

Bis[hydrazido(2-)] and related complexes of molybdenum(VI): towards alkene-metathesis catalysts based on hydrazido(2-) ligation

Jonathan R. Dilworth,^{*,a} Vernon C. Gibson,^{*,b} Canzhong Lu,^a John R. Miller,^a Carl Redshaw^b and Yifan Zheng^a

^a Department of Biological and Chemical Sciences, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

^b Department of Chemistry, Imperial College, London SW7 2AY, UK

The complex $[\text{Mo}(\text{NBu})_2\text{Cl}_2(\text{dme})]$ ($\text{dme} = 1,2\text{-dimethoxyethane}$) underwent an imide-ligand exchange reaction with an excess of 1,1-diphenylhydrazine hydrochloride in refluxing dme to give the bis[hydrazido(2-)] complex $[\text{MoCl}_2(\text{NNPh}_2)_2(\text{dme})]$ **1**. Reaction of **1** with an excess of PMe_3 in CH_2Cl_2 gave $[\text{MoCl}_2(\text{NNPh}_2)_2(\text{PMe}_3)_2]$ **2**. Treatment of $\text{Na}_2[\text{MoO}_4]$ with 2 molar equivalents of $\text{Ph}_2\text{NNH}_2\cdot\text{HCl}$ in the presence of NEt_3 and SiMe_3Cl in refluxing dme afforded the salt $[\text{NHEt}_3][\text{MoCl}_4(\text{NNPh}_2)(\text{NHNPh}_2)]$ **3**. The crystal structures of **1-3** have been determined; all possess octahedral geometries with unidentate hydrazido groups. The hydrazido(2-) Mo-N bond distances vary from 1.749(2) and 1.771(2) Å in **1**, to 1.793(3) in **2** and 1.748(2) Å in **3**, with no simple correlation with the Mo-N_α-N_β angle. The anionic component of **3** contains a bent hydrazide(1-) ligand (Mo-N-N 136.0°) and a linear hydrazido(2-) group (Mo-N-N 174.4°).

Imide ligands play a central role in the stabilization of well-defined metathesis catalysts of molybdenum,¹ tungsten² and rhenium.³ The four-co-ordinate molybdenum complexes $[\text{Mo}(\text{NC}_6\text{H}_3\text{Pr}^i\text{-}2,6)(\text{CHCMe}_2\text{Ph})(\text{OR})_2]$ [$\text{R} = \text{CMe}_3$, $\text{CMe}_2(\text{CF}_3)$ or $\text{CMe}(\text{CF}_3)_2$] in particular have found widespread application in the controlled synthesis of polymers *via* ring-opening metathesis polymerization.⁴ In view of the close iso-electronic relationship between the hydrazido(2-) ligand and the imido (NR) group, we have embarked upon a programme of study aimed at exploring the potential of hydrazido ligands for stabilizing a new family of well defined metathesis catalysts. Here, we report the synthesis, characterization and crystal structures of several important precursors.

Results and Discussion

We have recently shown that the complex $[\text{MoCl}_2(\text{NBu})_2(\text{dme})]$ ($\text{dme} = 1,2\text{-dimethoxyethane}$) undergoes imide ligand exchange upon treatment with anilines in dme at 70 °C.⁵ This synthetic procedure is quite general and we show here that it can be extended to the synthesis of hydrazido(2-) complexes by treatment of bis(imido)molybdenum precursors with the hydrochloride salt of diphenylhydrazine.

