

Synthesis and reactions of $[\text{Mo}(\text{2,6-lutidine})(\eta\text{-allyl})]$ derivatives

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Abstract

The syntheses of the η -lutidine(η -allyl)molybdenum compounds $[\text{Mo}(\text{2,6-lutidine})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ **1**, $[\text{Mo}(\eta\text{-2,6-lutidine})(\eta\text{-C}_3\text{H}_5)(\eta^2\text{-O}_2\text{CR})]$ (**2**: R = CH₃, **3**: R = C(CH₃)₃) and $[\text{Mo}(\eta\text{-2,6-lutidine})(\eta\text{-C}_3\text{H}_5)_2]$ **4** are described. The sandwich compound $[\text{Mo}(\eta\text{-2,6-lutidine})_2]$ undergoes facile ligand displacement giving zero-valent compounds MoL_6 , where L = CO, CNR, and $\text{Mo}(\text{diene})_3$, where diene = 2,3-dimethyl-1,3-butadiene. The crystal structure of compound **1** has been determined.

Keywords: Molybdenum; Allyl; η -Arene; Crystal structure; Metal vapour synthesis

1. Introduction

The chemistry of bis(η -arene)metal sandwich compounds is well-established [1–3]. Analogous sandwich complexes which incorporate a heteroatom such as N, P or As into the arene ring [4–6] have been prepared but their chemistry is virtually unexplored. The complex $[\text{Mo}(\eta\text{-2,6-lutidine})_2]$, first prepared by Wucherer and Muetterties using metal vapour synthesis techniques [7], has been fully characterised [8] but no reaction chemistry was reported. Treatment of the well-known bis- η -arene molybdenum compound $[\text{Mo}(\eta\text{-arene})_2]$ with allyl chloride gives the compound $[\text{Mo}(\eta\text{-arene})(\eta\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$, which is a synthon for an extensive chemistry of the $\text{Mo}(\eta\text{-arene})$ moiety [1–3,9–16]. In an earlier paper [16] we described the analogous reaction between $[\text{Mo}(\eta\text{-2,6-lutidine})_2]$ and allylchloride which gave the dimer $[\text{Mo}(\text{2,6-lutidine})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ (**1**). Here we report further studies on the chemistry of **1**.

2. Results and discussion

The original preparation of $[\text{Mo}(\text{2,6-lutidine})_2]$ via co-condensation of molybdenum atoms with an excess of 2,6-lutidine using a rotating flask reactor gave a yield

of only 8% [7]. In order to attempt to improve the yield the experiment was repeated using a bell-jar reactor [17] supported by a turbomolecular pump. Molybdenum atoms were co-condensed with an excess of 2,6-lutidine over a period of 6 h onto the surface of a glass bell-jar cooled to -196°C . The resulting orange–brown matrix was brought to room temperature and washed from the reaction vessel using light petroleum ether to give a dark red–brown solution. The original work-up of the reaction mixture [7] was modified since the product yield was sensitive to temperature. Filtrations were carried out at low temperature since work-up at room temperature gave yields of only $\sim 20\%$. The low temperature procedure gave orange–brown, needle-shaped crystals in 39% yield, on a scale of 3–4 g.

The compound **1**, synthesised as described [16], is sparingly soluble in THF and toluene but insoluble in less polar solvents and stable below ca. 290°C . We were able to grow crystals of X-ray quality by slow cooling of a saturated toluene solution to -20°C , and the crystal structure of **1** has been determined. The asymmetric units in the crystals of **1** contain two crystallographically independent molecules (**A** and **B**) with similar geometrical parameters. The perspective view of molecule **1A** is shown in Fig. 1. Selected bond angles and distances for both molecules are listed in Table 1, and the fractional atomic coordinates are given in Table 2. Owing to the centre of symmetry the Mo_2Cl_2 group in **1** is ideally planar. The bond length and angle distributions in this group are similar to those in the

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Table 1
Selected interatomic distances (Å) and angles (°) for **1**

