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Synthesis and reactivity of molybdenocene isocyanide complexes; crystal structure of $(\eta^5\text{-}C_5H_5)_2MoCN^tBu$

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Abstract

Synthetic, structural and reactivity studies on Mo^{IV} and Mo^{II} alkyl isocyanide complexes of the types $[Cp_2Mo(X)CNR]Y$ and Cp_2MoCNR (X = H, Me, Et, Cl, I; R = Me, Et, ^tBu; Y = I, BF_4, PF_6) are reported. Reaction of $Cp_2Mo(H)I$ (**2**) with EtNC gives the hydrido-isocyanide complex $[Cp_2Mo(H)CNEt]I$ (**3**) in high yield. Complex **3** is converted by CHI_3 into the corresponding iodo derivative $[Cp_2Mo(I)CNEt]I$ (**4**). An alternative route to halo-isocyanide complexes of molybdenocene involves halide abstraction from Cp_2MoX_2 (**5**: X = Cl; **6**: X = I) by $TlPF_6$ in the presence of RNC (R = Et, ^tBu); this affords the complexes $[Cp_2Mo(X)CNR]PF_6$ (**7a–8b**) (**7**: X = Cl, **8**: X = I; **a**: R = Et, **b**: R = ^tBu) in high yield. Reduction of **7a–8b** by sodium amalgam in THF results in the formation of the Mo^{II} isocyanide complexes Cp_2MoCNR (**9a**: R = Et, **9b**: R = ^tBu). An alternative high yield route to these compounds involves reaction of the acetonitrile complex $Cp_2Mo(\eta^2\text{-}MeCN)$ (**10**) with RNC. Alkylation of **9a** with MeI or Et_3OBF_4 occurs exclusively at the metal centre to yield the Mo^{IV} alkyl complexes $[Cp_2Mo(Me)CNEt]I$ (**11**) and $[Cp_2Mo(Et)CNEt]BF_4$ (**12**), respectively. Similarly, complex **9a** reacts with $AuPPh_3Cl$ to give the heterobimetallic compound $[Cp_2Mo(AuPPh_3)CNEt]Cl$ (**13**). By contrast, a carbonyl/isocyanide exchange reaction occurs between **9a** and $Re(CO)_5Br$, to give Cp_2MoCO (**14**) and *cis*-$Re(CO)_4(CNEt)Br$ (**15**). The alkyl complexes **11** and **12**, when heated in CH_2Cl_2 undergo a clean isocyanide insertion to give the Mo^{IV} iminoacyl complexes $[Cp_2Mo[\eta^2\text{-}C(NEt)Me]]I$ (**16**) and $[Cp_2Mo[\eta^2\text{-}C(NEt)Et]]BF_4$ (**17**), respectively. Similarly the alkyl complexes $[Cp_2Mo(R)CNMe]I$ (**18**: R = Me; **19**: R = Et), which are obtained from $Cp_2MoCNMe$ (**9c**) and RI, rearrange in refluxing CH_2Cl_2 to the η^2-iminoacyl complexes $Cp_2Mo[\eta^2\text{-}C(NMe)R]]I$ (**20**: R = Me; **21**: R = Et), whereas the tert-butyl isocyanide derivative $[Cp_2Mo(Me)CN^tBu]I$ (**22**), obtained from **9b** and MeI, is stable even in refluxing acetonitrile. In the solid-state **9b** consists of a bent molybdenocene fragment with an 'end on' bound tert-butyl isocyanide ligand. The isocyanide ligand lies within the mirror plane of the molecule, which is perpendicular to the Cp–Mo–Cp direction. A short bond from molybdenum to C_α of the isocyanide ligand, a long C_α–N bond, and extensive bending of the isocyanide ligand at the nitrogen atom are observed. On the basis of these structural features and the 'carbene like' character of the 16e Cp_2Mo fragment, complexes **9a–9c** can be described as organometallic analogues of ketene imines.

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Introduction

We have recently shown that reductive coupling of alkyl isocyanide ligands in the seven-coordinate $[M(CNR)_6X]^+$ complexes ($M = Mo^{II}$, W^{II}; X = halide) to form coordinated bis(alkylamino)acetylenes [1] involves a sequence of reactions initiated by the two-electron reduction of the starting materials to give the octahedral M^0 isocyanide complexes $M(CNR)_6$ [2]. The reduction step is followed by the addition of a Lewis acid to the nitrogen atom of an isocyanide ligand in $M(CNR)_6$ to give an octahedral cationic aminocarbyne complex. Illustrative examples of this common mode of reaction of electron-rich isocyanide complexes [3] are provided by the ethylation of $M(CNEt)_6$ with Et_3OBF_4 to give the diethylaminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ (M = Mo, W) and the silylation of the tungsten derivatives $W(CNR)_6$ with $SiMe_3OTf$ to give $[(RNC)_5W{\equiv}CN(SiMe_3)R]OTf$ (R = Et, ^{t}Bu) [2a,c]. Addition of a second equivalent of an acid (HX) induces coupling of the aminocarbyne with the adjacent isocyanide ligand to give the bis(amino)acetylene complex, e.g. the aminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ and $[(^tBuNC)_5W{\equiv}CN(Et)^tBu]BF_4$ react with HI to yield the coupling products $[I(EtNC)_4M[\eta^2\text{-}Et_2NC{\equiv}CN(H)Et]]BF_4$ and $[I(^tBuNC)_4W[\eta^2\text{-}^tBu(Et)NC{\equiv}CN(H)^tBu]]BF_4$, respectively [2b,c].

The carbyne-isocyanide coupling reaction has been observed for a number of electron-rich Group VI transition metal carbyne complexes [4]. Recent mechanistic studies have revealed that this coupling reaction proceeds in two steps. The first step involves an electrophile-induced transformation of the aminocarbyne complex to a bis-aminocarbyne intermediate, and this is followed by the C–C bond-forming step, which is a nucleophile-induced carbyne–carbyne coupling reaction of the bis-aminocarbyne complex to yield the alkyne product [5].

These results reveal that factors favouring the consecutive transformation of an electron-rich isocyanide complex to an aminocarbyne and then to a bis-aminocarbyne complex also favour the reductive coupling of isocyanide ligands. We therefore embarked on a study of the influence of the nature of the electrophile, metal centre, and coordination sphere on the course of these reactions. For the electron-rich isocyanide metallates $Na[Cp^*M(CO)_2(CNEt)]$ (M = Mo, W) we have shown that "soft" electrophiles such as RI (R = Me, Et) add at the metal centre to give the alkyl complexes *cis/trans*-$Cp^*M(CO)_2(CNEt)(R)$. These then undergo a migratory isocyanide insertion reaction, forming η^2-iminoacyl and η^3-1-azaallyl compounds [6a,b]. In contrast, "hard" electrophiles have been found to add at the isocyanide nitrogen, forming aminocarbyne complexes [6c–e]. Representative examples of the latter pathway are the reactions of $Na[Cp^*W(CO)_n(CNEt)_{3-n}]$ with Et_3OBF_4 to give $Cp^*(CO)_n(EtNC)_{2-n}W{\equiv}CNEt_2$ ($n = 1, 2$) [3d,6c]. Similar trends have been observed in the reactions of the homoleptic isocyanide complexes $M(CNR)_6$ (M = Mo, W; R = Et, ^{t}Bu) with electrophiles [2a,2b,7].

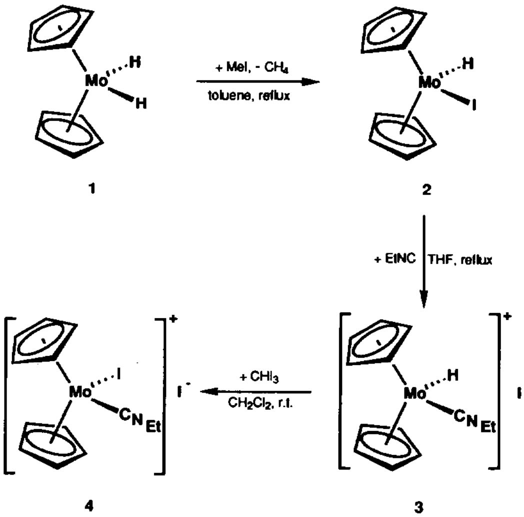
In order to extend this work to other electron-rich isocyanide complexes, we decided to prepare and study the reactions of the molybdenocene derivatives Cp_2MoCNR (R = alkyl). Although a wide variety of ligands have been used with the Cp_2M fragment (M = Mo, W) to give complexes of the general formula $[Cp_2M(X)L]^+$, $[Cp_2ML_2]^{2+}$ and Cp_2ML (X = 1e-donor ligand; L = 2e-donor ligand) [8,9], studies of analogous isocyanide complexes are very limited [10]. Our particular interest in these compounds arose from the fact that the marked π-back donating ability of the 16e molybdenocene fragment "Cp_2Mo" and the presence of the relatively inert cyclopentadienyl ligands allowed us to focus on the reactivity of the Mo–CNR moiety [9d]. The results of these studies are reported below.

Results and discussion

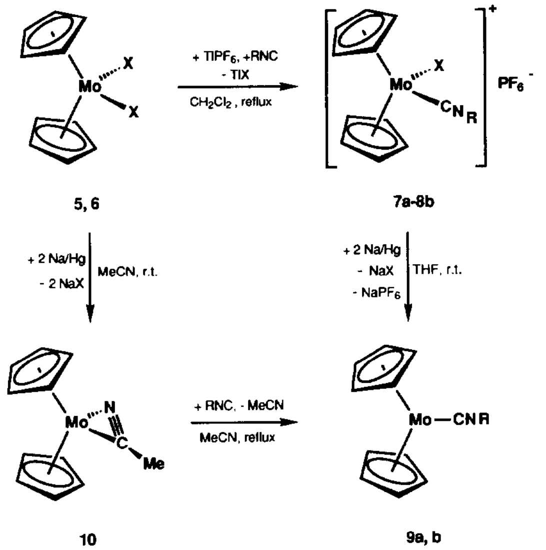
Two different methods were developed to prepare bis(cyclopentadienyl) molybdenum(IV) isocyanide complexes in high yield starting from Cp_2MoH_2 (**1**) [11]. The first route begins with the stochiometric reaction of **1** with MeI to give the iodo-hydride derivative $Cp_2Mo(H)I$ (**2**) (Scheme 1) [12,13]. Reaction of **2** with ethyl isocyanide in refluxing THF resulted in displacement of the iodo ligand from the coordination sphere to give the cationic Mo^{IV} complex $[Cp_2Mo(H)CNEt]I$ (**3**) in 87% yield (Scheme 1). No insertion of the isocyanide ligand in the Mo–H bond was observed under these conditions. Complex **3** was isolated as yellow microcrystals, sparingly soluble in MeCN and CH_2Cl_2 and insoluble in THF. An analogous reaction of **2** with MeNC has been previously reported to give the corresponding methyl isocyanide derivative $[Cp_2Mo(H)CNMe]I$ [10].