The reaction of $[\text{MoCl}_2(\text{NBu})_2(\text{dme})]$ with $\text{Ph}_2\text{NNH}_2\cdot\text{HCl}$ (2 equivalents) in refluxing dme (*ca.* 2 h) readily gives multigram quantities of $[\text{MoCl}_2(\text{NNPh}_2)_2(\text{dme})]$ **1** as an orange solid. Complex **1** shows a single ν_{NN} stretch at 1586 cm^{-1} . Crystals suitable for an X-ray analysis were grown from dme at -20 °C; the molecular structure is shown in Fig. 1. Bond lengths and angles are collected in Table 1 and crystal data are given in Table 4. The molecular geometry is distorted octahedral with *trans* chloride and *cis* hydrazido(2-) groups. The N(1)-Mo-N(3) angle is 105.56(10)°, the *cis* O(1)-Mo-Cl(2) and *trans* Cl(2)-Mo-Cl(1) angles are 85.99(5)° and 162.14(3)° respectively. The two hydrazido(2-) ligands are somewhat different: the Mo-N distances are short [Mo-N(1) 1.749(2), Mo-N(3) 1.771(2) Å], the former is the shortest reported to date for the *cis*-{M(NNR₂)₂} core.⁶ The corresponding Mo-N-N angles are 173.4(2) and 154.6(2)°. By comparison with analogous bis(imido)molybdenum complexes, the latter is likely to be at the lower limit for a linear hydrazido(2-) group.

Treatment of complex **1** with 1 equivalent of magnesium in

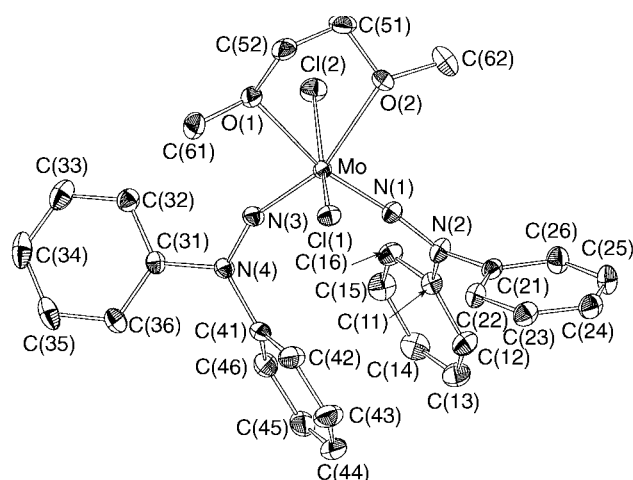


Fig. 1 Molecular structure of complex **1**, without H atoms and with key atoms labelled

thf in the presence of an excess of trimethylphosphine afforded orange crystalline $[\text{MoCl}_2(\text{NNPh}_2)_2(\text{PMe}_3)_2]$ **2**. Room-temperature NMR data reveal a virtually coupled triplet centred at δ 1.55 in the ¹H NMR spectrum and a singlet in the ³¹P NMR spectrum (δ 5.92) consistent with a structure in which the two phosphines are equivalent. Crystals of **2** suitable for a structure determination were grown by diffusion of heptane into a saturated CH_2Cl_2 solution. Fig. 2 shows the *cis* chloride, *trans* phosphine pseudo-octahedral geometry of **2**. The crystal data are given in Table 4 and selected bond lengths and angles are in Table 2. The molecules lie on crystallographic two-fold axes. The Mo-N separation of 1.793(3) Å and the associated Mo-N(1)-N(2) angle of 175.2(2)° are consistent with linear hydrazido(2-) units.

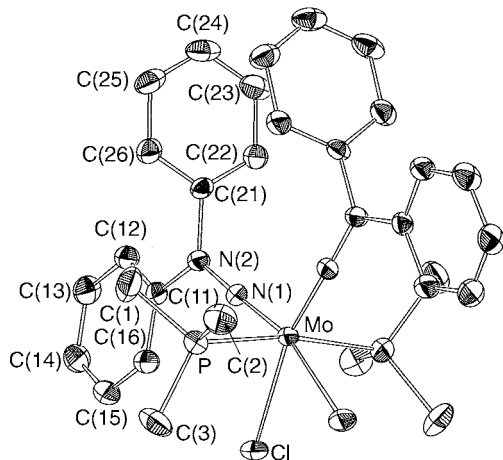
Attempts to isolate complex **1** by interaction of $\text{Na}_2[\text{MoO}_4]$ with $\text{Ph}_2\text{NNH}_2\cdot\text{HCl}$ in the presence of NEt_3 and SiMe_3Cl in refluxing dme led, after work-up, to a diamagnetic purple crystalline solid. Infrared data showed a N-H stretch at 3208 cm^{-1} and a strong ν_{NN} stretch at 1585 cm^{-1} , while the ¹H NMR spectrum contained resonances at δ *ca.* 8.2 (br) and *ca.* 12.9 (sharp) due to two different nitrogen-bound hydrogens. Analytical data

