

Preparation of imido pentamethylcyclopentadienyl molybdenum(IV) complexes

X-ray molecular structure of *cis*-[MoCp*Cl(μ -N^tBu)]₂ · C₆H₆

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Abstract

The reduction of [MoCp*Cl₂(N^tBu)] **1** with 1 equiv. of 10% sodium amalgam in the presence of CN(2,6-Me₂C₆H₃) yields the green crystalline compound [MoCp*Cl(N^tBu{CN(2,6-Me₂C₆H₃)}] **2** which can be alkylated by MgClMe to give [MoCp*Me(N^tBu){CN(2,6-Me₂C₆H₃)}] **3**. The same reduction in the absence of ligands leads to an almost equimolar mixture of compounds identified as *cis*- and *trans*-[MoCp*(μ -Cl)(N^tBu)]₂ **4** which are slowly and irreversibly transformed into *cis*-[MoCp*Cl(μ -N^tBu)]₂ **5** by heating a toluene solution at 90°C. Compounds (*cis* + *trans*)-**4** and *cis*-**5** are alkylated by MgClMe leading to the same final methyl derivative [MoCp*Me(μ -N^tBu)]₂ **6**, and react with ethylene to yield the adduct [MoCp*Cl(N^tBu)(C₂H₄)] **7**. All new complexes were characterized by their analytical composition, IR and NMR spectroscopy and mass spectrometry, and the structure of the benzene solvate of *cis*-[MoCp*Cl(μ -N^tBu)]₂ **5** was determined by X-ray diffraction methods.

Keywords: Molybdenum; X-ray structure; Imido complexes

1. Introduction

An extensive chemistry of halo imido cyclopentadienyl molybdenum and tungsten complexes in different oxidation states (d⁰–d²) has been developed in the last few years [1]. Most imido molybdenum(V) (d¹) compounds were synthesized by reaction of the tetrachloro complexes with the primary amine [2] and their reduction in the presence of different ligands to the related molybdenum(IV) (d²) compounds has been studied [3]. More recently we have reported [4] the isolation of terminal and bridging imido dinuclear molybdenum and tungsten complexes containing the monobridged and dibridged di(cyclopentadienyl) (η^5 -C₅H₄)₂SiMe₂ and (η^5 -C₅H₃)₂(SiMe₂)₂ ligands.

The synthesis of several analogous molybdenum and tungsten(V) imido complexes containing the pentamethylcyclopentadienyl ring MCp*(NR)Cl₂ (M = Mo, W;

R = ^tBu, ⁱPr, C₆F₅, 2,6-(ⁱPr)₂C₆H₃) were reported [5] during the preparation of this manuscript. Here we describe the reduction of [MoCp*(N^tBu)Cl₂] in the absence of ligands, followed by the addition of isocyanide and the alkylation of the resulting molybdenum(IV) compounds. The structural characterization of these compounds by ¹H and ¹³C NMR spectroscopy and the molecular structure of the dimeric complex [(MoCp*Cl)₂(μ -N^tBu)]₂ are reported.

2. Results and discussion

2.1. Synthesis of [MoCp*Cl₂(N^tBu)] (1)

The molybdenum(V) tetrachlorides [MoCp'Cl₄] (Cp' = C₅H₅ (Cp), C₅Me₅ (Cp*)) were prepared in more than 90% yield by a modification of the method previously reported [6] by Schrock and coworkers which involves the oxidation of [MoCp'(CO)₂]₂ or

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$[\text{MoCp}^*(\text{CO})_2]_2$ or any mixture of them with an excess of PCl_5 in toluene.

The title complex was prepared in high yield by treating a purple suspension of the molybdenum(V) chloride $[\text{MoCp}^*\text{Cl}_4]$ [5] in toluene with 3 equiv. of the amine which undergoes a double deprotonation, simultaneously acting as a proton acceptor agent (Scheme 1). Complex **1**, which was isolated as brown-yellow crystals from hexane, is a moderately stable compound as a solid and can be handled in air for short periods without observable decomposition. However its toluene solutions were much more reactive in the presence of air, being easily transformed into the reported molybdenum(VI) dioxo-chloride $[\text{MoCp}^*\text{Cl}(\text{O})_2]$ [7] by simultaneous oxidation and protonation of the imido group, which was eliminated as ammonium chloride.

Compound **1** is a paramagnetic d^1 complex with a ^1H NMR spectrum which shows two very broad signals at δ 2.45 (15H) and δ 45.0 (9H) with low relaxation times $T_1 = 0.0085$ s and < 100 μs respectively. Its IR spectrum shows a strong absorption band between 1206 and 1223 cm^{-1} which must be assigned to the $\nu(\text{N}-\text{C})$ stretching frequency [8] of a linear four-electron donor imido ligand.