Treatment of **3** with CHI_3 in CH_2Cl_2 gave the Mo^{IV} derivative $[Cp_2Mo(I)CNEt]I$ (**4**), which was obtained as a brown solid in 90% yield (Scheme 1). Halogenation by CHX_3 is known to be an effective method for the conversion of molybdenocene hydrido complexes into analogous halo compounds [12a,14].

The second route to bis(cyclopentadienyl)molybdenum(IV) isocyanide complexes involves halide abstraction from the dihalides Cp_2MoX_2 (**5**: X = Cl; **6**: X = I) by $TlPF_6$ and RNC (R = Et, ${}^tBu$) in refluxing CH_2Cl_2. The monocationic Mo^{IV} isocyanide complexes $[Cp_2Mo(X)CNR]PF_6$ (**7a–8b**) were thereby obtained as orange-red **7a** or brown **8a**, **8b** solids in high yield (Scheme 2). Formation of the dicationic complexes $[Cp_2Mo(CNR)_2](PF_6)_2$ was not observed even when excess of



Scheme 1. Synthesis of bis(cyclopentadienyl)molybdenum(IV) isocyanide complexes starting from Cp_2MoH_2 (**1**).



Scheme 2. Synthesis of bis(cyclopentadienyl)molybdenum(II) isocyanide complexes starting from the dihalides Cp_2MoX_2 (**5**, **6**). **5**, **7**: X = Cl; **6**, **8**: X = I; **a**: R = Et; **b**: R = ^tBu.

$TlPF_6$ and RNC was used. In contrast, the reaction of **6** with methyl isocyanide in refluxing MeCN was reported to afford the dicationic Mo^{IV} complex $[Cp_2Mo(CNMe)_2](I)_2$, which was subsequently converted by $TlPF_6$ into the analogous PF_6 salt $[Cp_2Mo(CNMe)_2](PF_6)_2$ [10].

The Mo^{IV} halo-isocyanide complexes **4** and **7a–8b** were found to be convenient starting materials for the preparation of molybdenocene isocyanide complexes. Reduction of the tert-butyl isocyanide derivative **8b** with an excess of sodium amalgam in THF afforded the Mo^{II} complex Cp_2MoCN^tBu **9b** in reproducibly high yields (80–90%). Similarly, reactions of **7a** and **8a** with an excess of sodium amalgam gave the ethyl isocyanide analogue $Cp_2MoCNEt$ (**9a**) (Scheme 2). Unfortunately, formation of a second product at the expense of **9a** was observed in the latter reactions. Evidence for this was given by the IR spectra of the reaction solutions, which revealed a gradual decrease in intensity of the two $\nu(C{\equiv}NEt)$ absorption bands of **9a** at 1878 and 1830 cm^{-1} and a concomitant increase in intensity of a new $\nu(C{\equiv}NEt)$ absorption band at 1900 cm^{-1}. The by-product can be easily separated from **9a** owing to its insolubility in n-pentane and Et_2O. It is presumably a HgX_2 adduct of **9a** [3d,15]. Evidence for this was provided by the fact that this by-product was not formed when lithium powder was used to reduce **7a** or **8a** in THF. However, the use of lithium did not increase the yield of **9a** (40%) because of the concomitant formation of brown, n-pentane-insoluble, isocyanide-free products [15].

A different, more effective route to **9a** was developed, starting from the dihalides **5** or **6**. These were reduced with sodium amalgam in MeCN to afford the Mo^{II} acetonitrile complex $Cp_2Mo(\eta^2\text{-}MeCN)$ (**10**) in high yield [16]. When complex **10** (prepared *in situ*) was treated with ethyl isocyanide in refluxing MeCN, a clean substitution reaction occurred to give **9a** in an overall yield of 80%. The tert-butyl isocyanide derivative **9b** was obtained similarly in an overall yield of 85%

(Scheme 2). The use of other solvents such as THF or toluene was found to lead to a considerable decrease in the yield in the latter reactions. This is probably due to decomposition of **10** under the conditions (60 °C) necessary to bring about the substitution reaction in these solvents.

We have previously reported that the methyl isocyanide analogue $Cp_2MoCNMe$ (**9c**) can be obtained either by dehydrohalogenation of the Mo(IV) hydride complex $[Cp_2Mo(H)CNMe]I$ with NaH or by reduction of the dichloride **5** with Na/Hg in methyl isocyanide [10]. Compared with these methods, the present routes to Cp_2MoCNR complexes have considerable advantages because the products are obtained analytically pure, thus avoiding tedious purification procedures, and yields are high.

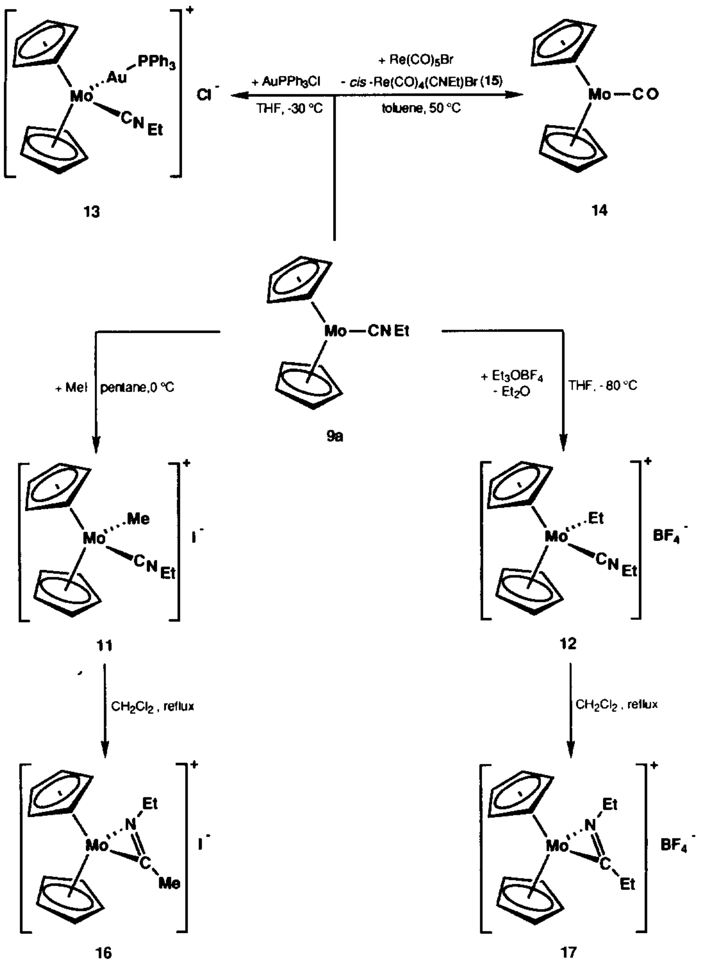
The molybdenocene isocyanide complexes **9a** and **9b** were isolated as brown, very air-sensitive solids, soluble in all common organic solvents.

As other electron-rich Cp_2ML derivatives (M = Mo, W; L = 2e-donor ligand), the isocyanide complexes **9a** and **9b** react readily with electrophiles [9b,e,i–k]. On the basis of ground state orbital control arguments an electrophile would be predicted to attack the metal-localized $1a_1$ HOMO orbital of Cp_2MoCNR (see molecular orbital study of $Cp_2MoCNMe$ (**9c**) below). As expected, treatment of **9a** with MeI in n-pentane resulted in quantitative formation of the Mo^{IV} methyl complex $[Cp_2Mo(Me)CNEt]I$ (**11**) (Scheme 3). This was isolated as a pale yellow solid, soluble in MeCN and CH_2Cl_2. Similarly, reaction of **9a** with Et_3OBF_4 in THF at −80 °C was accompanied by a fast colour change from brown to yellow and quantitative precipitation of the Mo^{IV} ethyl complex $[Cp_2Mo(Et)CNEt]BF_4$ (**12**) (Scheme 3).

Inorganic electrophiles also add to the metal centre, as shown by the immediate reaction of **9a** with $AuPPh_3Cl$ in THF at −30 °C to afford the yellow heterobimetallic complex $[Cp_2Mo(AuPPh_3)CNEt]Cl$ (**13**) in quantitative yield. In comparison, treatment of **9a** with $Re(CO)_5Br$ in toluene at 50 °C yielded the molybdenocene carbonyl complex Cp_2MoCO (**14**) and the Re^I derivative *cis*-$Re(CO)_4(CNEt)Br$ (**15**) (Scheme 3). Complexes **14** and **15** were separated by fractional crystallization from n-pentane and isolated as green (**14**) and white (**15**) microcrystals in high yield.

