a) The regioselectivity of the reactions of these electron-rich isocyanide complexes with electrophiles is strongly influenced by the nature of the electrophile, i.e. "soft" electrophiles such as MeI or EtI alkylate predominantly or exclusively the metal center leading to isocyanide-substituted metal-alkyl compounds, hard electrophiles such as Et₃OBF₄ alkylate the isocyanide nitrogen leading to dialkylaminocarbyne complexes [2,5,14]. (b) The site of the electrophilic attack is affected also by M, i.e. an alkylation of the

metal center is more preferred for molybdenum than for tungsten [2,5,14,16]. (c) An increase in the stability of the initial products from the metal-alkylation, the alkyl complexes *cis/trans*-Cp**M*(CO)₂(EtNC)(R), is observed in the series Mo < W and Et < Me [5].

The η^2 -iminoacyl complexes Cp*(CO)₂Mo[η^2 -C(NEt)R] (R = Me, Et) reveal interesting reaction patterns; e.g. they rearrange via an intramolecular hydrogen shift to the η^3 -1-azaallyl compounds Cp*(CO)₂Mo[η^3 -CH(R') \equiv CH \equiv NEt] (R' = H, Me) and afford, in a clean CC-coupling reaction with RNC, the η^2 -1,4-diaza-3-methylbutadien-2-yl complexes Cp*(CO)₂Mo[C(NR)C(NEt)Me] (R = Me, Et). Preliminary studies show that these products undergo a variety of CC-coupling reactions with unsaturated organic substrates leading to metalla-heterocycles. Extension of these studies with the goal of achieving metal-mediated synthesis of heterocycles is considerably facilitated by the new route to such complexes described here, starting from the readily accessible electron-rich metallate Na[Cp*Mo(CO)₂(EtNC)] [14].

Experimental

Standard Schlenk procedures were used for all syntheses and manipulations. The solvents were dried by standard methods (n-pentane, toluene, Et₂O and THF over Na/benzophenone), distilled under nitrogen, and stored over 4-Å molecular sieves prior to use. Column chromatography was carried out with neutral alumina (Merck, activity I, 0.063–0.2 mm, dried *in vacuo* and stored under nitrogen) as the stationary phase in a thermostated column of 30 cm length and 1.5 cm diameter.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were run on a Nicolet DX 5 FT spectrophotometer. ¹H NMR and ¹³C{¹H} NMR spectra were recorded in dry, deoxygenated methylene-*d*₂ chloride and benzene-*d*₆ on a Jeol GX 400 and Bruker WP 100 SY FT instrument. Chemical shifts were referenced to residual solvent signals (CD₂Cl₂ δ_H 5.32 and δ_C 53.8 ppm; C₆D₆ δ_H 7.15 and δ_C 128.0 ppm). Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer.

The synthesis of *cis/trans*-Cp*Mo(CO)₂(EtNC)I (**1a/1b**) has been reported previously [14]. Sodium powder was obtained as described previously [63]. Commercially supplied MeI and EtI were distilled prior to use. MeNC and EtNC were prepared by published procedures [64,65], distilled, and stored under nitrogen at –30 °C.

1. Cp*(CO)₂Mo[η^2 -C(NEt)Me] (**3**)

To a solution of 330 mg (0.70 mmol) of *cis/trans*-Cp*Mo(CO)₂(EtNC)I (**1a/1b**) in 30 ml of THF were added, with rigid exclusion of air and water, 50 mg (2.17 mmol) of sodium powder. The mixture was stirred at room temperature for 3 h during which the initially red solution turned yellow and a precipitate of NaI was formed. The precipitate was allowed to settle, and the supernatant yellow solution of the metallate **2** filtered through a filter canula, cooled to –78 °C and treated with 0.044 ml (0.70 mmol) of MeI. The mixture was then warmed to room temperature and stirred for 1 h, during which the colour of the solution changed from yellow to red and precipitation of NaI was observed. The solvent was stripped off under vacuum, the residue was taken up in Et₂O, and the NaI precipitate removed by

filtration through a filter canula. After removal of the solvent from the filtrate and recrystallization of the residue from n-pentane, complex **3** was isolated as a red, microcrystalline solid. M.p.: 110 °C. Yield: 220 mg (88% rel. to **1a/1b**). Found: C, 54.16; H, 6.38; Mo, 27.11; N, 3.87; O, 9.07. C₁₆H₂₃MoNO₂ (357.30) calc.: C, 53.79; H, 6.49; Mo, 26.85; N, 3.92; O, 8.96%.

2. $Cp^*(CO)_2Mo[\eta^2-C(NEt)Et]$ (**4**)

By the procedure described above, a yellow solution of the metallate **2** in 50 ml of THF was prepared from 350 mg (0.75 mmol) of **1a/1b** and 50 mg (2.17 mmol) of sodium powder, cooled to -78 °C, and treated with 0.059 ml (0.74 mmol) of EtI. The mixture was then allowed to warm to room temperature and stirred for 1 h. The resulting red solution containing a white precipitate of NaI was evaporated to dryness, and the residue extracted with Et₂O. The extract was then filtered through a filter canula and the solvent removed under reduced pressure. Recrystallization of the residue from n-pentane afforded red microcrystals of **4**. M.p.: 111 °C. Yield: 220 mg (79% rel. to **1a/1b**). The product was characterized by comparing its IR, ¹H NMR and ¹³C NMR spectra with that of a pure sample of **4**, obtained from **2** and Et₃OBf₄ by a previously published procedure [14].