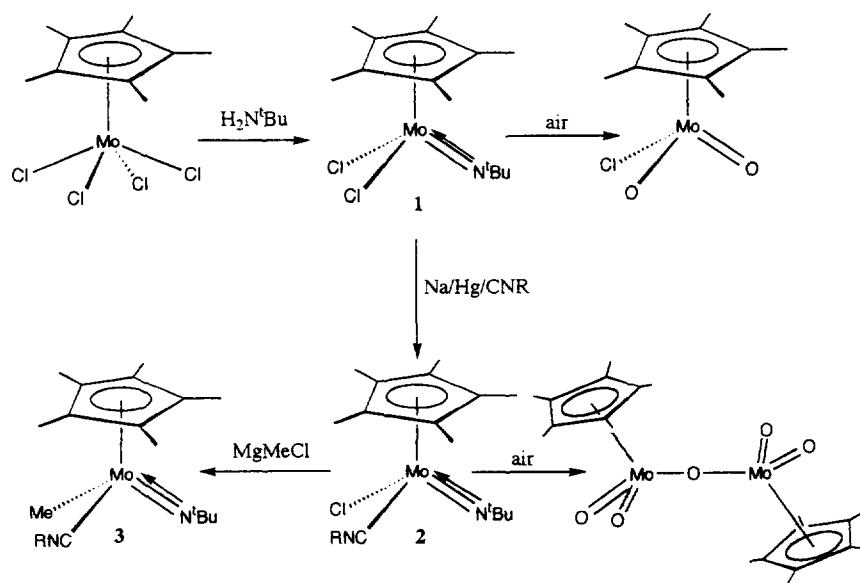
2.2. Reduction of $[\text{MoCp}^*\text{Cl}_2(\text{N}^t\text{Bu})]$ (**1**)

Reduction of hexane or toluene solutions of complex **1** with 1 equiv. of 10% sodium amalgam in the presence of $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ led to the imido molybdenum(IV) complex $[\text{MoCp}^*\text{Cl}(\text{N}^t\text{Bu})\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ **2** which was isolated as a very air-sensitive green solid highly soluble in pentane. The same reaction with CN^tBu took place in a similar way to give, after extraction with pentane, a brown solution containing the

related CN^tBu adduct as the unique component, which could not be isolated as a solid due to its extraordinarily high solubility in pentane and its extreme air sensitivity. Both compounds are immediately oxidized and hydrolysed in the presence of air to give the reported dioxo μ -oxo dinuclear molybdenum(VI) derivative $[\{\text{MoCp}^*(\text{O})_2\}_2(\mu\text{-O})]$ [9].

Complex **2** was characterized by IR and NMR spectroscopy (see Section 3) as the expected diamagnetic 18-electron molybdenum(IV) complex and similar behaviour was also observed for pentane solutions of the CN^tBu adduct. Alkylation of complex **2** with 1 equiv. of MgClMe in THF was a slow reaction that led to the methyl complex $[\text{MoCp}^*\text{Me}(\text{N}^t\text{Bu})\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}]$ **3**, which was isolated as a microcrystalline brown-green solid after extraction with toluene and crystallization from toluene–hexane. The same reaction with LiMe led to complex **3** always accompanied by a second almost equally abundant product which could not be separated and characterized.

Reduction of a pentane solution of complex **1** with 1 equiv. of 10% sodium amalgam stirred for 12 h in the absence of ligands led to a solution which after filtration and evaporation gave a brown solid, characterized by elemental analysis as the imido molybdenum(IV) complex $[\text{MoCp}^*\text{Cl}(\text{N}^t\text{Bu})]$ **4**. The dimeric structure $[\text{MoCp}^*\text{Cl}(\text{N}^t\text{Bu})]_2$ **4** was revealed by its mass spectrum which showed one peak at $m/e = 674$ and was also consistent with the observed NMR data. The ^1H NMR spectrum (C_6D_6) of **4** showed two singlets at δ 1.64 ($T_1 = 1.485$) and δ 1.62 ($T_1 = 1.376$) for the $\eta^5\text{-Cp}^*$ methyl protons and two singlets at δ 1.47 ($T_1 = 0.677$) and δ 1.33 ($T_1 = 0.722$) for the ^tBu protons, each with an intensity ratio 1/1. Similar behaviour was observed in the ^{13}C NMR spectrum from



Scheme 1.