Formation of **14** and **15** could be accounted for in terms of a three-step reaction sequence. The initial step would involve decarbonylation of $Re(CO)_5Br$ to give the halo-bridged dimer $[Re(CO)_4Br]_2$ [17]. This step would be followed by the fast carbonylation of **9a** by the released CO to give **14** and EtNC, which then would be expected to react rapidly with the dimer $[Re(CO)_4Br]_2$ to give **15** [18]. However such an "indirect" interaction of **9a** with $Re(CO)_5Br$ to give **14** and **15** can be excluded by the results of competition experiments. These show that $Re(CO)_5Br$ is stable under the reaction conditions necessary to achieve conversion of **9a** to **14** (toluene, 50 °C), and that carbonylation of **9a** with CO gas in toluene to give **14** is a slow process even at 100 °C [15]. Therefore a "direct" interaction of **9a** with $Re(CO)_5Br$ is suggested to account for the formation of **14** and **15**. Three mechanisms can be envisaged involving such a direct interaction as follows:

(a) One involving an addition-replacement reaction similar to that observed between **9a** and $AuPPh_3Cl$ to give the heterobimetallic intermediate "$[Cp_2Mo[Re(CO)_5]CNEt]Br$" **A** (Scheme 4). This step would be followed by a carbonyl/isocyanide exchange between the two metal centres in **A** to yield the

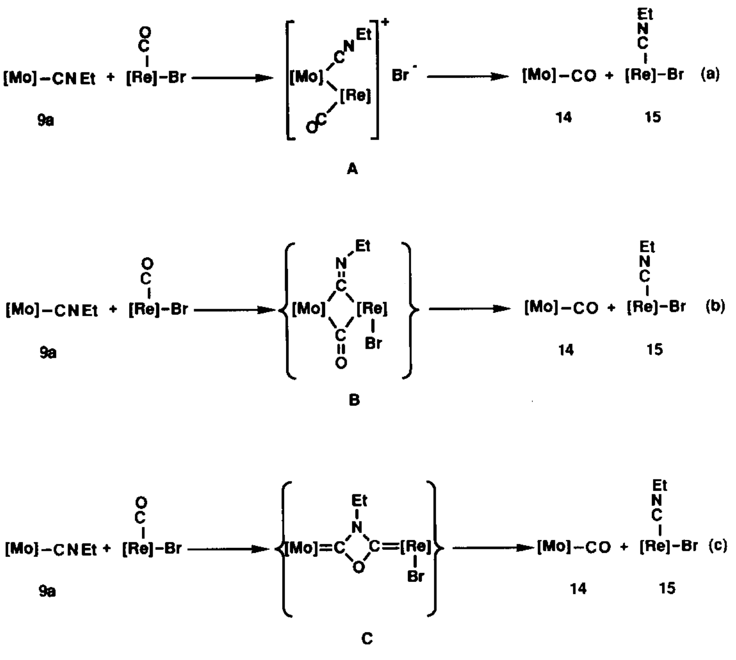


Scheme 3. Reactions of the molybdenocene ethyl isocyanide complex **9a** with organic and inorganic electrophiles.

products. The exchange process could proceed via intermediate **B** (see discussion of the second mechanism below).

(b) A mechanism involving a concerted 2 + 2 cycloaddition of the Mo–isocyanide bond across one of the four *cis* Re–carbonyl bonds to give the four-membered dimetallaheterocycle **B** (Scheme 4). Formation of **B** could also be accounted for by a stepwise mechanism involving nucleophilic attack of the metal centre in **9a** at the electrophilic carbon atom of a *cis* carbonyl ligand in $Re(CO)_5Br$ to give a zwitterionic intermediate, followed by ring closure. This reaction is closely related to the previously reported addition of heteroallenes to Cp_2WCO to give four-membered metallaheterocycles [9k]. Ring opening of the dimetallaheterocycle **B** by cleavage of the Mo–isocyanide and the Re–carbonyl bond would then result in the formation of **14** and **15** (Scheme 4).

(c) A mechanism involving a concerted 2 + 2 cycloaddition of the isocyanide ligand of **9a** across one of the C–O bonds of the *cis* carbonyl ligands in $Re(CO)_5Br$



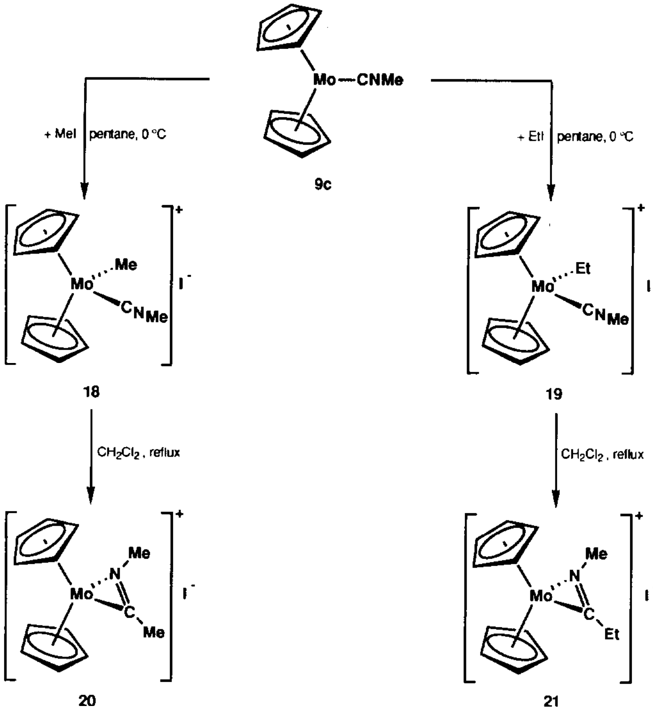
[Mo] = Cp_2Mo; [Re] = $Re(CO)_4$

Scheme 4. Possible pathways for the carbonyl/isocyanide exchange reaction of **9a** with $Re(CO)_5Br$.

to give the four-membered heterocycle **C**. This would subsequently open to give **14** and **15**. Formation of **C** could also be accounted for by a stepwise mechanism involving a nucleophilic attack of the nitrogen atom in **9a** at the electrophilic carbon atom of a *cis* CO ligand in $Re(CO)_5Br$ to give a zwitterionic intermediate, followed by ring closure (Scheme 4).

Route c involves a cleavage of the isocyanide C–N bond in **9a** and a C–O bond of a *cis*-arranged CO ligand in $Re(CO)_5Br$. It thus differs from the other two mechanisms, which involve a cleavage of the Mo–isocyanide bond in **9a** and a Re–carbonyl bond in $Re(CO)_5Br$. Labelling studies should therefore discriminate between these possibilities, and are currently being carried out.

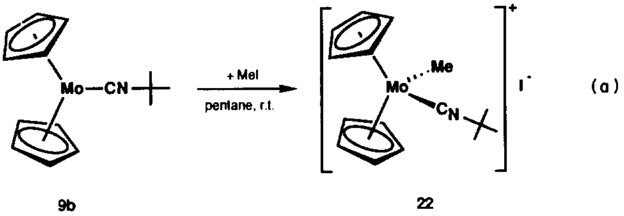
Metal alkyl complexes containing isocyanide ligands such as **11** and **12** have been previously suggested to be key intermediates in the metal-assisted polymerization of isocyanides [19]. Isolation has been achieved only in a few cases owing to the ease with which these compounds undergo C–C coupling reactions, the most common of which involves migratory insertion of the isocyanide ligand into the metal–alkyl bond [3f,6,7,20 and references cited therein]. In keeping with these observations, complexes **11** and **12** were found to be thermally labile, undergoing in refluxing CH_2Cl_2 a clean insertion of the ethyl isocyanide ligand into the metal–alkyl bond to give the Mo^{IV} iminoacyl complexes $Cp_2Mo[\eta^2\text{-}C(NEt)Me]]I$ (**16**) and $[Cp_2Mo[\eta^2\text{-}C(NEt)Et]]BF_4$ (**17**), respectively (Scheme 3). The latter were isolated as orange solids, soluble in MeCN and CH_2Cl_2. Similarly, the alkyl complexes $[Cp_2Mo(R)CNMe]I$ (**18**: R = Me; **19**: R = Et), which are obtained by alkylation of $Cp_2MoCNMe$ (**9c**) with RI in n-pentane, were found to rearrange in



Scheme 5. Reactions of $Cp_2MoCNMe$ (**9c**) with alkvlating agents.

refluxing CH_2Cl_2 to yield the orange iminoacyl complexes $[Cp_2Mo[\eta^2\text{-}C(NMe)R]]I$ (**20**: R = Me; **21**: R = Et) (Scheme 5).

In contrast, the analogous Mo^{IV} tert-butyl isocyanide derivative $[Cp_2Mo(Me)\text{-}CN^tBu]I$ (**22**), obtained from **9b** and MeI (equation a), did not rearrange to an η^2-iminoacyl complex even after several days' refluxing in acetonitrile.



These results are consistent with previous observations, which indicate that the ease of insertions of isocyanides into metal–alkyl bonds is strongly dependent on the isocyanide substituent [20a].

Spectroscopic investigations

IR spectra

The IR spectra are consistent with the structures suggested for **3–22**. All the isocyanide complexes exhibit characteristic absorptions for the $\nu(C\equiv NR)$ vibrations (Table 1).

Table 1

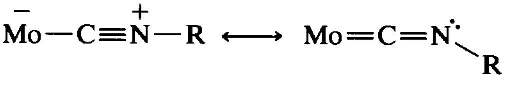
ν(C≡NR), ν(C≡O) and ν(C=N) absorptions for the molybdenum complexes **3**, **4**, and **7a–22** in cm^{-1}; solvents: CH_3CN (a), CH_2Cl_2 (b), THF (c), n-pentane (d), toluene (e) and KBr (f)

Complex	ν(C≡NR)	ν(C≡O)	ν(C=N)	Solvent
$[Cp_2Mo(H)CNEt]I$ (**3**)	2203 w, sh, 2180 s	–	–	a
$[Cp_2Mo(I)CNEt]I$ (**4**)	2213 s, 2196 m, sh	–	–	a
$[Cp_2Mo(Cl)CNEt]PF_6$ (**7a**)	2209 m, 2176 s	–	–	b
$[Cp_2Mo(I)CNEt]PF_6$ (**8a**)	2207 s, 2192 m, sh	–	–	a
$[Cp_2Mo(I)CN^tBu]PF_6$ (**8b**)	2181 s	–	–	a
$Cp_2MoCNEt$ (**9a**)	1878 m, 1830 s	–	–	c
$Cp_2MoCNEt$ (**9a**)	1881 m, 1841 s	–	–	d
Cp_2MoCN^tBu (**9b**)	1845 s	–	–	c
Cp_2MoCN^tBu (**9b**)	1852 s	–	–	d
$Cp_2MoCNMe$ (**9c**)	1834 s	–	–	e
$Cp_2Mo(\eta^2\text{-}MeCN)$ (**10**)	–	–	1780 s	a
$[Cp_2Mo(Me)CNEt]I$ (**11**)	2198 sh, 2173 s	–	–	b
$[Cp_2Mo(Et)CNEt]BF_4$ (**12**)	2176 s	–	–	b
$[Cp_2Mo(AuPPh_3)CNEt]I$ (**13**)	2136 s, 2080 m	–	–	b
Cp_2MoCO (**14**)	–	1929 s	–	d
cis-$Re(CO)_4(CNEt)Br$ (**15**)	2226 w	2110 w, 2017 vs, 1953 s	–	c
$[Cp_2Mo[\eta^2\text{-}C(NEt)Me]]I$ (**16**)	–	–	1744 s	b
$[Cp_2Mo[\eta^2\text{-}C(NEt)Et]]BF_4$ (**17**)	–	–	1737 s	b
$[Cp_2Mo(Me)CNMe]I$ (**18**)	2180 s	–	–	f
$[Cp_2Mo(Et)CNMe]I$ (**19**)	2170 s	–	–	f
$[Cp_2Mo[\eta^2\text{-}C(NMe)Me]]I$ (**20**)	–	–	1750 s	f
$[Cp_2Mo[\eta^2\text{-}C(NMe)Et]]I$ (**21**)	–	–	1740 s	f
$[Cp_2Mo(Me)CN^tBu]I$ (**22**)	2154 s	–	–	b

A considerable decrease in the ν(C≡NR) frequencies is observed on going from the Mo^{IV} to the Mo^{II} isocyanide complexes (compare for example the ν(C≡NR) absorptions of **3**, **7a** or **8a** with those of **9a**, of **8b** or **22** with those of **9b**, and of **18** and **19** with those of **9c**). This decrease is a consequence of the higher electron density around the metal centre in the Mo^{II} compounds **9a–9c** which results in a stronger metal–isocyanide back bonding.