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mo–N(1)	1.749(2)	Mo–N(3)	1.771(2)
Mo–O(1)	2.322(2)	Mo–O(2)	2.331(2)
Mo–Cl(2)	2.4380(9)	Mo–Cl(1)	2.4451(9)
N(1)–N(2)	1.324(3)	N(2)–C(11)	1.430(3)
N(2)–C(21)	1.435(3)	N(3)–N(4)	1.326(3)
N(4)–C(31)	1.421(3)	N(4)–C(41)	1.440(3)
N(1)–Mo–N(3)	105.56(10)	N(1)–Mo–O(1)	164.13(8)
N(3)–Mo–O(1)	89.75(9)	N(1)–Mo–O(2)	94.46(9)
N(3)–Mo–O(2)	159.68(9)	O(1)–Mo–O(2)	70.60(7)
N(1)–Mo–Cl(2)	97.19(7)	N(3)–Mo–Cl(2)	92.88(8)
O(1)–Mo–Cl(2)	85.99(5)	O(2)–Mo–Cl(2)	80.98(6)
N(1)–Mo–Cl(1)	94.23(7)	N(3)–Mo–Cl(1)	97.23(8)
O(1)–Mo–Cl(1)	79.40(5)	O(2)–Mo–Cl(1)	84.49(5)
Cl(2)–Mo–Cl(1)	162.14(3)	N(2)–N(1)–Mo	173.4(2)
N(1)–N(2)–C(11)	120.0(2)	N(1)–N(2)–C(21)	116.3(2)
C(11)–N(2)–C(21)	122.2(2)	N(4)–N(3)–Mo	154.6(2)
N(3)–N(4)–C(31)	118.3(2)	N(3)–N(4)–C(41)	118.6(2)
C(31)–N(4)–C(41)	122.6(2)		

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

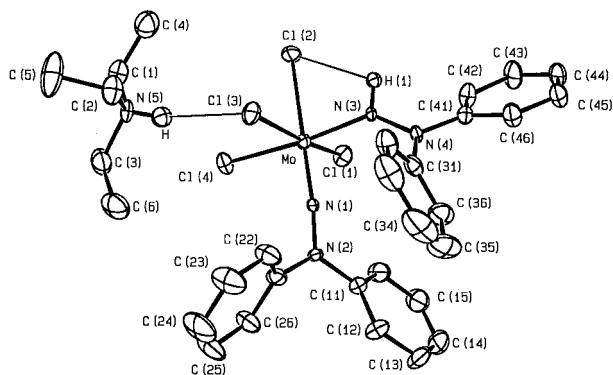
Mo–N(1)	1.793(3)	P–C(3)	1.811(4)
Mo–P	2.5141(12)	N(1)–N(2)	1.306(4)
Mo–Cl	2.5625(11)	N(2)–C(11)	1.432(4)
P–C(2)	1.805(5)	N(2)–C(21)	1.450(4)
P–C(1)	1.810(4)		
N(1)–Mo–N(1 [†])	103.6(2)	P–Mo–Cl	90.42(4)
N(1)–Mo–P	92.59(9)	Cl [†] –Mo–Cl	76.76(5)
N(1)–Mo–P [†]	93.02(9)	N(2)–N(1)–Mo	175.2(2)
P–Mo–P [†]	170.92(5)	N(1)–N(2)–C(11)	121.4(3)
N(1)–Mo–Cl [†]	165.80(9)	N(1)–N(2)–C(21)	119.7(3)
P–Mo–Cl [†]	82.45(4)	C(11)–N(2)–C(21)	118.8(3)
N(1)–Mo–Cl	90.03(9)		