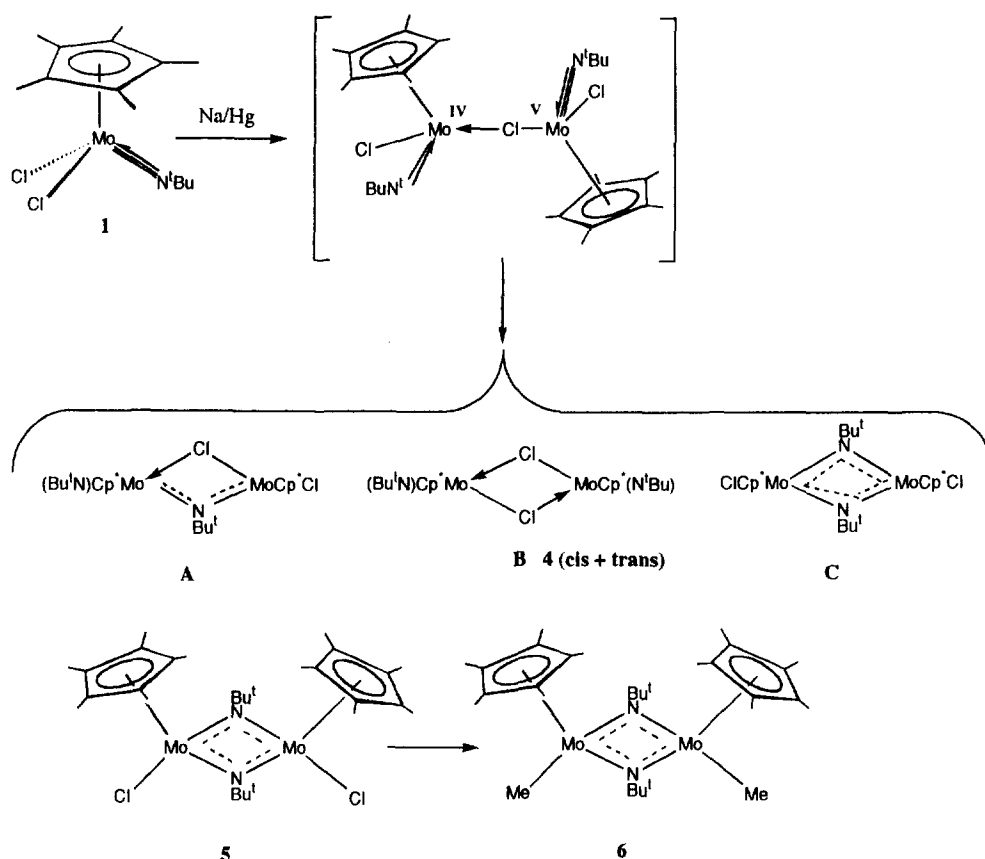
which a difference $\delta C_\alpha - \delta C_\beta = \Delta$ of 40.9 and 40.6 was observed for the two signals due to the ^1Bu groups. Two possible explanations are consistent with the observed NMR behaviour of **4** (see Scheme 2): one corresponds to the structure (A), with one chloro and one imido bridges and therefore one chloro and one imido terminal groups, and the second considers **4** to be a 1/1 molar mixture of two *cis*- and *trans*-stereoisomers containing two chloro (B) or two imido (C) bridges.

When **4** was kept as solid under dry argon it was partially and slowly transformed into a second green product **5** with the same analytical composition and mass spectrum but having a different NMR behaviour. The ^1H NMR spectrum (C_6D_6) of **5** showed one singlet at δ 1.67 ($T_1 = 0.693$) for the $\eta^5\text{-Cp}^*$ methyl protons and one singlet at δ 1.81 ($T_1 = 0.496$) for the ^1Bu protons, as expected for a symmetric dinuclear species. Conversion of **4** into **5** was followed by ^1H NMR (C_6D_6) spectroscopy in a sealed tube between -70 and 90°C . Starting from a pure sample of **4**, no conversion was observed between -70 and 20°C . Upon heating the sample to 90°C for 10 min the intensity of all the four singlets of **4** decreased with simultaneous appearance and increasing intensity of the singlets for **5**, which is quantitatively formed as a pure compound after heating for 2 h at 90°C . This was an irreversible transforma-

tion as no reconversion into **4** was ever observed on cooling again to room temperature. We conclude that **5** is the thermodynamic product of the reaction, whereas formation of **4** is kinetically controlled.

Reduction of complex **1** in toluene gave a solution which after evaporation to dryness provided a mixture of **4** and **5**, from which **4** could be isolated by extraction into pentane and further evaporation of the solvent. The maximum yield of complex **4** was obtained when the reaction was carried out below 10°C . The same products were also obtained more rapidly (4 h) when THF was used as solvent. Both species **4** and **5** were moderately air-stable compounds as solids for short periods but they were easily transformed into $[\{\text{MoCp}^*(\text{O})_2\}_2(\mu\text{-O})]$ [**4**] in solution.