The ν(C≡NR) absorptions for **9a–9c** were found at considerably lower frequency than those for the free alkyl isocyanides [ν(C≡NEt) in THF: 2149 cm^{-1}; ν(C≡N^{t}Bu) in THF: 2140 cm^{-1}; ν(C≡NMe) in CH_2Cl_2: 2168 cm^{-1}]. Comparable low ν(C≡NR) frequencies have been so far observed only for electron-rich Mo^0 isocyanide complexes such as $Na[CpMo(CO)(CNMe)_2]$ [ν(C≡NMe) in THF: 1855, 1745 cm^{-1}] [21], *trans*-$Mo(CNMe)_2(dppe)_2$ [ν(C≡NMe) in THF: 1886 cm^{-1}] [22], $Mo(CNEt)_6$ [ν(C≡NEt) in THF: 1991, 1868 cm^{-1}] [2a] and $Na[Cp^*Mo(CO)_2(CNEt)]$ [ν(C≡NEt) in THF: 1860 cm^{-1}] [6e].

In terms of the valence bond theory the low ν(C≡NR) absorptions of **9a–9c** can be attributed to a strong contribution of the canonical form **b** to the structure of these compounds:



$$\overset{-}{Mo}-C\equiv\overset{+}{N}-R \longleftrightarrow Mo=C=\ddot{N}\diagdown_{R}$$

(a) (b)

Table 2. ^{1}H NMR data for the complexes **3**, **4**, **7a**–**9b** and **11**–**22** in CD_3CN (a), CD_2Cl_2 (b) or C_6D_6 (c) at +20 °C; relative intensities and multiplicities in parentheses, coupling constants in Hz.

Complex	Mo*H*; MoC*H*$_3$; Mo*Et*	NCH$_2$C*H*$_3$; CCH$_2$C*H*$_3$	CNC(C*H*$_3$)$_3$	C*H*$_3$; CC*H*$_2$CH$_3$	NC*H*$_2$CH$_3$; NC*H*$_3$	*Cp*; P*Ph*$_3$	Solvent
3	−9.02 (1,s)	1.31 (3,t) ^3J(H,H) 7.3	–	–	3.72 (2,q) ^3J(H,H) 7.3	5.26 (10,s)	a
4	–	1.39 (3,t) ^3J(H,H) 7.3	–	–	3.96 (2,q) ^3J(H,H) 7.3	5.78 (10,s)	a
7a	–	1.40 (3,t) ^3J(H,H) 7.3	–	–	3.93 (2,q) ^3J(H,H) 7.3	5.73 (10,s)	a
8a	–	1.38 (3,t) ^3J(H,H) 7.3	–	–	3.92 (2,q) ^3J(H,H) 7.3	5.71 (10,s)	a
8b	–	–	1.53 (9,s)	–	–	5.70 (10,s)	a
9a	–	1.00 (3,t) ^3J(H,H) 7.3	–	–	3.12 (2,q) ^3J(H,H) 7.3	4.36 (10,s)	c
9b	–	–	1.14 (9,s)	–	–	4.36 (10,s)	c
11	−0.07 (3,s)	1.38 (3,t) ^3J(H,H) 7.3	–	–	3.85 (2,q) ^3J(H,H) 7.3	5.24 (10,s)	a
12	1.02 (2,m); 1.12 (3,m)	1.35 (3,t) ^3J(H,H) 7.3	–	–	3.81 (2,q) ^3J(H,H) 7.3	5.21 (10,s)	a
13	–	1.19 (3,t) ^3J(H,H) 7.3	–	–	3.56 (2,q) ^3J(H,H) 7.3	5.20 (10,s); 7.49–7.51 (15,m)	b
14	–	–	–	–	–	4.15 (10,s)	c
15	–	0.28 (3,t) ^3J(H,H) 7.3	–	–	2.21 (2,q) ^3J(H,H) 7.3	–	c
16	–	1.10 (3,t) ^3J(H,H) 7.3	–	2.71 (3,s)	3.49 (2,q) ^3J(H,H) 7.3	5.17 (10,s)	a
17	–	1.10 (3,t) ^3J(H,H) 7.3; 1.34 (3,t) [a] ^3J(H,H) 7.3;	–	2.85 (2,q)	3.49 (2,q) ^3J(H,H) 7.3	5.15 (10,s)	a
18	−0.07 (3,s)	–	–	–	3.54 (3,s)	5.22 (10,s)	a
19	1.12 (5,m)	–	–	–	3.54 (3,s)	5.23 (10,s)	a
20	–	–		2.65 (3,s)	3.40 (3,s)	5.15 (10,s)	a
21	–	1.34 (3,t) ^3J(H,H) 7.3		2.84 (2,q) ^3J(H,H) 7.3	3.38 (3,s)	5.15 (10,s)	a
22	−0.08 (3,s)	–	1.52 (9,s)	–	–	5.26 (10,s)	a

[a] Methyl protons of the carbon-bonded ethyl group.

Table 3

^{13}C NMR data for the complexes **3**, **4**, **7a–9b**, **11–17** and **22** in CD_3CN (a), CD_2Cl_2 (b) or C_6D_6 (c) at +20 ° C; multiplicities in parentheses, coupling constants in Hz

Complex	Mo*Me*; Mo*C*H_2CH_3	NCH_2*C*H_3; CCH_2*C*H_3	*C*Me; C*Me*$_3$; $MoCH_2$*C*H_3; *C*CH_2CH_3	N*C*H_2CH_3;	*C*Me$_3$	*Cp*; P*Ph*$_3$	*C*NR	*C*=N	CO	Solvent
3	–	14.7	–	42.0	–	86.8	–[a]	–	–	a
4	–	14.9	–	42.8	–	96.7	148.0	–	–	a
7a	–	15.0	–	42.7	–	99.7	–[a]	–	–	a
8a	–	14.9	–	42.5	–	96.7	147.7	–	–	a
8b	–	–	30.0	–	61.7	96.8	148.4	–	–	a
9a	–	15.9	–	43.8	–	76.1	245.5	–	–	c
9b	–	–	30.7	–	57.1	76.0	241.0	–	–	c
11	−19.0	15.4	–	42.2	–	93.2	160.2	–	–	a
12	−3.2	15.4	22.3	42.1	–	93.1	159.8	–	–	a
13	–	15.0	–	42.1	–	80.1; 129.4 (d) ^3J(P,C) 8.6; 131.6 [b]; 134.1 (d) ^2J(P,C) 13.4	174.7	–	–	b
14	–	–	–	–	–	74.6	–	–	244.9	c
15	–	13.9	–	38.9	–	–	177.9		180.9; 182.1 [c]; 183.1	c
16	–	13.1	21.1	46.1	–	92.2	–	188.9	–	a
17	–	11.0 [d] 13.3	27.0	46.7	–	92.0		194.2	–	a
22	−18.9	–	30.3	–	60.7	93.3	161.2	–	–	a

[a] The isocyanide carbon resonance could not be observed because of the low solubility of **3** and **7a** in CD_3CN. [b] C_p-resonance. [c] carbon resonance of the mutually *trans*-oriented carbonyl ligands. [d] methyl carbon resonance of the carbon-bonded ethyl group.

Further experimental support for this interpretation is provided by the solid state structure of **9b**, which shows a) a considerably shorter Mo–C_α bond length than is observed for a Mo–C(*sp*) single bond; b) a longer C_α–N bond than expected for a C(*sp*)–N(*sp*) triple bond; and c) an extensive bending of the isocyanide ligand at the nitrogen atom (see discussion of the crystal structure of **9b** below).

Complex **3** is distinguished by a weak, sharp absorption at 1862 cm^{-1} (KBr), which can be assigned to the ν(Mo–H) vibration. For comparison, the Mo(IV) η^2-iminoacyl complexes **16**, **17**, **20** and **21** exhibit a characteristic absorption at 1744, 1737, 1750 and 1740 cm^{-1}, respectively (Table 1), which can be assigned to the ν(C=N) vibration of the iminoacyl ligand. Similar low frequency absorptions have been observed in the IR spectra of the Mo^{IV} η^2-iminoacyl complexes $Cp^*(Br)_2(CO)Mo[\eta^2$-C(NEt)R] [R = Me, ν(C=N) in CH_2Cl_2: 1741 cm^{-1}; R = Et, ν(C=N) in CH_2Cl_2: 1732 cm^{-1}] [23].

The *cis*-isomer **15** was identified from the observed pattern of the ν(CO) absorptions, which are consistent with group theory predictions. The ν(CO) bands of **15** are found to lie close to those for the analogous methyl isocyanide complex *cis*-$Re(CO)_4(CNMe)Br$ [ν(CO) in CH_2Cl_2: 2118, 2018 and 1960 cm^{-1}] [18].

^{1}H NMR spectra

Further support for the assigned structures to the molybdenocene derivatives **3–14** and **16–22** is provided by the ^{1}H NMR spectra, which display a characteristic singlet resonance for the protons of the two equivalent Cp ligands (Table 2). This resonance is shifted to higher field on going from the Mo^{IV} to the Mo^{II} complexes. In addition, the chemical shift of the Cp protons of the Mo^{IV} isocyanide complexes is found to be strongly dependent on the 1e-donor ligand X [X = halogen (**4**, **7a–8b**): $\delta \sim 5.70$; X = hydride, alkyl, $AuPPh_3$ (**3**, **11–13**, **18**, **19**, **22**): $\delta \sim 5.20$].