	Molecule A	Molecule B
Mo–Cl	2.5132(8)	2.5245(8)
Mo–Cl'	2.5251(8)	2.5241(8)
Mo–N	2.264(3)	2.261(3)
Mo–C(1)	2.351(3)	2.354(3)
Mo–C(2)	2.311(4)	2.325(3)
Mo–C(3)	2.176(4)	2.193(4)
Mo–C(4)	2.316(3)	2.319(4)
Mo–C(5)	2.338(3)	2.334(3)
Mo–C(8)	2.236(4)	2.240(4)
Mo–C(9)	2.155(3)	2.161(4)
Mo–C(10)	2.243(4)	2.232(4)
Mo–CEN	1.823	1.826
C(8)–C(9)	1.423(6)	1.419(6)
C(9)–C(10)	1.418(6)	1.432(7)
Cl–Mo–Cl'	78.83(3)	78.24(3)
Cl–Mo–C(8)	120.8(1)	120.0(1)
Cl'–Mo–C(8)	80.2(1)	81.2(1)
Cl–Mo–C(9)	85.8(1)	85.5(1)
Cl'–Mo–C(9)	85.7(1)	86.9(1)
Cl–Mo–C(10)	81.1(1)	80.9(1)
Cl'–Mo–C(10)	120.8(1)	122.2(1)
Cl–Mo–CEN	119.6	119.3
Cl'–Mo–CEN	119.3	118.8
C(8)–Mo–CEN	119.1	120.1
C(9)–Mo–CEN	145.9	146.2
C(10)–Mo–CEN	119.1	118.4
Mo–Cl–Mo'	101.17(3)	101.76(3)
C(8)–C(9)–C(10)	113.6(4)	113.5(4)

CEN denotes the centroid of the NC(1)–C(5) ring.

compound $[\text{Mo}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ [18]. The dimethylpyridine groups in complex **1** are not exactly planar. The nitrogen atom and *para* carbon atom C(3) are bent ca. 0.16 Å out of the C(1)C(2)C(4)C(5) plane towards the molybdenum atoms, whereas the methyl atoms C(6) and C(7) are displaced from this plane by 0.14–0.18 Å in the opposite direction. The molybdenum–ring distances indicate that the metal atom is not equally bonded to the ring atoms: the Mo–C(3) distance (av. 2.185 Å) is

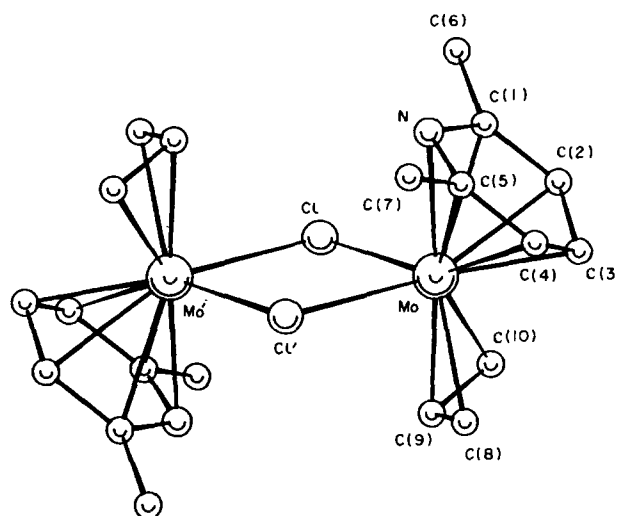


Fig. 1. Perspective view of molecule **1A** with labelling scheme. The primed atoms are generated from the asymmetric unit using the inversion centre. Hydrogen atoms are omitted for clarity.

noticeably shortened, whereas the Mo–C(1) and Mo–C(5) distances (av. 2.185 Å) are slightly elongated in comparison with the Mo–C(2) and Mo–C(4) distances (av. 2.318 Å). In the pyridine ring the N–C(1) and N–C(5) bonds lengths are almost the same as C(1)–C(2) and C(4)–C(5), whereas the C(2)–C(3) and C(3)–C(4) bonds are noticeably elongated. Similar observations have been made for the related vanadium and titanium compounds $\text{V}(\text{lutidine})_2$ and $\text{Ti}(\text{lutidine})_2$ [8]. The allyl ligand is symmetrically bound to the Mo atom with Mo–C(8) and Mo–C(10) distances of 2.232–2.243(4) Å. The distance between Mo and the central carbon atom C(9) is slightly shorter (ca. 0.07–0.08 Å), as is unexceptional in other metal allyl complexes [19]. The dihedral angle between Mo_2Cl_2 and C(8)C(9)C(10) planes is 114.08° for **1A** and 113.95° for **1B**.