The structure found for complex **5** by X-ray diffraction methods (Fig. 1) corresponds to the dimeric imido bridged *cis*- $[\text{MoCp}^*\text{Cl}(\mu\text{-N}^t\text{Bu})_2]$ complex (structure C). In contrast the NMR data show an upfield shift for the H_β protons of the organoimido ligand, a smaller difference Δ for their $\text{C}_\alpha - \text{C}_\beta$ resonances [10] and larger relaxation times T_1 for all Cp^* and ^1Bu signals, consistent with **4** having terminal imido groups. Therefore it seems reasonable to propose that **4** is a mixture of the two *cis*-*trans* isomers of the dimeric-chloro bridged complex $[\text{MoCp}^*(\mu\text{-Cl})(\text{N}^t\text{Bu})_2]$ in an approx-



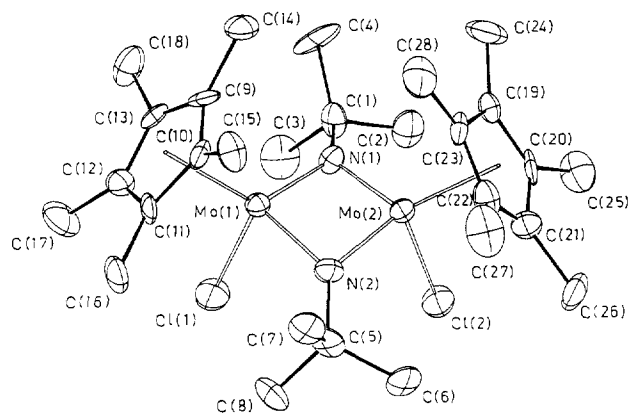


Fig. 1. View of the molecular structure of complex *cis*-[MoCp*Cl(μ-N^tBu)]₂ (**5**) with the atomic labelling scheme.

imately 1/1 molar ratio. Formation of the dinuclear di-chloro bridged species is consistent with the first step of the reduction pathway leading to a dinuclear μ-chloro di-molybdenum(IV)(V) complex whose further reduction leads to the kinetically controlled product.

Methylation of complexes **4** and **5** with 2 equiv. of MgClMe should lead to the same final product containing two imido bridges as it is the only substituent having electron pairs able to form the bridge. In fact, pentane or diethyl ether solutions of **4** react with MgClMe at room temperature to give brown bluish solutions, which after work-up provide the dimethyl derivative [(MoCp*Me(μ-N^tBu))₂] **6** as a microcrystalline solid, highly soluble in all organic solvents. The same reaction with complex **5** takes place in a similar way to give complex **6**, but is slower and decomposition products are observed when heated to reflux. The ¹H NMR spectrum of complex **6** shows the expected singlets for the Cp* and ^tBu protons along with a new high field singlet, due to the equivalent methyl protons, which is observed at δ = 1.48 (see Section 3).

Reaction of both complexes **4** and **5** with ethylene was monitored by ¹H NMR spectroscopy in a sealed tube in benzene-*d*₆. Reaction of complex **4** takes place easily and is complete after heating to 60 °C for 1 h whereas the same reaction with complex **5** requires heating to 100 °C for several days to give the same product, characterized by NMR spectroscopy as the adduct [MoCp*Cl(N^tBu)(C₂H₄)] **7**, analogous to the previously reported [3] derivatives [Mo(C₅H₄R)Cl(N^tBu)(C₂H₄)] (R = H, Me, ⁱPr). When the reaction of complex **4** was carried out on a preparative scale, stirring the solution under an ethylene atmosphere (1 atm), the starting product could not be totally transformed even after 3 h. This behaviour confirms that ethylene coordinates to the metal centre, breaking the double μ-chloro bridging system in complexes **4** more easily than the double μ-imido system in complex **5**.

2.3. X-ray structure of *cis*-[MoCp*Cl(μ-N^tBu)]₂ · C₆H₆ (5 · C₆H₆)

In the crystals, dimeric *cis*-[MoCp*Cl(μ-N^tBu)]₂ complexes and benzene molecules of solvation are present. The structure of the complex is shown in Fig. 1 together with the atomic labelling scheme. Selected bond distances and angles are given in Table 1. In the complex **5** each molybdenum is bound to a pentamethylcyclopentadienyl ring in a slightly asymmetric η⁵-fashion [the Mo(1)–C distances range from 2.325(16) to 2.551(18) Å; those of Mo(2)–C are in the range 2.345(18)–2.501(17) Å], the distance between the metal and the centroid of the ring being 2.109(16) Å for Mo(1) and 2.126(18) Å for Mo(2). Each Mo atom is bound also to one terminal Cl atom with Mo(1)–Cl(1) and Mo(2)–Cl(2) bond lengths of 2.391(5) Å and 2.394(5) Å respectively. The coordination around the Mo atoms is completed by two N atoms from two N^tBu imido groups acting as nearly symmetric bridging ligands [Mo(1)–N(1) = 1.951(13) and Mo(2)–N(1) = 1.948(12), Mo(1)–N(2) = 1.974(14) and Mo(2)–N(2) = 1.950(13) Å]. The Mo(1)–N–Mo(2) angles at the bridges are rather narrow [85.8(6) and 85.1(6)°], and the value of the Mo(1)–Mo(2) separation is very short, 2.655(3) Å, in agreement with most values reported for metal–metal single bonds, even if the short Mo–Mo separation could be imposed by the Mo₂(μ-N)₂ core itself [11]. The Mo₂(μ-N)₂ core is roughly planar, the two Mo(1)Mo(2)N(1) and Mo(1)Mo(2)N(2) triangles being folded by 14.9(4)°. The coordination geometry around each Mo atom can be described as of three-legged piano-stool-type or pseudotetrahedral if the centroid of the Cp* ring is considered as occupying one coordination site. In the three compounds *trans*-[MoCpO(μ-NCOOEt)]₂ [12], *trans*-[Mo(η⁵-