Complex **3** is distinguished by a high field singlet resonance (δ −9.02) of the molybdenum-bound hydrogen. The methyl complexes **11**, **18** and **22** also display a characteristic high field singlet for the protons of the molybdenum-bonded methyl group at δ *ca.* −0.07. Similarly, the methylene protons of the molybdenum-bonded ethyl group in **12** and **19** give rise to a multiplet at high field (δ 1.02 and 1.12). Rearrangement of the alkyl complexes **11**, **12**, **18** and **19** to the iminoacyl compounds **16**, **17**, **20** and **21** results in a considerable deshielding of the protons of the metal-bonded methyl and methylene groups (Table 2).

^{13}C NMR spectra

The ^{13}C NMR spectra are also consistent with the proposed structures for the new compounds (Table 3).

A considerable deshielding of the isocyanide carbon is observed on going from the Mo^{IV} to the Mo^{II} isocyanide complexes (compare for example the isocyanide carbon resonance of **4**, **8a**, **11** or **12** with that of **9a**, and of **8b** or **22** with that of **9b**). This trend is consistent with previous NMR studies on isocyanide complexes of Group VI transition metals, which have shown that a stronger metal–isocyanide back bonding causes an increased deshielding of the isocyanide carbon [24,25]. Notably, an extremely low-field resonance is observed for the isocyanide-carbon in **9a** and **9b** at δ 245.5 and 241.0, respectively. These chemical shifts are the largest so far reported for 'end-on' bound isocyanide ligands. Comparable low-field

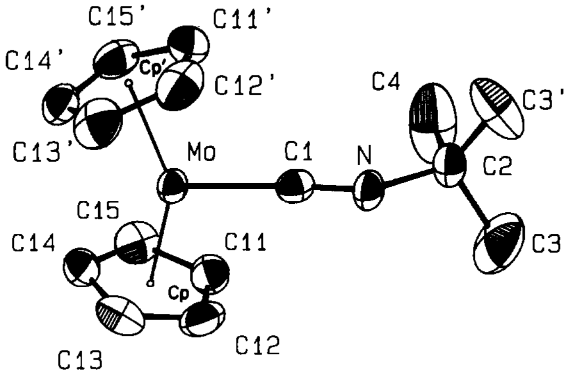


Fig. 1. ORTEP drawing of the molecular structure of **9b** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity reasons.

resonances have been observed for the isocyanide-carbons of other electron-rich isocyanide complexes such as $Cp^*(CO)(RNC)W{\equiv}CNEt_2$ ($R = Et$: δ 209.7; $R = {}^tBu$: δ 215.4) [3d], $Cp^*(RNC)_2W{\equiv}CNEt_2$ ($R = Et$: δ 223.9; $R = {}^tBu$: δ 221.8) [5] and *trans*-$Mo(CNPh)_2(Me_8[16]aneS_4)$ (δ 197.6 and 233.2) [26].

The Mo^{IV} η^2-iminoacyl complexes **16** and **17** are distinguished by a low-field resonance for the imino-carbon at δ 188.9 and 194.2, respectively. Comparable chemical shifts have been previously found for the imino-carbons of other Mo^{IV} η^2-iminoacyl complexes such as $Cp^*(Br)_2(CO)Mo[\eta^2\text{-}C(NEt)R]$ ($R = Me$: δ 194.7; $R = Et$: δ 196.0) [23] as well as for the iminocarbons of Mo^{II} η^2-iminoacyl complexes such as $Cp^*(CO)_2Mo[\eta^2\text{-}C(NEt)R]$ ($R = Me$: δ 200.6; $R = Et$: δ 206.0) [6b,e] and $HB(3,5\text{-}Me_2pz)_3(CO)_2Mo[\eta^2\text{-}C(N{}^tBu)Me]$ (δ 204.7) [3f].

Crystal structure of 9b

The molecular structure of **9b** was confirmed by a single crystal X-ray diffraction study. Two views of a single molecule with the atomic numbering scheme are given in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 4 and fractional coordinates in Table 5.

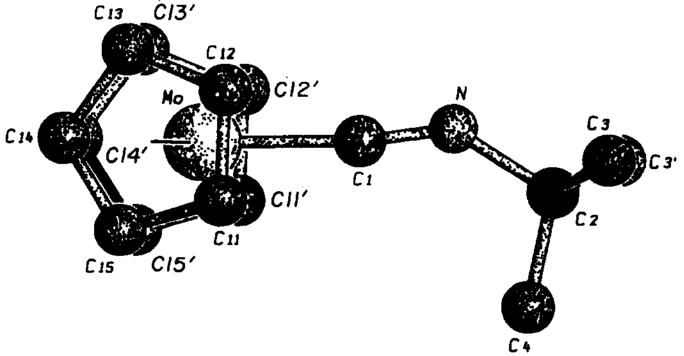


Fig. 2. SCHAKAL plot of the molecular structure of **9b** (top view).

Table 4

Selected bond lengths (pm) and bond angles (°) with estimated standard deviations for **9b** [a]

Mo–C(1)	199.7(4)	Mo–C(1)–N	173.1(3)
Mo–C(11)	230.0(4)	C(1)–N–C(2)	139.5(4)
Mo–C(12)	228.0(4)	cp–Mo–cp	147.7
Mo–C(13)	228.1(4)	cp–Mo–C(1)	106.2
Mo–C(14)	226.4(3)		
Mo–C(15)	227.2(4)		
Mo–cp	194.1		
C(1)–N	119.3(4)		
N–C(2)	148.9(4)		
C(2)–C(3)	150.3(7)		
C(2)–C(4)	149.8(7)		

[a] cp denotes the centroid of the cyclopentadienyl ring.

The molecule contains a bent molybdenocene unit with an 'end on' bound tert-butyl isocyanide ligand. It has C_s symmetry, the mirror plane being defined by the molybdenum centre and the C_1, N, C_2 and C_4 atoms of the isocyanide ligand.

The geometry at molybdenum is typical for a bent metallocene complex. The cp–Mo–cp angle (cp = centroid of the cyclopentadienyl ring) is to our knowledge the largest (147.7 °) so far observed for a Cp_2ML complex (M = Mo, W; L = monohapto bonded, 2e-donor ligand). It is, for example, larger than that in the tungstenocene carbene complex $Cp_2W{=}C(H)Ph$ (cp–W–cp = 143.6 °) [27] and the trimethylphosphine compound Cp_2MoPMe_3 (cp–Mo–cp = 142.8 °) [15]. It is also larger than that in Cp_2MoL complexes containing a dihapto bonded, 2e-donor ligand L such as $Cp_2Mo(\eta^2\text{-}H_2CO)$ (cp–Mo–cp = 139.0 °) [9g], $Cp_2Mo(\eta^2\text{-}MeCN)$ (cp–Mo–cp = 141.6 °) [16], $(Cp')_2Mo[C_2(CF_3)_2]$ (cp'–Mo–cp' = 134.6 °) (Cp' = $\eta^5\text{-}C_5H_4Me$) [28] and $Cp_2Mo[\eta^2\text{-}Ph(H)CNPh]$ (cp–Mo–cp = 136 °) [29]. The Cp ligands adopt an eclipsed conformation (Fig. 2). They are coordinated in a

Table 5

Fractional atomic coordinates and their estimated standard deviations for non-hydrogen atoms in **9b** [a]

Atom	x	y	z	B_{eq} (Å^2)
Mo	0.68690(3)	$\frac{1}{4}$	0.16073(3)	2.410(8)
N	0.9050(3)	$\frac{1}{4}$	−0.0402(3)	3.02(8)
C1	0.8190(3)	$\frac{1}{4}$	0.0271(4)	2.71(9)
C2	0.9433(3)	$\frac{1}{4}$	−0.1921(4)	3.2(1)
C3	1.0163(3)	0.1541(3)	−0.2103(3)	7.2(1)
C4	0.8442(4)	$\frac{1}{4}$	−0.2923(5)	8.8(2)
C11	0.6696(2)	0.0811(3)	0.0760(3)	4.07(8)
C12	0.7490(3)	0.0816(3)	0.1888(3)	4.66(9)
C13	0.6950(3)	0.1117(3)	0.3157(3)	4.56(9)
C14	0.5804(2)	0.1298(3)	0.2783(3)	3.74(8)
C15	0.5653(2)	0.1132(3)	0.1312(3)	4.07(8)
cp	0.6518	0.1034	0.1979	

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

conventional pentahapto coordination mode, with $\mathrm{Mo{-}C_{Cp}}$ distances ranging from 226.4(3) to 230.0(4), very close to those in other $\mathrm{Cp_2MoL}$ complexes [16,28,29].

Striking features of the structure are the bonding parameters of the isocyanide ligand in **9b**:

(a) The Mo–C(1) bond [199.7(4) pm] is considerably shorter than the Mo–CNR bond of other $\mathrm{Mo^{II}}$ isocyanide complexes such as $\mathrm{[Mo(CN^tBu)_7](PF_6)_2}$ $\mathrm{[(Mo{-}CN^tBu)_{av} = 211.5\ pm]}$ [30], $\mathrm{[I(^tBuNC)_4Mo[\eta^2{-}^tBu(H)NC{\equiv}CN(H)^tBu]]I}$ $\mathrm{[(Mo{-}CN^tBu)_{av} = 212.0\ pm]}$ [31] or $\mathrm{[Mo(CNMe)_7](BF_4)_2}$ $\mathrm{[(Mo{-}CNMe)_{av} = 210.7\ pm]}$ [32]. Moreover it is shorter than the Mo–C(*sp*) bond of $\mathrm{Mo^{II}}$ alkynyl complexes such as *trans*-$\mathrm{Mo(C{\equiv}CPh)_2(dppe)_2}$ [Mo–C = 209.3(8) pm] [33]. This bond length is also well below the value of a Mo–C(*sp*) single bond (228 pm) estimated from the sum of the covalent radii of a single bonded molybdenum and a *sp*-hybridized carbon atom ($r_{\mathrm{Mo}} = 158$ pm; $r_{\mathrm{C}} = 70$ pm) [34,35]. In contrast, it is only slightly longer than the Mo–C(*sp*) double bond of mononuclear $\mathrm{Mo^{II}}$ vinylidene complexes such as $\mathrm{Cp(I)[P(OMe)_3]_2Mo{=}C{=}C(H)^tBu}$ [Mo–C = 192.7(3) pm] [36,37].