The mass spectrum of the dimer **1**, recorded under FAB(+) conditions, showed the successive loss of the

Table 2
Fractional atomic coordinates for compounds **1A** and **1B** with e.s.d.s in parentheses

Atom	Molecule 1A			Molecule 1B		
	x	y	z	x	y	z
Mo	–0.06107(3)	0.65359(2)	0.08283(2)	0.51185(3)	0.17724(2)	0.42793(2)
Cl	0.09795(9)	0.43367(7)	0.10680(7)	0.37428(9)	0.05490(8)	0.59598(7)
N	0.1296(3)	0.7473(3)	–0.0109(3)	0.3377(3)	0.1680(3)	0.3056(3)
C(1)	0.1538(4)	0.7312(4)	0.1087(3)	0.4595(4)	0.1859(4)	0.2279(3)
C(2)	0.0457(5)	0.7745(4)	0.1937(3)	0.5420(5)	0.2798(4)	0.2346(3)
C(3)	–0.0956(5)	0.8367(4)	0.1586(4)	0.4968(5)	0.3685(4)	0.3231(4)
C(4)	–0.1057(4)	0.8765(3)	0.0348(4)	0.3529(5)	0.3695(4)	0.3806(4)
C(5)	0.0058(4)	0.8265(3)	–0.0466(3)	0.2777(4)	0.2709(3)	0.3724(3)
C(6)	0.3038(5)	0.6619(5)	0.1387(4)	0.5021(5)	0.0879(4)	0.1403(4)
C(7)	–0.0019(6)	0.8610(4)	–0.1785(4)	0.1299(4)	0.2643(4)	0.4352(4)
C(8)	–0.3059(4)	0.6740(4)	0.0997(4)	0.7473(5)	0.1913(5)	0.4408(4)
C(9)	–0.2382(4)	0.5567(4)	0.1633(4)	0.6712(4)	0.1720(5)	0.5552(4)
C(10)	–0.1623(5)	0.5762(4)	0.2599(4)	0.5546(5)	0.2766(5)	0.5796(4)

Table 3
Analytical and spectroscopic data

Compound ^a	Spectroscopic data ^b
1. Purple-black C, 43.0 (42.95) H, 5.2 (5.05) Cl, 12.6 (12.7) M/e 588 P ⁺ (FAB)	¹ H ^c : 1.85 (12, s, C _o CH ₃), 2.71 [4, d (J = 7.7) H _{anti}], 2.27 [4, d (J = 6.1) H _{syn}], 3.40 [2, t (J = 5.1) H _p], 5.12 (2, m, H _c), 4.10 (4, d (J = 5.1) H _m) ¹³ C at 75.5 MHz ^c : 21.8 (C _o CH ₃), 56.4 (C _i), 88.1 (C _c), 93.8 (C _p), 95.0 (C _m), 128.6 (C _o) IR: 1545m ^d
2. Purple-black C, 47.8 (47.5) H, 5.8 (5.65) N, 4.6 (4.6)	¹ H ^c : 1.59 (3, s, O ₂ CCH ₃), 1.71 (6, s, C _o CH ₃), 2.71 [2, d (J = 8.0) H _{anti}], 2.77 [2, d (J = 6.5) H _{syn}], 2.76 [1, t (J = 5.5) H _p], 3.72 (1, m, H _c), 3.78 (2, d (J = 5.3) H _m) ¹³ C at 125.7 MHz ^c : 21.4 (C _o CH ₃), 54.6 (C _i), 23.6 (O ₂ CCH ₃), 91.6 (C _c), 92.6 (C _p), 97.6 (C _m), 127.1 (C _o), 187.7 (O ₂ CC) IR: 1530w ^d , 1558w ^f
3. Purple-black C, 52.6 (52.2) H, 6.85 (6.7) N, 4.1 (4.1) M/e 347 P ⁺ (FAB)	¹ H ^c : 1.13 [9, s, C(CH ₃) ₃], 1.67 (6, s, C _o CH ₃), 2.68 [2, d (J = 7.7) H _{anti}], 2.78 [2, d (J = 6.0) H _{syn}], 2.80 [1, t (J = 5.3) H _p], 3.60 (1, m, H _c), 3.79 [2, d (J = 5.3) H _m) ¹³ C at 75.5 MHz ^c : 21.3 (C _o CH ₃), 26.6 [C(CH ₃) ₃], 39.9[C(CH ₃) ₃], 54.5 (C _i), 91.6 (C _c), 91.9 (C _p), 97.6 (C _m), 127.4 (C _o), 195.0 (O ₂ CC) IR: 1546m ^d , 1657w ^f
4. Orange C, 54.8 (54.7) H, 6.7 (6.7) Mo, 33.05 (33.6) N, 5.25 (4.9) M/e 287 P ⁺ (EI)	¹ H ^e : 1.11 [4, d (J = 10.5) H _{anti}], 1.90 (6, s, C _o CH ₃), 2.03 [4, d (J = 7.5) H _{syn}], 2.89 [1, t (J = 5.5) H _p], 3.67 (2, m, H _c), 4.61 (2, d (J = 5.5) H _m) ¹³ C at 125.7 MHz ^e : 22.8 (C _o CH ₃), 43.4 (C _i), 93.5 (C _c), 84.1 (C _p), 94.9 (C _m) IR: 1548m ^g