Table 1

Selected bond lengths (Å) and angles (deg) for complex *cis*-[MoCp*Cl]₂(μ-N^tBu)₂ **5**

Mo(1)–CE(1)	2.109(16)	Mo(2)–CE(2)	2.126(18)
Mo(1)–Cl(1)	2.391(5)	Mo(2)–Cl(2)	2.394(5)
Mo(1)–N(1)	1.951(13)	Mo(2)–N(1)	1.948(12)
Mo(1)–N(2)	1.974(14)	Mo(2)–N(2)	1.950(13)
N(1)–C(1)	1.515(20)	N(2)–C(5)	1.499(22)
Mo(1)–Mo(2)	2.655(3)		
CE(1)–Mo(1)–Cl(1)	106.5(5)	CE(2)–Mo(2)–Cl(2)	107.6(5)
CE(1)–Mo(1)–N(1)	126.5(6)	CE(2)–Mo(2)–N(1)	127.1(6)
CE(1)–Mo(1)–N(2)	128.8(6)	CE(2)–Mo(2)–N(2)	127.8(6)
Cl(1)–Mo(1)–N(1)	98.9(4)	Cl(2)–Mo(2)–N(1)	96.5(4)
Cl(1)–Mo(1)–N(2)	96.1(4)	Cl(2)–Mo(2)–N(2)	96.2(4)
N(1)–Mo(1)–N(2)	93.1(5)	N(1)–Mo(2)–N(2)	93.9(5)
Mo(1)–N(1)–Mo(2)	85.8(5)	Mo(1)–N(2)–Mo(2)	85.1(6)
Mo(1)–N(1)–C(1)	137.1(10)	Mo(1)–N(2)–C(5)	137.9(11)
Mo(2)–N(1)–C(1)	135.6(9)	Mo(2)–N(2)–C(5)	136.0(10)

CE(1) and CE(2) are the centroids of the C(9)–C(13) and C(19)–C(23) cyclopentadienyl rings respectively.

$C_5H_4Me(NPh)(\mu-NPh)_2$ [13] and $[Mo(O^iBu)_2(\mu-NAr)_2]$ (Ar = 2,6-diisopropylphenyl) [11], comparable structural features of the $Mo_2(\mu-N)_2$ core determined by imido-bridges have been found. In fact in these three complexes this core is roughly planar, the bridges are symmetrical and the values of the Mo–Mo distances, 2.724(1) Å, 2.719(1) Å and 2.654(1) Å respectively are comparable to those found in **5** as well as those of the Mo–N bonds, 1.971(4) and 1.978(3) Å in *trans*- $[MoCpO(\mu-NCOOEt)]_2$, 1.964(2) and 1.964(2) Å in *trans*- $[Mo(\eta^5-C_5H_4Me)(NPh)(\mu-NPh)]_2$, 1.955(4) and 1.952(4) Å in $[Mo(O^iBu)_2(\mu-NAr)]_2$. Extended Hückel molecular orbital calculations carried out on the complex *trans*- $[Mo(\eta^5-C_5H_4Me)(NPh)(\mu-NPh)]_2$ [13] were in agreement with the presence of a metal–metal single bond.

3. Experimental

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a glovebox. Solvents used were previously dried and freshly distilled. Reagent grade H_2N^iBu (freshly distilled) and $MgClMe$ (3 M in THF) and Na (without further purification) were purchased from Aldrich Chemical Co; Hg, from Panreac. Isocyanide [14] ($2,6-Me_2C_6H_3$)NC and the starting material $[MoCp^*Cl_4]$ [15] were prepared as described previously.