(b) The C(1)–N bond is longer (119.3(4) pm) than the corresponding C–N bond of other $\mathrm{Mo^{II}}$ isocyanide complexes such as $\mathrm{[Mo(CN^tBu)_7](PF_6)_2}$ $\mathrm{[(C{-}N)_{av.} = 114.7\ pm]}$ [30], $\mathrm{[I(^tBuNC)_4Mo[\eta^2{-}^tBu(H)NC{\equiv}CN(H)^tBu]]I}$ $\mathrm{[(C{-}N)_{av.} = 114.2\ pm]}$ [31] or $\mathrm{[Mo(CNMe)_7](BF_4)_2}$ $\mathrm{[(C{-}N)_{av.} = 114.2\ pm]}$ [32] and longer than a normal C–N triple bond (116 pm) [38].

(c) An extensive bending of the isocyanide ligand is observed at the nitrogen atom. The C(1)–N–C(2) angle is, at 139.5(4)°, even more acute than the smallest angle so far observed for an alkyl isocyanide ligand bound 'end-on' to molybdenum [*trans*-$\mathrm{Mo(CNMe)_2(dppe)_2}$, $\mathrm{(C{-}N{-}C)_{av.} = 156(1)^\circ}$] [39]. This bending is probably steric in origin, resulting from a more efficient crystal packing (Fig. 3) (see also molecular orbital study of **9c** below).

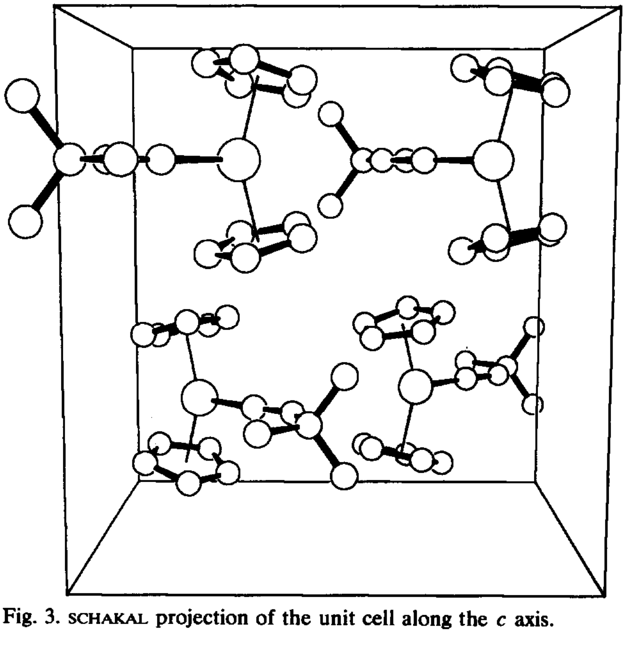
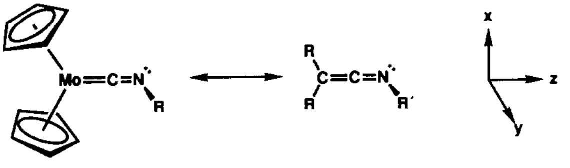


Fig. 3. SCHAKAL projection of the unit cell along the *c* axis.



9a-c

Fig. 4. Analogy between the molybdenocene isocyanide complexes **9a–9c** and ketene imines.

On the basis of these structural features and the 'carbene-like' character of the 16e species molybdenocene (Cp_2Mo) [9a,40,41] complexes **9a–9c** can be described as organometallic analogues of ketene imines ($R_2C{=}C{=}NR'$) [42] (Fig. 4).

Additional support for this analogy is provided by: (a) the almost equal lengths found for the C_1–N bond in **9b** [119.3(4) pm] and the C–N double bond in ketene imines [e.g. $Ph_2C{=}C{=}N(p\text{-}C_6H_4Me)$: $d(C{=}N) = 120.6$ pm] [43]; (b) the extensive bending of ketene imines at the nitrogen atom [e.g. $Ph_2C{=}C{=}N(p\text{-}C_6H_4Br)$: $(C{=}N\text{-}(p\text{-}C_6H_4Br) = 123.1°$] [43]; and (c) the conformation of the tert-butyl substituent of the isocyanide ligand in **9b**, i.e. the coplanar arrangement of the atoms Mo, C(1), N and C(2) (*yz* plane, Fig. 4), perpendicular to the plane defined by the molybdenum centre and the centroids of the Cp rings (*xz* plane, Fig. 4). This conformational preference is a consequence of the strong interaction between the filled b_2 orbital of the Cp_2Mo fragment and the empty π^* orbital of the isocyanide ligand (metal–ligand back bonding), both orbitals lying in the *yz* plane (Fig. 4) (see discussion of the molecular orbital study of **9c** below).

Molecular orbital study of $Cp_2MoCNMe$ (9c)

Extended Hückel molecular orbital calculations [44] were carried out on complex **9c** in order to assist understanding of some of the points related to the bonding in these complexes. In a previous study the "end-on" and "side-on" coordinations were compared [10]. The most interesting point to address now is the bending of the isocyanide ligand.

Figure 5 shows the interaction diagram between a d^4 Cp_2Mo fragment and a linear (left side) or a bent (right side) methyl isocyanide.

The frontier orbitals of the molybdenocene fragment are those described by Lauher and Hoffmann [9c] and are shown at the centre of the diagram. The Mo–C_α and C_α–N bond lengths were taken as 210 and 115 pm, respectively, which are in the range normally found for Mo^{II} isocyanide complexes (see discussion of the crystal structure of **9b** above). The cp–Mo–cp angle (cp = centroid of the Cp-ring) was kept at 132°, which is a usual value for Bis(cyclopentadienyl)molybdenum derivatives.

Five orbitals are presented for the linear isocyanide. The HOMO may be described in a very simplified approach [45] as a carbon-localized lone pair, while the other orbitals are two π and two π^* levels, the orbitals in each pair being degenerate. Donation from the isocyanide HOMO to the empty $2a_1$ orbital of Cp_2Mo takes place, while the $1a_1$ orbital of Cp_2Mo remains approximately non-bonding. Simultaneously one of the π^* orbitals, the one lying in the bisecting plane, receives electrons from the filled b_2 orbital of Cp_2Mo, indicating the existence of back donation even in this linear coordination mode. The other π^*

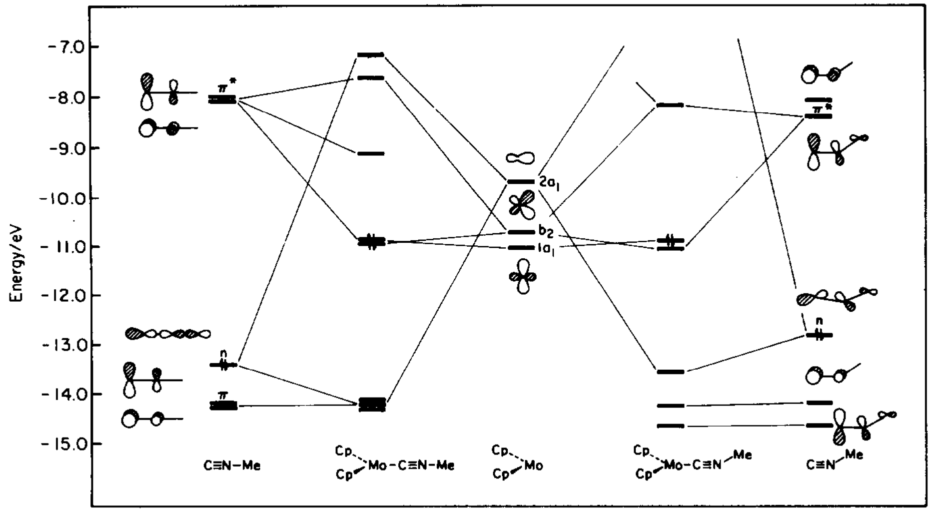


Fig. 5. Diagram of interaction between a d^4 Cp_2Mo fragment and a linear or bent methyl isocyanide.

orbital is involved in an interaction with an empty orbital of molybdenocene, and this is of no further consequence.

Let us now consider the right side of the diagram. Bending of the isocyanide leads to loss of degeneracy of the two orbitals in both the π and π^* set [46]. The bonding pattern is the same as in the linear case, i.e. donation from the isocyanide HOMO to the empty $2a_1$ orbital and back donation from the b_2 orbital of molybdenocene to the empty π^* orbital of the isocyanide. What is different now is the contribution of these two interactions to global bonding; the population of the isocyanide HOMO falls to 1.629 electrons in the linear and to 1.676 electrons in the bent case, while the π^* orbital receives 0.258 and 0.363 electrons, respectively. This implies that fewer electrons are donated from the bent isocyanide to the metal, whereas back donation increases.

If the Mo–C_α bond is allowed to shorten to 200 pm and the C_α–N bond to increase to 120 pm (the experimental values found for **9b**), the back donation component of the bonding in the bent case is reinforced, as indicated by the increase of the population of the π^* orbital to 0.715 electrons. At the same time the population of the isocyanide HOMO increases to 1.727 electrons. All these results imply that loss of donation is compensated by better back donation, so that a strong bond is formed between metal and the bent isocyanide. Changing the cp–Mo–cp angle to the value observed in the crystal structure of **9b**, however, has no significant effect.

We should point out that there is no clear cut energetic preference for the bent vs. the linear structure, and the potential energy surface for bending is very soft. The reason for this is that formation of a much stronger Mo–C_α bond in the bent structure is not enough to overcome the amount of energy required for bending the isocyanide ligand, at least at this level of calculation. We can say, as a conclusion, that electronic effects do not clearly favour bending of the isocyanide ligand. The observed bending of the tert-butyl isocyanide ligand of **9b** in the crystal structure may therefore originate from other effects, such as crystal packing forces.

The molecular orbital diagram may also help to provide qualitative understanding of the preference for electrophilic attack in **9c**. The HOMO of the complex, which is mainly localized on the metal, has a much higher energy than the lone pair assigned to the isocyanide nitrogen (not shown in Fig. 5, but appearing at ca. -14 eV). It is therefore expected that the metal centre in **9c** will behave as a better donor towards the incoming electrophile.