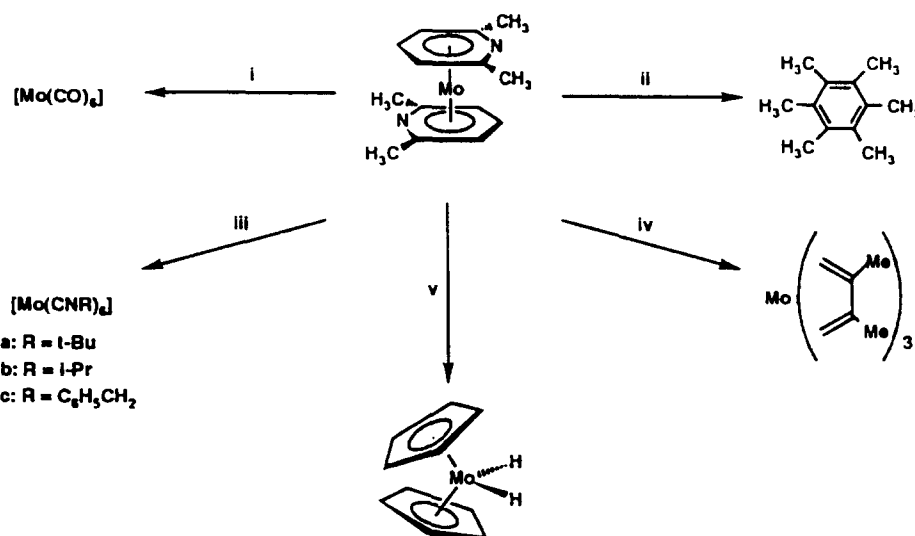
^a Analytical data given as: Found (Calc.) (%). ^b ¹H NMR at 300 MHz, ¹³C at 75.5 or 125.7 MHz. NMR data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (Hz) and assignment. The labelling of atoms is given in the structure of 1 in Scheme 1. ¹H-¹³C correlation spectra enabled the precise assignment of all resonances in the ¹³C NMR spectra of compounds 1–4. IR data in Nujol mulls (cm⁻¹). The M/e values refer to the ⁹⁸Mo isotope. ^c In [2H₂] dichloromethane. ^d Assigned to ν (C–C) of the η -allyl ligand [20]. ^e In [2H₆] benzene. ^f Assigned to ν (C–O) of the carboxylato ligand [20]. ^g In [2H₈]toluene.

two allyl and lutidine ligands from the parent molecule ion M⁺ (M/z = 588).

The analytical and spectroscopic data characterising the compounds 1–4 are given in Table 3. ¹H-¹³C

correlation spectra assisted in the assignment of all the resonances in the ¹³C NMR spectra of compounds 1–4.