Infrared spectra were recorded on a Perkin–Elmer 883 spectrophotometer ($4000–200\text{ cm}^{-1}$) as Nujol mulls between CsI pellets or as a pentane solution between CaF_2 pellets. 1H and ^{13}C NMR spectra were recorded on Varian Unity VXR-300 or Varian Unity 500 Plus instruments. 1H and ^{13}C NMR shifts were measured relative to residual 1H and ^{13}C resonances in the deuterated solvents: C_6D_6 (δ 7.15) and C_5D_5 (δ 128), C_7D_8 (δ 127, 124, 20) respectively. Sequence inversion recovery [16] was used to measure relaxation times T_1 .

Mass spectra were recorded on an HP 5890 instrument. C, H and N analyses were carried out with a Perkin–Elmer 240 C microanalyser.

3.1. $MoCp^*Cl_2(N^iBu)$ (**1**)

To a toluene (40 ml) suspension of **1** (2 g, 5.36 mmol) was added the stoichiometric amount of freshly distilled H_2N^iBu (1.69 ml, 16.1 mmol) and the mixture was stirred for 2 h. The purple colour of the mixture changed to give a brown solution. The ammonium salt formed was filtered and the solution was evaporated in vacuo to give a brown oil which was washed with pentane and extracted with *n*-hexane (4×30 ml). The solution was concentrated to ca. 20 ml and cooled to $-40^\circ C$ to give **1** as brown-yellow crystals (1.5 g, 75% yield). Anal.

Calc. for $C_{14}H_{24}Cl_2MoN$: C, 45.05; H, 6.43; N, 3.75. Found: C, 45.04; H, 6.34; N, 3.74. IR (Nujol mull, $\nu\text{ cm}^{-1}$): 1223 (s), 1206 (s), 1027 (m), 929 (m), 802 (w), 386 (s), 334 (s). 1H NMR (δ ppm, in C_6D_6): -2.45 (br, 1200 Hz, $T_1 = 0.0085$ s, 15H, C_5Me_5), 45 (br, 12000 Hz, $T_1 < 100$ ms, 9H, $NCMe_3$). MS (EI, 70 eV): m/e 374 (6), 318 (44), 287 (21), 119 (100), 57 (18).

3.2. $MoCp^*Cl(N^iBu)\{CN(2,6-Me_2C_6H_3)\}$ (**2**)

A THF (40 ml) solution of **1** (0.68 g, 1.28 mmol) was added to a mixture of 10% sodium amalgam (0.050 g, 1.28 mmol) and $CN(2,6-Me_2C_6H_3)$ (0.17 g, 1.28 mmol). After stirring for 5 h the resulting green solution was filtered and the solvent removed in vacuo to give a green oil, which was washed with the minimum amount of pentane because **2** is partially soluble in this solvent. After evaporation and cooling complex **2** was obtained as a green solid (0.42 g, 70% yield). Anal. Calc. for $C_{23}H_{33}ClMoN_2$: C, 58.91; H, 7.04; N, 5.97. Found: C, 58.40; H, 7.10; N, 6.00. IR (Nujol mull, $\nu\text{ cm}^{-1}$): 2080 (sh), 2005 (s), 1909 (s), 1228 (s), 1027 (m), 785 (s), 671 (m), 580 (w), 513 (w), 493 (m), 423 (m). 1H NMR (δ ppm, in C_6D_6): 6.8 (s, 3H, $2,6-Me_2C_6H_3$), 2.42 (s, 6H, $2,6-Me_2C_6H_3$), 1.84 (s, 15H, C_5Me_5), 1.32 (s, 9H, $NCMe_3$).

3.3. $MoCp^*Me(N^iBu)\{CN(2,6-Me_2C_6H_3)\}$ (**3**)

A sample of **2** (0.47 g, 1 mmol) was dissolved in THF (50 ml) and 0.33 ml of a 3 M solution of $MgClMe$, in THF was added. The mixture was heated under reflux for 20 h. The resulting solution was allowed to cool to room temperature and the solution was evaporated to dryness. The resulting brown solid was extracted into an approximately 1/2 mixture of toluene–*n*-hexane (40 ml). The solution was cooled and brown-green microcrystals of **3** were obtained (0.3 g, 67% yield). Anal. Calc. for $C_{24}H_{36}MoN_2$: C, 64.28; H, 8.03; N, 6.25. Found: C, 64.50; H, 7.98; N, 6.28. IR (pentane solution, $\nu\text{ cm}^{-1}$): 1988 (sh), 1829 (br), 1250 (s), 1101 (m), 1059 (m), 1016 (s). 1H NMR (δ ppm, in C_6D_6): 6.88 (m, 3H, $2,6-Me_2C_6H_3$), 2.47 (s, 6H, $2,6-Me_2C_6H_3$), 1.82 (s, 15H, C_5Me_5), 1.22 (s, 9H, $NCMe_3$), 0.45 (s, 3H, Mo–Me).