Symmetry relation: $I - x, y, -z + \frac{1}{2}$.**Fig. 2** Molecular structure of complex **2**, without H atoms and with key atoms labelled

were consistent with the stoichiometry $[\text{NHET}_3][\text{MoCl}_4(\text{NNPh}_2)(\text{NHNPh}_2)]$ **3**. The structure was determined by X-ray diffraction and a view of the ion pair is shown in Fig. 3. Selected bond lengths and angles and crystal data are given in Tables 3 and 4 respectively. The structure contains a pseudo-octahedral anionic molybdenum fragment with *cis* NNPh₂ units bound in two different ways. One has the linear Mo–N–N arrangement, with short M–N and N–N bonds and a trigonal-planar arrangement of the N(2) atom, and may be described as a ‘hydrazide(2–)’ ligand, or better related to its geometry, as an ‘isodiazene’.⁷ The other ligand is notably different, with a Mo–N–N angle of 136.0(2)°, a Mo–N distance of 1.958(2) Å and a N–N distance of 1.358(3) Å. Atom N(4) has a trigonal-

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Mo–Cl(1)	2.4448(7)	Mo–Cl(2)	2.4788(7)
Mo–Cl(3)	2.4213(7)	Mo–Cl(4)	2.4641(7)
Mo–N(1)	1.748(2)	Mo–N(3)	1.958(2)
N(1)–N(2)	1.304(3)	N(3)–N(4)	1.358(3)
H–Cl(3)	2.579(1)	H(1)–Cl(2)	2.573(1)
Cl(1)–Mo–Cl(2)	84.51(3)	C(1)–Mo–Cl(3)	169.31(3)
Cl(1)–Mo–Cl(4)	85.73(3)	Cl(1)–Mo–N(1)	94.82(7)
Cl(1)–Mo–N(3)	86.43(7)	Cl(2)–Mo–Cl(3)	86.07(3)
Cl(2)–Mo–Cl(4)	87.70(3)	Cl(2)–Mo–N(1)	179.32(7)
Cl(2)–Mo–N(3)	82.97(6)	Cl(3)–Mo–Cl(4)	88.85(3)
Cl(3)–Mo–N(1)	94.58(7)	Cl(3)–Mo–N(3)	97.43(7)
Cl(4)–Mo–N(1)	92.10(7)	Cl(4)–Mo–N(3)	168.34(7)
N(1)–Mo–N(3)	97.15(9)	Mo–N(1)–N(2)	174.4(2)
N(1)–N(2)–C(11)	119.8(2)	N(1)–N(2)–C(21)	118.8(2)
C(11)–N(2)–C(21)	121.3(2)	Mo–N(3)–N(4)	136.0(2)
N(3)–N(4)–C(31)	118.5(2)	N(3)–N(4)–C(41)	119.0(2)
C(31)–N(4)–C(41)	120.7(2)		

**Fig. 3** Molecular structure of complex **3**, without H atoms and with key atoms labelled

planar environment. The atoms Mo, Cl(2), N(1), N(2), N(3) and N(4) are virtually coplanar [maximum deviation through the best plane 0.026 Å for N(3)], and the Mo–N(3)–N(4) unit bends towards the Mo–N(1)–N(2) fragment most likely in order to accommodate a bond to a hydrogen atom (see below).

In order to account for the diamagnetism of the compound and the presence of N–H stretching frequencies in the infrared spectrum, the anion has to contain a hydrogen atom not detected by the X-rays but attached to a nitrogen atom; we have placed this hydrogen atom on the first N atom, N(3), of the bent NNPh₂ ligand, which would normally imply its description as a ‘*N,N*-diphenylhydrazido(1–)’ group; the internal geometry, particularly the coplanarity of N(4) with N(3), C(31) and C(41), suggests however that it could also be described as a protonated diphenylisodiazene. The calculated position of H(1) places it 2.57 Å from Cl(2), consistent with an internal hydrogen bond. The C and N atoms of the triethylammonium cation are very well defined in the structure determination and the N-bound hydrogen atom was placed in a calculated position 0.9 Å from the N atom. This position indicates that it is hydrogen bonded to Cl(3) and Cl(4), with H···Cl distances of 2.58 and 2.72 Å respectively; thus in the solid state **3** is an ion pair.