Treatment of the dimer 1 with sodium acetate or sodium pivalate at room temperature in a mixture of



Scheme 1. (i) Carbon monoxide at 1 atm. and room temperature in toluene, yield > 90%. (ii) But-2-yne in toluene at room temperature for 1 h, yield 50%. (iii) ¹BuNC in MeCN, 0–40°C, yield 72%. (iv) 2,3-Dimethyl-1,3-butadiene in toluene at 60°C, yield 76%. (v) Cyclopentadiene in toluene at 60°C, yield 52%.

toluene and ethanol leads to the formation of the carboxylato derivatives $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})(\eta\text{-C}_3\text{H}_5)(\eta^2\text{-O}_2\text{CR})]$ ($\text{R} = \text{CH}_3$ (**2**) or $\text{R} = \text{CMe}_3$ (**3**)). The complexes **2** and **3** were formed as black–purple crystals in ca. 40% yields. The crystals of **2** and **3** were air-sensitive and soluble in common organic solvents; they melt without decomposition at 65 and 75°C respectively. Attempts to synthesise **2** directly by treating $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ with allyl acetate failed.

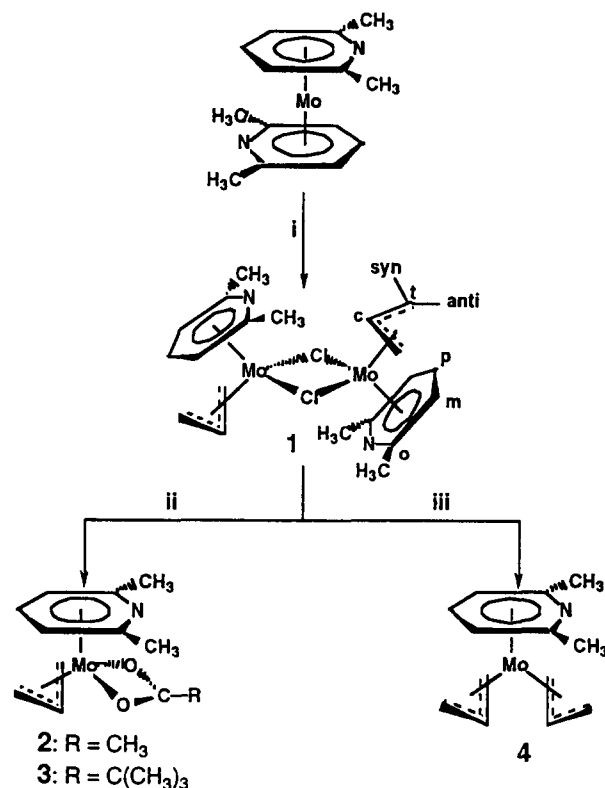
Treatment of the dimer **1** with allylmagnesium chloride at -30°C gives the bis- η -allyl complex $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})(\eta\text{-C}_3\text{H}_5)_2]$ **4** as orange–brown crystals in 41% yield. The orange complex **4** is moderately soluble in *n*-pentane and very soluble in benzene, CH_2Cl_2 and THF; it melts without decomposition in a sealed capillary at 123°C .

2.1. Reactivity studies of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$

The compound $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ **5** is thermally fragile and decomposes in solution at 60°C . This facile loss of the $\eta\text{-}2,6\text{-lutidine}$ ligands suggested that the compound **5** might be a useful synthon for low valent molybdenum complexes. Therefore, some reactions of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ with ligands known to form stable molybdenum compounds were explored, and these reactions are summarised in Scheme 1.

Treatment of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ in light petroleum with an excess of cyclopentadiene gave the well-known $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ [21–23]. The best yield of 52% was obtained using a reaction temperature of $\geq 60^\circ\text{C}$. The dihydride $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ and the other reaction products shown in Scheme 1 were characterised by comparison of their IR and NMR spectra with previously reported data [21].