3.4. $[MoCp^*Cl(N^iBu)]_2$ (**4** *cis* + *trans*)

To a freshly prepared 10% sodium amalgam (0.20 g, 8.85 mmol) was added complex **1** (3 g, 8.05 mmol) and pentane (40 ml). The reaction mixture was stirred for 20 h and after filtration of the sodium salt formed, the solvent was removed in vacuo to give a yellow-brown microcrystalline solid. The same reaction was more rapid (4 h) when carried out in THF but extraction into

pentane is required to obtain the same solid (2 g, 75% yield). Anal. Calc. for $C_{28}H_{48}Cl_2Mo_2N_2$: C, 49.77; H, 7.10; N, 4.10. Found: C, 49.05; H, 6.90; N, 3.88. IR (Nujol mull, ν cm^{-1}): 1218 (s), 1179 (m), 1023 (m), 339 (w), 325 (w). 1H NMR (δ ppm, in C_6D_6): 1.71 (s, 15H, C_5Me_5), 1.66 (s, 15H, C_5Me_5), 1.55 (s, 9H, $NCMe_3$), 1.42 (s, 9H, $NCMe_3$). ^{13}C NMR (δ ppm, in C_6D_6): 113.11 (s, C_5Me_5), 108.7 (s, C_5Me_5), 77.2 (s, $NCMe_3$), 72.9 (s, $NCMe_3$), 36.3 (s, $NCMe_3$), 32.3 (s, $NCMe_3$), 13.7 (s, C_5Me_5), 12.9 (s, C_5Me_5). Relaxation times (T_1 s): 1.71 ppm (Cp^*), 1.485 ± 0.03 ; 1.66 ppm (Cp^*), 1.376 ± 0.06 ; 1.55 ppm (tBu), 0.677 ± 0.016 ; 1.42 ppm (tBu), 0.722 ± 0.02 . MS (EI, 70 eV): m/e 674 (1), 619 (2), 564 (2.5), 318 (15), 282 (12), 119 (27), 57 (100).

3.5. *cis*-[MoCp*Cl] $_2(\mu-N^tBu)_2$ (**5**)

A toluene (40 ml) solution of complex **4** (1 g, 2.96 mmol) was heated with stirring at ca. 80 °C for 15 h. The brown colour of the solution changed to give a green solution. After removal of the solvent, 1 g (2.96 mmol) of a dark green crystalline solid identified as **5** was obtained (1 g, 100% yield). Complex **5** can also be obtained by reduction of **1** with 10% sodium amalgam in THF, as a by-product of **4**, but it is always contaminated with the sodium salt formed in the reaction. Anal. Calc. for $C_{28}H_{48}Cl_2Mo_2N_2$: C, 49.77; H, 7.10; N, 4.10. Found: C, 49.21; H, 6.90; N, 3.97. IR (Nujol mull, ν cm^{-1}): 2013 (m), 1179 (s), 1020 (m), 337 (s). 1H NMR (δ ppm, in C_6D_6): 1.73 (s, 15 H, C_5Me_5), 1.91 (s, 9 H, $NCMe_3$). ^{13}C NMR (δ ppm, in C_6D_6): 113.6 (s, C_5Me_5), 34.2 (s, $NCMe_3$), 13.2 (s, C_5Me_5). Relaxation times (T_1 s): 1.73 ppm (Cp^*), 0.693 ± 0.02 ; 1.91 ppm (tBu), 0.496 ± 0.01 . MS (EI, 70 eV): m/e 674 (0.5), 619 (1), 564 (1), 318 (11.5), 282 (17), 119 (32), 57 (100).

3.6. [MoCp*Me] $_2(\mu-N^tBu)_2$ (**6**)

A 3 M solution of MgMeCl in THF (1.00 ml, 3.00 mmol) was added to a solution of **4** (1.00 g, 1.50 mmol) in hexane (50 ml) cooled to -60 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. After filtration, the solvent was evaporated to give a blue solid which was characterized as **6** (0.55 g, 98% yield). Anal. Calc. for $C_{30}H_{54}Mo_2N_2$: C, 34.57; H, 4.44. Found: C, 34.81; H, 5.00. 1H NMR (300 MHz, C_6D_6 , 25 °C) δ -1.48 (s, 6 H, Mo-Me), 1.74 (s, 18H, - CMe_3), 1.75 (s, 30H, C_5Me_5).

3.7. [MoCp*Cl(N^tBu)](C_2H_4) (**7**)

Ethylene was condensed into an NMR tube containing a solution of **4** in C_6D_6 and the tube was sealed. The reaction started immediately and was complete

after heating for 1 h to 60 °C. The same reaction with complex **5** required heating for 2 days to 100 °C to be complete. 1H NMR (300 MHz, C_6D_6 , 25 °C) δ 0.99 (s, 9H, CMe_3), 1.62 (s, 15H, C_5Me_5 + 1H, C_2H_4), 1.90, 2.72, 2.84 (m, 3H, C_2H_4). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C) δ 10.6 (C_5Me_5), 28.7 (CMe_3), 41.1 (C_2H_4), 50.9 (C_2H_4), 70.5 (CMe_3), 110.7 (C_5Me_5).