The internal geometry of the N_αN_βPh₂ units in complexes **1–3** and in many other complexes of this type, supports the suggestion⁷ that these ligands are described more accurately as ‘isodiazene’ than as ‘hydrazido(2–)’. The coplanarity of the three bonds to N_β is a constant theme, pointing to N_β being conjugated. The N_α–N_β bond distances are intermediate between those for single and double bonds⁸ (single bond, 1.40–1.46; double bond, 1.22–1.26 Å). Even in the protonated ligand of **3**, N_β is trigonal planar and the N–N distance is only 1.358(3) Å. Isoelectronic with ketones, isodiazenes would be

Table 4 Crystal structure determinations for complexes **1–3**

	1	2	3
Empirical formula	C ₂₈ H ₃₀ Cl ₂ MoN ₄ O ₂	C ₁₅ H ₁₉ ClMo _{0.5} N ₂ P	C ₃₀ H ₃₇ Cl ₄ MoN ₅
<i>M</i>	621.40	341.71	705.4
Crystal size/mm	0.25 × 0.5 × 0.56	0.39 × 0.72 × 0.83	0.2 × 0.3 × 0.7
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2₁/n</i>	<i>Pbcn</i>	<i>P2₁/n</i>
<i>a</i> /Å	15.981(5)	9.278(3)	12.1775(36)
<i>b</i> /Å	9.984(2)	21.692(7)	10.6011(9)
<i>c</i> /Å	17.688(5)	16.097(9)	26.4756(97)
β/°	97.78(2)		99.44(2)
<i>U</i> /Å ³	2796.1(13)	3240(2)	3371.5(1.6)
<i>Z</i>	4	8	4
<i>D_c</i> /g cm ⁻³	1.476	1.401	1.390
μ(Mo-Kα)/mm ⁻¹	0.692	0.694	0.725
<i>F</i> (000)	1272	1408	1448
<i>T</i> /K	291	291	291
2θ Range/°	1.61–25.02	1.88–24.98	1.5–25.0
<i>hkl</i> Range	0–18, 0–11, –21 to 20	0–11, –25 to 19, 0–19	0–14, –12–0, –31 to 31
Reflections collected	5096	5419	6620
Independent reflections (<i>R</i> _{int})	4910 (0.0121)	2827 (0.0414)	6305 (0.013)
Reflections observed	4004 [<i>I</i> > 2 σ(<i>I</i>)]	2240 [<i>I</i> > 2 σ(<i>I</i>)]	5016 [<i>I</i> > 1.5 σ(<i>I</i>)]
Absorption correction <i>T</i> _{max} , <i>T</i> _{min}	1.00, 0.92	1.00, 0.857	1.00, 0.93
Weighting scheme, <i>w</i>	1/[σ ² (<i>F</i> _o ²) + (0.0299 <i>P</i>) ² + 1.4945 <i>P</i>], <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	1/[σ ² (<i>F</i> _o ²) + (0.0475 <i>P</i>) ² + 0.9756 <i>P</i>], <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3	1/[σ ² (<i>F</i> _o ²) + (0.02 <i>F</i> _o) ²]
Data, restraints, parameters	4910, 0, 454	2827, 0, 177	5016, 0, 361
<i>R</i> 1, <i>wR</i> 2 ^a	0.0267, 0.0678	0.0475, 0.1033	0.034, 0.046 ^b
<i>S</i> ^c	1.193	1.251	1.80 ^d

^a $R1 = \sum |F_o - F_c| / \sum |F_o|$, $wR2 = \{[\sum w(F_o)^2 - (F_c)^2] / \sum w(F_o)^2\}^{1/2}$. ^b $wR = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$. ^c $[\sum w(F_o)^2 - (F_c)^2] / (n - p)$ where *n* = number of reflections and *p* = total number of parameters. ^d $[\sum w(F_o - F_c)^2 / (n - p)]^{1/2}$.

expected to have two N_α lone pairs in the N_αN_βC₂ plane (alternatively regarded as a combination of a σ lone pair on the NN vector and a π pair in the NNC₂ plane); N_α would be expected to be more basic, and therefore a better donor, than the O atom of a ketone as it carries an effective negative charge. We suggest that the difference between the isodiazenes and hydrazido(2–) descriptions is real because hydrazido(2–) complexes should have pyramidally bound N_β atoms and distinctly longer N–N distances. Assignment of the ligands as electronically neutral isodiazenes implies that they are derived from hydrazines by oxidation rather than *via* reductive deprotonation.