Treatment of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ with 2,3-dimethyl-1,3-butadiene in toluene at 60°C for 15 h gave *tris*(2,3-dimethyl-1,3-butadiene)molybdenum [24–29] in 76% yield. Similarly, treatment of **5** with an excess of *tert*-butyl isocyanide in acetonitrile gave $[\text{Mo}(\text{tBuNC})_6]$ [30–37]. Acetonitrile was chosen as the solvent since ^1H NMR studies had shown that **5** decomposes in CD_3CN at 0°C after 3 h. Attempts to carry out this reaction in toluene at 60°C failed due to the decomposition of the thermally sensitive product $[\text{Mo}(\text{tBuNC})_6]$. The highest yield (72%) for preparation of $[\text{Mo}(\text{tBuNC})_6]$ was obtained by keeping the acetonitrile solution at 0°C for 4 h before warming to 40°C for 15 h. The related isonitrile complexes $[\text{Mo}(\text{tPrNC})_6]$ and $[\text{Mo}(\text{PhCH}_2\text{NC})_6]$ were prepared similarly. The compound **5** reacts readily with CO at room temperature giving $[\text{Mo}(\text{CO})_6]$. Also, treatment of **5** with but-2-yne in acetonitrile at room temperature causes rapid trimerization giving hexamethylbenzene [38–40]. Analogous reactions using 3-hexyne and phenylacetylene as the alkyne were unsuccessful.



Scheme 2. (i) Allyl chloride in toluene at -30°C , then at room temperature for 48 h, yield 45%. (ii) For $\text{R} = \text{CH}_3$, sodium acetate in toluene/ethanol for 12 h, yield 40%. For $\text{R} = \text{O}_2\text{CC}(\text{CH}_3)_3$, sodium pivalate in toluene/ethanol at room temperature for 5 h, yield 39%. (iii) Allylmagnesium chloride in THF at room temperature, yield 41%.

In conclusion, we have described an improved synthesis of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ and used it to develop the chemistry of the $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})(\eta\text{-allyl})]$ moiety. The new compounds and their proposed structures are shown in Scheme 2. Generally it is found that the chemistry of $[\text{Mo}(\eta\text{-}2,6\text{-lutidine})_2]$ is similar to that of $[\text{Mo}(\eta\text{-toluene})_2]$ but the $\eta\text{-lutidine}$ compounds are more labile and substitution occurs under milder conditions.

3. Experimental

All preparations and manipulations were carried out under an inert atmosphere of dinitrogen using either standard Schlenk techniques or a dry box, unless otherwise stated. All solvents were thoroughly deoxygenated before use either by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through the solvent for approximately 15 min. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled over sodium (toluene), sodium/potassium alloy and benzophenone (benzene), sodium and benzophenone (diethyl ether, THF, diglyme), or calcium hydride (pentane, petroleum ether (b.p. $40\text{--}60^\circ\text{C}$), hep-

tane, dichloromethane) under a slow continuous stream of dinitrogen. Predeuterated solvents for NMR spectroscopy were deoxygenated and then dried over calcium hydride (dichloromethane) or potassium (benzene and toluene). Activated, neutral, Brockmann I, standard grade, ca. 150 mesh alumina (Al_2O_3) was used for chromatography and deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Celite 545 filtration aid (Koch-Light) was pre-dried at 140°C and similarly deoxygenated before use.

^1H , ^{13}C and ^{31}P NMR spectra were recorded using a Bruker AM 300 (^1H 300 MHz, ^{13}C 75.5 MHz, ^{31}P 121.6 MHz). Spectra were referenced internally using residual protio solvent resonances (^1H and ^{13}C) relative to tetramethylsilane ($\delta = 0$ ppm) or externally using trimethylphosphate in D_2O (^{31}P). All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, relative integration and assignment). Electron impact mass spectra were recorded on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectrometry Services Ltd. Fast atom bombardment (FAB) mass spectra were obtained by the EPSRC Mass Spectrometry Service Centre at University College of Swansea under the supervision of Dr. J.A. Ballantine. IR spectra were recorded on a Perkin-Elmer 1510 FT interferometer. Elemental analyses were performed by the Oxford Analytical Laboratory.

3.1. Synthesis of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$

A modification of a previously published method [7] was used. Molybdenum metal (2.93 g, 30.5 mmol) and pure 2,6-lutidine (200 ml) were co-condensed onto the surface of a glass bell-jar which was cooled by liquid nitrogen [18]. An orange-brown matrix developed over a 6 h period. The matrix was allowed to warm to room temperature and was washed from the reaction vessel using light petroleum (1.5 l). Since the complex $[\text{Mo}(2,6\text{-lutidine})_2]$ is sensitive towards thermal decomposition, purification by sublimation was disfavoured and work-up procedures including filtrations were carried out at low temperatures. The petroleum ether extract was filtered immediately after the extraction through a bed of Celite at -50°C . This freed the mixture from unreacted molybdenum metal which is known to catalyse the decomposition of the complex. The clear orange-brown filtrate was evaporated to dryness under reduced pressure, extracted into petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) (500 ml) and the extract was filtered a second time through a bed of Celite at -50°C . The second filtration was necessary to remove insoluble residues and the last traces of unreacted metal. The orange filtrate was concentrated to 200 ml and cooled to

-80°C to give orange-brown, needle-shaped crystals. Yield 3.7 g (39%).