Summary

High-yield synthetic routes to Mo^{IV} and Mo^{II} isocyanide complexes of the type $[Cp_2Mo(X)CNR]Y$ and Cp_2MoCNR ($X = H$, Me, Et, Cl, I; $Y = I$, BF_4, PF_6; $R =$ Me, Et, ${}^tBu$) have been developed, allowing detailed studies of the reactivity of these rare compounds. Reactions of the electron-rich molybdenocene isocyanide complexes Cp_2MoCNR with organic and inorganic electrophiles have been shown to be frontier-orbital controlled, i.e. the entering electrophile accepts electron density from the high-lying metal-localized $1a_1$ HOMO orbital, converting the organometallic substrate to a Mo^{IV} isocyanide complex. The latter displays interesting reactivity patterns, as shown for example by the clean isocyanide insertion rearrangement of the alkyl complexes $[Cp_2Mo(R)CNR']Y$ (R, $R' =$ Me, Et; $Y = I$, BF_4) to give η^2-iminoacyl compounds.

Structural data suggest an analogy between the molybdenocene isocyanide complexes Cp_2MoCNR and ketene imines. Implications of this analogy for the reactions of these compounds are currently being investigated.

Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane, toluene, Et_2O and THF over Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy; MeCN over P_2O_5 and K_2CO_3) and distilled under nitrogen prior to use or stored in bottles over 4 Å (MeCN over 3 Å) molecular sieves.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were recorded on a Nicolet DX 5 FT spectrophotometer. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded in dry, deoxygenated acetonitrile-d_3, methylene-d_2-chloride and benzene-d_6 on a Jeol GX 400 FT instrument; the ^1H NMR spectrum of **18** was recorded on a Jeol FX 90Q FT instrument. Chemical shifts were referenced to residual solvent signals (CD_3CN δ_H 1.93 and δ_C 118.2; CD_2Cl_2 δ_H 5.32 and δ_C 53.8 ppm; C_6D_6 δ_H 7.15 and δ_C 128.0 ppm). Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer; m/z values are relative to the ^{98}Mo isotope.

The complexes Cp_2MoH_2 (**1**), $Cp_2Mo(H)I$ (**2**), Cp_2MoX_2 (**5**: $X = Cl$; **6**: $X = I$), $Cp_2MoCNMe$ (**9c**), $AuPPh_3Cl$ and $Re(CO)_5Br$ were prepared as described in references 11, 12b, 12a, 10, 47 and 48, respectively. EtNC and ${}^tBuNC$ were made by published procedures [49,50], distilled, and stored under nitrogen. Et_3OBF_4 was obtained by Meerwein's method [51].

1. $[Cp_2Mo(H)CNEt]I$ (3). A solution of 160 mg (0.45 mmol) of **2** in 30 ml of THF was treated with 0.044 ml (0.59 mmol) of EtNC and the mixture was refluxed for 3 h, during which a yellow solid separated. The suspension was allowed to cool to room temperature and the supernatant colourless solution decanted from the yellow precipitate, which was dried *in vacuo*. Yield: 160 mg (87%). Found: C, 38.20; H, 4.06; I, 30.17; Mo, 23.66; N, 3.27. $C_{13}H_{16}IMoN$ (409.12) calc.: C, 38.17; H, 3.94; I, 31.02; Mo, 23.45; N, 3.42%. FD-MS: m/z 284 (K^+).

2. [$Cp_2Mo(I)CNEt$]I (4). A yellow solution of 120 mg (0.29 mmol) of **3** in 40 ml of CH_2Cl_2 was treated with 150 mg (0.38 mmol) of CHI_3 and the mixture stirred for 2 h at room temperature. The resulting orange-brown solution was reduced in volume and Et_2O was added to bring about complete precipitation of **4**. The solid was recrystallized from CH_2Cl_2/Et_2O to give complex **4** as brown microcrystals. Yield: 140 mg (90%). Found: C, 28.76; H, 2.88; I, 46.65; Mo, 18.07; N, 2.53. $C_{13}H_{15}I_2MoN$ (535.02) calc.: C, 29.18; H, 2.83; I, 47.44; Mo, 17.93; N, 2.62%.

3. [$Cp_2Mo(Cl)CNEt$]PF_6 (7a). A suspension of 1.01 g (3.40 mmol) of **5** in 50 ml of CH_2Cl_2 was treated with 1.19 g (3.41 mmol) of $TlPF_6$ and 0.30 ml (4.05 mmol) of EtNC and the mixture refluxed for 6 h until all the green solid had dissolved. The white precipitate of TlCl was allowed to settle and the supernatant orange-brown solution filtered through a filter cannula. The filtrate was reduced in volume and Et_2O was slowly added until precipitation of complex **7a** was complete. The solid was recrystallized from CH_2Cl_2/Et_2O to give **7a** as orange-red needles. Yield: 1.30 g (83%). Found: C, 34.42; H, 3.48; N, 2.91. $C_{13}H_{15}ClF_6MoNP$ (461.62) calc.: C, 33.82; H, 3.28; N, 3.03%.

4. [$Cp_2Mo(I)CNEt$]PF_6 (8a). A suspension of 1.01 g (2.10 mmol) of **6** in 50 ml of CH_2Cl_2 was treated with 770 mg (2.20 mmol) of $TlPF_6$ and 0.20 ml (2.70 mmol) of EtNC and the mixture refluxed for 6 h until all the green solid had dissolved. The resulting mixture was worked up as described for the preparation of **7a** to give complex **8a** as a brown solid. Yield: 1.01 g (87%). Found: C, 28.50; H, 2.80; I, 21.96; Mo, 17.20; N, 2.68. $C_{13}H_{15}F_6IMoNP$ (553.07) calc.: C, 28.23; H, 2.73; I, 22.95; Mo, 17.35; N, 2.53%.

5. [$Cp_2Mo(I)CN^tBu$]PF_6 (8b). A suspension of 680 mg (1.42 mmol) of **6** in 35 ml of CH_2Cl_2 was treated with 520 mg (1.49 mmol) of $TlPF_6$ and 0.162 ml (1.43 mmol) of ^tBuNC and the mixture refluxed for 4 h until all the green solid had dissolved. The resulting mixture was worked up as described for **7a** to give complex **8b** as a brown solid. Yield: 725 mg (88%). Found: C, 31.21; H, 3.42; I, 20.68; Mo, 16.17; N, 2.56. $C_{15}H_{19}F_6IMoNP$ (581.13) calc.: C, 31.00; H, 3.30; I, 21.84; Mo, 16.51; N, 2.41%.

6. $Cp_2MoCNEt$ (9a) from 7a and Na / Hg. A suspension of 250 mg (0.54 mmol) of **7a** in 40 ml of THF was treated with 6.13 g of 0.92% (w/w) Na/Hg (2.45 mmol Na) and the mixture stirred at room temperature until all the solid had dissolved (ca. 30 min). After addition of Et_2O to the suspension the grey precipitate, consisting of NaCl and residual sodium amalgam, was allowed to settle and the supernatant brown solution filtered through a filter cannula. The filtrate was evaporated to dryness and the residue extracted with n-pentane. The extract was filtered, reduced in volume, and cooled to $-78\,^\circ C$ to bring about precipitation of **9a**. Brown microcrystals. Yield: 70 mg (46%). Found: C, 55.50; H, 5.53; Mo, 33.25; N, 4.65. $C_{13}H_{15}MoN$ (281.21) calc.: C, 55.52; H, 5.38; Mo, 34.12; N, 4.98%.

7. Cp_2MoCN^tBu (9b) from 8b and Na / Hg. A suspension of 340 mg (0.59 mmol) of **8b** in 40 ml of THF was stirred for 30 min in the presence of 7.61 g of 0.92% Na/Hg (3.05 mmol Na). The resulting mixture was worked up as described above for the synthesis of **9a** to give complex **9b** as brown microcrystals. Yield: 155 mg (86%). Found: C, 58.43; H, 6.18; Mo, 31.38; N, 4.55. $C_{15}H_{19}MoN$ (309.26) calc.: C, 58.26; H, 6.19; Mo, 31.02; N, 4.53%. EI-MS: m/z 311 (M^+), 255 ($[M-Me_2C{=}CH_2]^+$), 228 ($[M-{}^tBuNC]^+$).

*8. $Cp_2MoCNEt$ (**9a**) from $Cp_2Mo(\eta^2\text{-}MeCN)$ (**10**) and EtNC.* A suspension of 950 mg (3.20 mmol) **5** in 30 ml of MeCN was stirred for 45 min in the presence of 15.51 g of 0.92% Na/Hg (6.21 mmol Na). The grey precipitate, consisting of NaCl and residual sodium amalgam, was allowed to settle down and the supernatant red solution of **10** filtered through a filter cannula. The filtrate was treated with 0.245 ml (3.30 mmol) of EtNC and refluxed. Monitoring by IR spectroscopy showed when reaction was complete (disappearance of the $\nu(C{=}N)$ absorption of **10** at 1780 cm^{-1}). The brown solution was evaporated to dryness and the residue extracted with n-pentane. The solvent was then removed from the extract to leave **9a** as brown microcrystals. Yield: 720 mg (80% rel. to **5**).

*9. Cp_2MoCN^tBu (**9b**) from $Cp_2Mo(\eta^2\text{-}MeCN)$ (**10**) and ^tBuNC.* By the procedure described for the preparation of **9a**, 810 mg (2.73 mmol) of **5** were reduced with 15.04 g of 0.92% Na/Hg (6.02 mmol Na) in 30 ml of MeCN to give **10**, which was then treated with 0.37 ml (3.27 mmol) of ^tBuNC to afford 720 mg of **9b**. Yield: (85% rel. to **5**).

*10. $[Cp_2Mo(Me)CNEt]I$ (**11**).* To a solution of 260 mg (0.92 mmol) of **9a** in 25 ml of n-pentane at 0 °C was added 0.061 ml (0.98 mmol) of MeI. There was immediate colour change from brown to yellow and separation of a pale yellow solid. The suspension was stirred for 15 min at ambient temperature, the precipitate then allowed to settle, and the supernatant colourless solution decanted off. The precipitate was washed with n-pentane and dried *in vacuo*. Yield: 390 mg (quantitative). Found: C, 39.87; H, 4.30; I, 29.60; Mo, 21.72; N, 3.21. $C_{14}H_{18}IMoN$ (423.15) calc.: C, 39.74; H, 4.29; I, 29.99; Mo, 22.67; N, 3.31%. FD-MS: m/z 298 (K^+).