The Mo–N distances in all the complexes suggest multiple-bond character except for the protonated ligand of **3**, where the distance of 1.958(2) Å is readily assigned to a single bond; this is also consistent with the Mo–N_α–N_β angle of 136.0(2)°, *i.e.* one of the N_α lone pairs co-ordinates to Mo, the other to H⁺. Among the unprotonated ligands there is no correlation between bond distances and the Mo–N_α–N_β angle.

The derivative chemistry of these hydrazido(2–) complexes is under development and will be reported at a future date.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the micro-analytical services of the Department of Chemistry at Durham and Medac Ltd. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (¹H) and 162.0 MHz (³¹P, referenced to dilute aqueous H₃PO₄, δ 0) and a Bruker DRX 300 machine at 75.0 MHz (¹³C); chemical shifts are referenced to the residual protio impurity of the deuterated solvent. The IR spectra (Nujol mulls, CsI or KBr windows) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. The complex [Mo(NBu)₂Cl₂·dme]⁹ was prepared by the literature method. All other chemicals were obtained commercially and used as received unless stated otherwise.

Syntheses

[MoCl₂(NNPh)₂(dme)] 1. The complex [MoCl₂(NBu)₂(dme)] (1.0 g, 2.5 mmol) and Ph₂NNH₂·HCl (1.1 g, 5.0 mmol) in dme (30 cm³) were refluxed for 12 h. After filtration and concentration (to *ca.* 20 cm³) deep orange prisms of the product were deposited on standing at room temperature. Yield 0.48 g, 31%. Further crops can be obtained from the mother-liquor; overall yield 70% (Found: C, 54.1; H, 4.9; N, 9.1. C₂₈H₃₀Cl₂MoN₄O₂ requires C, 54.1; H, 4.9; N, 9.0%). IR: 2711w, 2600w, 2500w, 2078w, 1586s, 1511w, 1328w, 1298m, 1262s, 1158s, 1087 (br) bs, 1043s, 922w, 862s, 848m, 801s, 760s, 692s, 654w, 634m, 530w and 494m cm⁻¹. NMR (CDCl₃): ¹H (400 MHz), δ 7.31 (m, 8 H, *o*-H), 7.13 (m, 8 H, *m*-H), 6.94 (m, 4 H, *p*-H), 3.96 (s, 4 H, CH₂) and 3.52 (s, 6 H, CH₃); ¹³C-{¹H} (75 MHz), δ 142.77, 128.39, 125.58, 120.87, 71.01 (s, CH₂ of dme) and 63.86 (s, CH₃ of dme).

[MoCl₂(NNPh)₂(PMe₃)₂] 2. Trimethylphosphine (0.21 cm³, 2.0 mmol) was added to [MoCl₂(NNPh)₂(dme)] (0.5 g, 0.8 mmol) and Mg (0.02 g, 0.83 mmol) in thf (30 cm³). After stirring for 12 h, the volatiles were removed under reduced pressure and the residue was taken up in CH₂Cl₂ (20 cm³). Diffusion of heptane into CH₂Cl₂ gave orange prisms. Yield 0.4 g, 82% (Found: C, 52.5; H, 5.7; N, 8.0. C₃₀H₃₈MoN₄P₂·CH₂Cl₂ requires C, 53.3; H, 5.8; N, 8.0%). IR: 1587w, 1338w, 1294m, 1250w, 1163w, 948m, 755w, 692w, 497w, 476w, 358w 330w, 314w, 294m and 251vs cm⁻¹. NMR (CDCl₃): ¹H (400 MHz), δ 7.19 (m, 16 H, *o,m*-H), 7.06 (tt, 4 H, *J* = 6.8, *J* = 1.6, *p*-H) and 1.55 (t, 18 H, *J* = 4.0 Hz, PMe₃); ¹³C-{¹H} (75 MHz), δ 146.39, 131.64, 128.66, 124.29, 17.72 (t, *J* = 13.0 Hz, PMe₃); ³¹P (162 MHz), δ 5.92 (s).