3.2. Synthesis of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ (**1**)

A solution of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$ (2.97 g, 9.57 mmol) in toluene (150 ml) was treated with an excess of allyl chloride (28.17 g, 368 mmol) at -30°C . The initial dark orange reaction mixture turned purple after warming to room temperature and was left stirring for an additional 48 h. The resulting mixture was evaporated to dryness, extracted into 300 ml warm toluene and crystallised at -20°C to yield black-purple crystals. Yield 1.2 g (45%).

3.3. Synthesis of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)(\eta^2\text{-O}_2\text{CCH}_3)]$ (**2**)

The complex $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ (70 mg, 0.13 mmol) and sodium acetate (20.5 mg, 0.25 mmol) were suspended in a 1:1 mixture of toluene:ethanol (50 ml) and left stirring for 12 h. The resulting purple solution was evaporated to dryness, extracted into petroleum ether (b.p. $40\text{--}60^\circ\text{C}$) and crystallised at -80°C to give black-purple crystals. Yield 30 mg (40%). Crucial to the success of this synthesis is the use of the mixed solvent system, toluene/ethanol. If ethanol alone is used as the solvent then higher temperatures are needed to dissolve the dimer **1**. This results in the decomposition of the sensitive product. The presence of toluene in the reaction mixture increases the solubility of the dimer **1** and allows the reaction to proceed at room temperature.

3.4. Synthesis of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)\text{O}_2\text{C}(\text{CH}_3)_3]$ (**3**)

A purple suspension of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ (170 mg, 0.30 mmol) in a 1:1 mixture of toluene:ethanol (40 ml) was treated with solid sodium pivalate (75 mg, 0.60 mmol) and the mixture was stirred for 5 h. The volatiles of the reaction mixture were evaporated under reduced pressure and the resulting residue was extracted into *n*-pentane. Crystallisation at -80°C yielded black-purple crystals. Yield 80 mg (39%).

3.5. Synthesis of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)_2]$ (**4**)

A purple suspension of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})(\eta\text{-C}_3\text{H}_5)\text{Cl}]_2$ (400 mg, 0.72 mmol) in THF (50 ml) was treated with a solution of allylmagnesium chloride (2 M, 0.8 ml, 1.6 mmol) in THF at room temperature. After stirring for 3 h the resulting red mixture was treated with 3 drops of distilled H_2O at -30°C in order

to hydrolyse the excess of Grignard reagent. The volatiles of the resulting suspension were evaporated under reduced pressure and the residue was extracted into *n*-pentane. Cooling to -80°C gave orange–brown crystals which were further purified by vacuum sublimation (130°C 10^5 Torr) to yield an orange, microcrystalline solid. Yield 170 mg (41%).

3.6. Preparation of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$

A solution of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$ (390 mg, 1.25 mmol) in light petroleum (b.p. $40\text{--}60^{\circ}\text{C}$) was treated with an excess of cyclopentadiene (3 ml). After refluxing the orange–brown mixture for 15 h the solvent was evaporated in vacuo. The residue was chromatographed at -25°C using a mixture of toluene : THF (3 : 2) as eluant. A yellow band was collected and the solvent was removed under reduced pressure. The residue was extracted into *n*-pentane and cooling gave yellow, needle crystals. Yield 150 mg (52%).

3.7. Preparation of $[\text{Mo}(\text{CH}_2=\text{CMeCMe}=\text{CH}_2)_3]$

A mixture of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$ (480 mg, 1.55 mmol) in 10 ml toluene and 2,3-dimethyl-1,3-butadiene (726 mg, 8.84 mmol) was heated for 15 h at 80°C . The resulting grey solution was evaporated to dryness, the residue was extracted into light petroleum (b.p. $40\text{--}60^{\circ}\text{C}$) and the extract was filtered through a bed of Celite. The solvent was removed from the filtrate under reduced pressure giving a white microcrystalline powder. This was extracted into pentane and the solution was cooled to -80°C giving white–yellow crystals. Yield 400 mg (76%).