3.8. X-ray data collection, structure determination and refinement for complex **5** · C_6H_6

Crystals suitable for the X-ray study were obtained by recrystallization from benzene, so in the crystals benzene molecules of solvation were found. The crystallographic data of **5** · C_6H_6 are summarized in Table 2. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the graphite-monochromated MoK α radiation and the θ - 2θ scan type. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects; no correction for absorption was necessary. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms excepting for the carbon atoms of the benzene molecule of solvation. Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, a final refinement was carried out using the coordinates $-x, -y, -z$; an increasing of the R and R_w values was obtained [$R(x,y,z) = 0.0541$, $R_w(x,y,z) = 0.0594$; $R(-x, -y, -z) = 0.0549$, $R_w(-x, -y, -z) = 0.0601$]. The former model was selected and the reported data

Table 2
Summary of crystallographic data for complex **5** · C_6H_6

Formula	$C_{28}H_{48}Cl_2Mo_2N \cdot C_2H_6$
Mol. wt.	753.60
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	10.898(6)
b (Å)	15.867(4)
c (Å)	20.411(9)
V (Å 3)	3529(3)
Z	4
D_{calc} (g cm $^{-3}$)	1.418
$F(000)$	1560
Crystal size (mm 3)	0.20 × 0.25 × 0.30
μ (MoK α) (cm $^{-1}$)	8.86
θ range (deg)	3–27
Unique total data	4286
Unique observed data	2160 [$I > 2\sigma(I)$]
$R = \sum \Delta F / \sum F_o $	0.0541
$R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$	0.0594

refer to this model. All hydrogen atoms were placed at their geometrically calculated positions (C–H = 0.96 Å) and refined 'riding' on the corresponding carbon atoms. Unit weights were used in all stages of the refinement. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from Ref. [17]. All calculations were carried out on the Gould Povernode 6040 of the 'Centro di Studio per la Strutturistica Diffraattometrica' del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [18]. The final atomic coordinates for the non-hydrogen atoms are given in Table 3. Additional data (atomic coordinates of the hydrogen

atoms, thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre or are available from the authors.

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Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for complex *cis*-[MoCp*Cl]₂(μ -N^tBu)₂ **5**

	x	y	z	U ^a
Mo(1)	1817(1)	1032(1)	2038(1)	356(4)
Mo(2)	4056(1)	558(1)	1681(1)	353(4)
Cl(1)	1981(5)	2207(3)	2767(3)	681(19)
Cl(2)	5484(4)	1447(3)	2244(3)	640(18)
N(1)	3039(12)	297(8)	2439(6)	384(42)
N(2)	2984(14)	1463(8)	1378(6)	435(45)
C(1)	3248(17)	-110(11)	3101(7)	487(58)
C(2)	4591(17)	-279(13)	3210(9)	691(80)
C(3)	2849(21)	511(15)	3612(7)	799(88)
C(4)	2542(19)	-934(13)	3153(9)	868(89)
C(5)	3115(21)	2218(11)	943(9)	574(69)
C(6)	4493(18)	2355(13)	772(11)	751(87)
C(7)	2332(19)	2111(11)	325(9)	654(76)
C(8)	2693(21)	3000(11)	1333(11)	800(90)
C(9)	250(16)	52(10)	1883(9)	468(63)
C(10)	187(14)	654(11)	1364(8)	449(56)
C(11)	-217(14)	1440(10)	1636(10)	479(58)
C(12)	-428(17)	1297(11)	2326(10)	516(64)
C(13)	-153(14)	453(11)	2458(8)	428(55)
C(14)	426(17)	-861(10)	1776(9)	580(66)
C(15)	289(18)	474(14)	648(9)	692(78)
C(16)	-597(17)	2262(12)	1279(10)	659(77)
C(17)	-957(23)	1926(11)	2778(11)	898(98)
C(18)	-489(19)	25(14)	3088(9)	781(88)
C(19)	4830(15)	-885(10)	1474(8)	426(54)
C(20)	5872(15)	-380(11)	1509(8)	500(59)
C(21)	5809(20)	239(11)	981(9)	572(66)
C(22)	4778(19)	80(14)	608(10)	603(72)
C(23)	4127(15)	-575(12)	944(8)	473(53)
C(24)	4572(22)	-1685(10)	1830(11)	880(101)
C(25)	6955(19)	-467(13)	1982(10)	793(83)
C(26)	6889(18)	792(13)	820(11)	855(94)
C(27)	4537(22)	400(16)	-63(9)	972(108)
C(28)	3010(21)	-1017(14)	646(10)	861(90)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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