[NHET₃[MoCl₄(NNPh)₂(NHNPh₂)] 3. Triethylamine (13.6 cm³, 97.6 mmol) and SiMe₃Cl (24.5 cm³, 193.0 mmol) were added to Na₂[MoO₄] (5.0 g, 24.3 mmol) and Ph₂NNH₂·HCl (10.72 g, 48.5 mmol) in dme (*ca.* 20 cm³). After refluxing for 12 h the suspension was filtered whilst hot. Purple lustrous crystals of complex **3** were deposited on standing at room temperature (2.81 g, 16.4% isolated yield) (Found: C, 51.2; H, 5.3; N, 9.8.

C₃₀H₃₇Cl₄MoN₅ requires C, 51.0; H, 5.3; N, 9.9%. IR: 3208w, 1585m, 1460s, 1377s, 1261s, 1154m, 806m, 758s, 734m, 693s, 654s, 610m, 522w and 496m cm⁻¹. NMR (CDCl₃): ¹H (400 MHz), δ 12.94 (s, 1 H, NHNPh₂), 8.29 (br s, 1 H, Et₃NH), 7.17–7.05 (m, 18 H, *o,m*-H), 6.89 (t, 2 H, *J* = 7.4, *p*-H), 3.21 (m, 6 H, CH₂CH₃) and 1.31 (t, 9 H, *J* = 7.2 Hz, CH₂CH₃); ¹³C-{¹H} (75 MHz), δ 144.48, 137.98, 129.49, 128.96, 127.89, 127.36, 124.02, 122.57, 47.12 and 9.13.

X-Ray crystallography

Numerical data are summarised in Table 4.

Data collection. Intensity data were collected on an Enraf-Nonius diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $20 < \theta < 25^\circ$ for complex **1**, $20 < \theta < 22^\circ$ for **2** and $22 < \theta < 25^\circ$ for **3**. The data were collected in the ω - 2θ scan mode and three standard reflections were measured every 3 h of exposure; 4.5 (for **1**), 0 (**2**) and 6.0% (**3**) loss of intensity was observed which was linearly corrected during processing. Three standard reflections were measured every 200 to check the crystal orientation. The data were corrected for Lorentz-polarization factors and an absorption correction was applied using ψ scans of nine reflections.

Structure analysis and refinement. Structures **1** and **2** were solved *via* direct methods (core atoms)¹⁰ and refined on F_o^2 by full-matrix least squares.¹¹ All non-hydrogen atoms were anisotropic. The hydrogen atoms were revealed by Fourier-difference synthesis and isotropically refined. The weighting scheme gave satisfactory agreement. Final *R* indices [$I > 2\sigma(I)$]: for **1**, *R*1 (on *F*) 0.0267, *wR*2 (on F^2) 0.0678; for **2**, 0.0475, 0.1033. Largest difference peak and hole: for **1**, 0.0245 and -0.447 ; for **2**, 0.679 and $-0.429 \text{ e \AA}^{-3}$. Maximum shift/e.s.d. was -0.212 (for **1**) and -0.001 (for **2**). Sources of scattering factors were as in ref. 11.

Structure **3** was solved by the Patterson heavy-atom method and refined on F_o by full-matrix least squares.¹² All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in calculated positions. Final *R* indices [$F_o > 3\sigma(F_o)$]: *R*1 (on *F*) 0.034, *R'* (on *F*) 0.046. Largest difference peak and

hole: 0.710 and $-0.229 \text{ e \AA}^{-3}$. The maximum shift/e.s.d. was < 0.01 .

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1977, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/293.

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