3.8. Preparation of hexakis(isocyanide)molybdenum complexes $[\text{Mo}(\text{CNR})_6]$

The compound $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$ (360 mg, 1.16 mmol) was treated with *tert*-butyl isocyanide (735 mg, 8.84 mmol) in 40 ml acetonitrile at 0°C . After 4 h the solution was warmed to 40°C and stirred for an additional 15 h. The dark orange reaction mixture was evaporated to dryness, the residue was extracted into a mixture of Et_2O : *n*-pentane (1 : 1) and the extract was filtered through a bed of Celite at -50°C . The volatiles were removed from the filtrate under reduced pressure. The residue was extracted into pentane and cooling to -80°C gave orange crystals of $[\text{Mo}(\text{}^t\text{BuNC})_6]$. Yield 500 mg (72%). The compounds $[\text{Mo}(\text{}^i\text{PrNC})_6]$ and $[\text{Mo}(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_6]$ [37] were prepared in a similar manner, giving similar yields.

3.9. Cyclisation of but-2-yne to $[\text{C}_6(\text{CH}_3)_6]$

A solution of $[\text{Mo}(\eta\text{-NC}_5\text{H}_3\text{Me}_2\text{-2,6})_2]$ (210 mg, 0.68 mmol) in 20 ml acetonitrile and 2-butyne (345.5

mg, 6.4 mmol) was stirred at room temperature for 15 h. The solvent was removed under reduced pressure and the residue was extracted into pentane. The extract was filtered through a bed of Celite at -50°C and the solvent was removed from the filtrate under reduced pressure. The residue was crystallised from pentane at -80°C to give silver-coloured crystals. Yield 55 mg (50%).

3.10. Crystal structure determination of 1

Crystal data. $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{Mo}_2\text{N}_2$, $M = 559.24$, triclinic, $a = 9.291(2)$, $b = 10.560(3)$, $c = 11.332(5)$ Å, $\alpha = 82.42(3)$, $\beta = 83.98(2)$, $\gamma = 79.49(2)^{\circ}$, $U = 1080.2(6)$ Å³ (by the least-squares refinement of the setting angles for 24 automatically centred reflections), space group $P\bar{1}$, $Z = 2$, $D_c = 1.72$ g cm⁻³, $F(000) = 560$, $\mu = 13.88$ cm⁻¹. Crystals dimensions $0.22 \times 0.35 \times 0.38$ mm³.

Data collection and processing. CAD4 diffractometer, ω - 2θ mode with scan width $0.88 + 0.35 \tan \theta$, ω scan speed $1.5\text{--}10.1^{\circ}$ min⁻¹, graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å); 4872 reflections were measured ($1.0 < \theta < 26^{\circ}$, $-h, h, -k, k, -l, l$), 4228 unique (merging $R = 0.016$), giving 3695 with $I > 3\sigma(I)$. Linear and approximate isotopic crystal decay, ca. 24% corrected during processing.

Structural analysis and refinement. Direct methods, full-matrix least-squares refinement with all non-hydrogens atoms in anisotropic approximation (235 variables, observations/variables = 15.7). All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with fixed positional and thermal parameters. The Chebyshev weighting scheme [41] with parameters 18.5, -3.5 , 15.4 was applied. Corrections for Lorentz and polarization effects, as well as empirical correction for absorption [42], were applied. Anomalous-dispersion contributions were included in the calculated structure factors. Final R and R' values were 0.040 and 0.048. Maximum and minimum peaks in the final difference synthesis were 1.11 and -1.32 eÅ⁻³. Crystallographic calculations were carried out using the CRYSTALS [43] program package on a Micro VAX 3800 computer. Neutral atom scattering factors were taken from the usual sources [44]. Fractional atomic coordinates are presented in Table 2. Additional material is available from the Cambridge Crystallographic Data Centre, comprising thermal parameters and remaining bond lengths and angles.

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