3. $Cp^*(CO)_2Mo(\eta^3-CH_2\equiv CH\equiv NEt)$ (**5**)

A solution of 160 mg (0.45 mmol) of **3** in 20 ml of toluene was refluxed for 24 h, during which the colour turned from red to yellow-brown. After removal of the solvent the residue was purified by column chromatography on alumina at +5 °C. Elution with n-pentane/Et₂O (2.5/1) afforded a yellow band, from which complex **5** was isolated as a yellow, microcrystalline solid by evaporation of the solvent. M.p.: 72 °C. Yield: 140 mg (88%). Found: C, 53.85; H, 6.65; Mo, 27.52; N, 3.84. C₁₆H₂₃MoNO₂ (357.30) calc.: C, 53.79; H, 6.49; Mo, 26.85; N, 3.92%.

4. $Cp^*(CO)_2Mo[\eta^3-CH(Me)\equiv CH\equiv NEt]$ (**6**)

A solution of 110 mg (0.30 mmol) of **4** in 25 ml of toluene was refluxed for 24 h. The resulting yellow-brown solution was evaporated to dryness under vacuum and the residue purified by column chromatography as described under 3. Complex **6** was obtained as a yellow, microcrystalline solid. M.p.: 84 °C. Yield: 100 mg (91%). Found: C, 54.72; H, 6.23; N, 3.55. C₁₇H₂₅MoNO₂ (371.33) calc.: C, 54.99; H, 6.79; N, 3.77%.

5. $Cp^*(CO)_2\overline{Mo[C(NMe)C(NEt)Me]}$ (**7**)

A solution of 190 mg (0.53 mmol) of **3** in 25 ml of toluene was treated with 0.058 ml (1.06 mmol) of MeNC and the mixture was heated at 80 °C for 3 h. The resulting red-brown solution was evaporated to dryness and the residue purified by column chromatography on alumina at 0 °C. Elution with THF gave a red solution, from which complex **7** was obtained as a red, microcrystalline solid after evaporation of the solvent and recrystallization of the residue from n-pentane/Et₂O. M.p.: 152 °C. Yield: 160 mg (76%). Found: C, 54.41; H, 6.69; Mo, 24.83; N, 7.02; O, 8.44. C₁₈H₂₆MoN₂O₂ (398.35) calc.: C, 54.27; H, 6.58; Mo, 24.09; N, 7.03; O, 8.03%.

6. $Cp^*(CO)_2\overline{Mo[C(NEt)C(NEt)Me]}$ (**8**)

A solution of 160 mg (0.33 mmol) of **3** in 25 ml of toluene was treated with 0.051 ml (0.69 mmol) of EtNC and the mixture refluxed for 4 h. The resulting red-brown

solution was worked up as described under 5 to give complex **8** as a red, microcrystalline solid. M.p.: 97°C. Yield: 120 mg (89%). Found: C, 55.21; H, 6.79; Mo, 23.53; N, 6.56; O, 7.93. $C_{19}H_{28}MoN_2O_2$ (412.38) calc.: C, 55.34; H, 6.84; Mo, 23.27; N, 6.79; O, 7.76%.

7. Structure determination of **8**

Suitable crystals were obtained as red plates by cooling a saturated n-pentane/ Et_2O solution of **8** from room temperature to $-78^\circ C$. Complex **8** crystallizes in the triclinic space group $P\bar{1}$ (International Tables. No. 2, no systematic absences). Unit cell constants were obtained by centering and least-squares refinement using a set of 25 reflections in the range $39.86^\circ \leq 2\theta \leq 46.90^\circ$ ($a = 863.8(2)$ pm, $b = 1040.8(2)$ pm, $c = 1202.4(3)$ pm, $\alpha = 87.11(2)^\circ$, $\beta = 80.65(2)^\circ$, $\gamma = 66.96(2)^\circ$; $V = 981 \times 10^6$ pm³, $Z = 2$, $\rho_{calc} = 1.395$ g cm⁻³).

Data collection was performed on an Enraf-Nonius CAD4 four circle diffractometer with graphite monochromated Mo- K_α radiation ($\lambda = 71.073$ pm) at room temperature ($23 \pm 3^\circ C$). Intensity data for 3689 reflections in the range $1.0^\circ \leq \theta \leq 25.0^\circ$ ($h, \pm k, \pm l$) were collected by ω -scan with a scan range of $(1.20 + 0.30 \tan \theta)^\circ \pm 25\%$ before and after each reflection for background determination. Maximum scan time amount, t_{max} , was 60 s. The intensity data were corrected for Lorentz and polarisation effects and for absorption (empirical correction, 8 reflections, $\mu = 6.6$ cm⁻¹). During data collection a slight decay of 1.9% was observed but no correction was made for this. After merging all 3360 unique reflections ($I > 0.0$) were used in the refinement. The structure was solved by the Patterson method and subsequent least squares refinement cycles and difference Fourier syntheses. All atoms were refined with anisotropic displacement parameters. Refinement of the extinction was included ($\epsilon = 4.552 \cdot 10^{-7}$). Hydrogen atoms were located and were freely refined (330 parameters). Refinement minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ and converged yielding R -values of $R = 0.018$ and $R_w = 0.020$ (goodness of fit parameter = 3.095). Residual electron density maxima and minima were 0.283 and -0.244 e⁻/Å³. Atomic scattering parameters were taken from ref. 66. Anomalous dispersion effects were included for all non-hydrogen atoms [67]. All calculations were performed on a MicroVAX 3100 computer using standard programs [68–72]. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55319, the names of the authors, and the journal citation.

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