*11. $[Cp_2Mo(Et)CNEt]BF_4$ (**12**).* To a solution of 430 mg (1.53 mmol) of **9a** in 25 ml of THF at −80 °C were added 290 mg (1.53 mmol) of Et_3OBF_4. The mixture was allowed to warm to room temperature during which a colour change from brown to yellow and separation of a yellow solid were observed. The supernatant colourless solution was then decanted off and the residue dried *in vacuo* and dissolved in CH_2Cl_2 at 0 °C. The orange solution was filtered at 0 °C, the filtrate reduced in volume, and Et_2O was added to precipitate complex **12**. Yellow solid. Yield: 605 mg (quantitative). Found: C, 44.80; H, 4.95; Mo, 23.90; N, 3.50. $C_{15}H_{20}BF_4MoN$ (397.07) calc.: C, 45.37; H, 5.08; Mo, 24.16; N, 3.53%.

*12. $[Cp_2Mo(AuPPh_3)CNEt]Cl$ (**13**).* A solution of 490 mg (0.99 mmol) $AuPPh_3Cl$ in 20 ml of THF was added slowly to a solution of 280 mg (1.00 mmol) of **9a** in 20 ml of THF at −30°C. There was immediate colour change from brown to yellow and separation of a yellow solid. The mixture was then allowed to warm to room temperature and the solvent removed *in vacuo*. The residue was extracted with CH_2Cl_2, the extract filtered and reduced in volume, and Et_2O added to precipitate complex **13**. Yellow solid. Yield: 750 mg (97%). Found: C, 48.42; H, 4.34; Cl, 5.10; Mo, 12.08; N, 1.74. $C_{31}H_{30}AuClMoNP$ (775.92) calc.: C, 47.99; H, 3.90; Cl, 4.57; Mo, 12.36; N, 1.81%.

*13. Cp_2MoCO (**14**) and* cis-*$Re(CO)_4(CNEt)Br$ (**15**) from **9a** and $Re(CO)_5Br$.* To a brown solution of 250 mg (0.89 mmol) of **9a** in 30 ml of toluene were added

360 mg (0.89 mmol) of Re(CO)$_5$Br, and the mixture was heated at 50°C until reaction was complete (ca. 30 min, IR monitoring). The resulting green solution was evaporated to dryness, the residue dissolved in n-pentane and the solution concentrated *in vacuo*. Upon cooling to −78°C white crystals of **15** separated, and these were washed with cold (−80 °C) n-pentane and dried *in vacuo*. Yield: 340 mg (89% rel. to Re(CO)$_5$Br). Found: C, 19.49; H, 1.45; N, 3.11; Re, 42.53. $C_7H_5BrNO_4Re$ (433.23) calc.: C, 19.41; H, 1.16; N, 3.23; Re, 42.98%.

The supernatant green solution was evaporated to dryness and the residue recrystallized from a minimum amount of n-pentane to give complex **14** as green microcrystals. Yield: 210 mg (93% rel. to **9a**). The product was characterized by IR, NMR spectroscopy and mass spectrometry.

*14. [Cp$_2$Mo[η^2-C(NEt)Me]]I (**16**).* A solution of 210 mg (0.50 mmol) of **11** in 20 ml of CH_2Cl_2 was refluxed for 30 h; reaction was shown to be complete by IR spectroscopy (disappearance of the ν(C≡NEt) absorption of **11** at 2173 cm^{-1}). The orange solution was concentrated under reduced pressure and Et$_2$O added to precipitate complex **16**. Orange solid. Yield: 200 mg (95%). Found: C, 39.61; H, 4.44; N, 3.20. $C_{14}H_{18}IMoN$ (423.15) calc.: C, 39.74; H, 4.29; N, 3.31%.

*15. [Cp$_2$Mo[η^2-C(NEt)Et]]BF$_4$ (**17**).* A solution of 350 mg (0.88 mmol) of **12** in 25 ml of CH_2Cl_2 was refluxed for ca. 30 h and the reaction shown to be complete by IR spectroscopy (disappearance of the ν(C≡NEt) absorption of **12** at 2176 cm^{-1}). The orange solution was worked up as described above for **16** to give complex **17** as an orange solid. Yield: 325 mg (93%). Found: C, 44.95; H, 5.33; N, 3.49. $C_{15}H_{20}BF_4MoN$ (397.07) calc.: C, 45.37; H, 5.08; N, 3.53%. FD-MS: m/z 312 (K$^+$).

*16. [Cp$_2$Mo(Me)CNMe]I (**18**).* To a solution of 160 mg (0.60 mmol) of **9c** in 50 ml of n-pentane at 0 °C was added 0.05 ml (0.08 mmol) of MeI. There was immediate colour change from brown to yellow and a solid separated. The suspension was worked up as described for the preparation of **11** to give complex **18** as a cream solid. Yield: 245 mg (quantitative). Found: C, 38.50; H, 4.00; N, 3.40. $C_{13}H_{16}IMoN$ (409.12) calc.: C, 38.17; H, 3.94; N, 3.42%.

*17. [Cp$_2$Mo(Et)CNMe]I (**19**).* To a solution of 310 mg (1.16 mmol) of **9c** in 50 ml of n-pentane at 0 °C was added 0.096 ml (1.20 mmol) of EtI and the mixture stirred for 30 min. The resulting suspension was worked up as described for the preparation of **11** to give complex **19** as a cream solid. Yield: 365 mg (quantitative). Found: C, 40.08; H, 4.29; N, 3.28. $C_{14}H_{18}IMoN$ (423.15) calc.: C, 39.74; H, 4.29; N, 3.31%.

*18. [Cp$_2$Mo[η^2-C(NMe)Me]]I (**20**).* A solution of 210 mg (0.51 mmol) of **18** in 20 ml of CH_2Cl_2 was refluxed for 30 h. The resulting orange solution was worked up as described for the preparation of **16** to give complex **20** as an orange solid. Yield: 200 mg (95%). Found: C, 38.40; H, 4.05; N, 3.36. $C_{13}H_{16}IMoN$ (409.12) calc.: C, 38.17; H, 3.94; N, 3.42%.

*19. [Cp$_2$Mo[η^2-C(NMe)Et]]I (**21**).* A solution of 230 mg (0.54 mmol) of **19** in 25 ml of CH_2Cl_2 was refluxed for 30 h. The resulting orange solution was worked up as described for the preparation of **16** to give complex **21** as an orange solid. Yield: 225 mg (98%). Found: C, 39.98; H, 4.32; N, 3.27. $C_{14}H_{18}IMoN$ (423.15) calc.: C, 39.74; H, 4.29; N, 3.31%.

*20. [Cp$_2$Mo(Me)CN^{t}Bu]I (**22**).* A brown solution of 270 mg (0.87 mmol) of **9b** in 10 ml of n-pentane was treated with 0.065 ml (1.04 mmol) of MeI at room temperature. The resulting white suspension was worked up as described for the synthesis of **11** to give complex **22** as a cream solid. Yield: 380 mg (96%). Found: C, 42.20; H, 4.92; I, 27.46; Mo, 21.63; N, 2.91. $C_{16}H_{22}IMoN$ (451.20) calc.: C, 42.59; H, 4.91; I, 28.13; Mo, 21.26; N, 3.11%.

21. Structure determination of ***9b***. Suitable crystals were obtained as red-brown cubes when a saturated n-pentane solution of **9b** was cooled from room temperature to $-78\,^{\circ}$C. Complex **9b** crystallizes in the orthorhombic space group *Pnma* (Inter. Tables. No.: 62). Unit cell constants were obtained by the centring and least-squares refinement of 25 reflections at high θ values ($a = 1179.1(<1)$, $b = 934.2(<1)$, $c = 1272.6(<1)$ pm; $V = 1401 \cdot 10^{6}$ pm^{3}, $Z = 4$, $\rho_{\text{calc}} = 1.465$ g/cm^{-3}). Data collection was performed on a CAD4 four circle diffractometer (Enraf–Nonius) with graphite monochromated Cu-K_{α} radiation ($\lambda = 154.18$ pm) at ambient temperature (23 ± 3°C). Intensity data for 3995 reflections in the range $1.0^{\circ} \leq \theta \leq 65.0^{\circ}$ ($\pm h$, $\pm k$, $-l$) were collected by $\omega/2\theta$-scan with a scan range of $(1.00 + 0.30 \tan\theta)^{\circ} \pm 25\%$ for background determination. Maximum scan time was 60 sec. The intensity data were corrected for Lorentz and polarization effects and for absorption (empirical correction, 7 reflections, $\mu = 76.05$ cm^{-1}). During data collection a slight decay of 6.8% was observed, and correction was made for this. After merging, all 1177 unique reflections ($I > 0.0$) were used in the refinement. The structure was solved by direct methods and subsequent least squares refinement and difference Fourier syntheses. All atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps and refined freely (141 parameters). Refinement minimized the function $\Sigma w(|F_{o}| - |F_{c}|)^{2}$, where $w = 1/\sigma^{2}(F)$ and converged yielding R-values of $R = 0.034$ and $R_{w} = 0.024$. Residual electron density maxima and minima were 0.53 and -0.93 e^{-} Å^{-3} near the molybdenum atom. Atomic scattering parameters were taken from ref. 52. Anomalous dispersion effects were included for all non-hydrogen atoms [53]. All calculations were performed on a MicroVAX 3100 computer with standard programs [54–57]. 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-55906, the names of the authors, and the journal citation.

22. Molecular orbital calculations of ***9c***. All the calculations were of the extended Hückel type [44] with modified Hij's [58]. The basis set for the metal atoms consisted of *ns*, *np* and $(n-1)d$ orbitals. The *s* and *p* orbitals were described by single Slater type wave functions and the *d* orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometry for complex **9c** was taken from the crystal structure described in this work. Standard parameters were used for C, N and H. The parameters for Mo were the following (H_{ii}/eV, C_1): 5*s*, -8.77, 1.96; 5*p* -5.60, 1.90; 4*d* -11.06, 4.54; C_2 1.90; ζ_1 0.5899; ζ_2 0.5899.

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