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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 [Mo(NBu^t)$_2$Cl$_2$(dme)] (dme = 1,2-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 [MoCl$_2$(NNPh$_2$)$_2$(dme)] **1**. Reaction of **1** with an excess of PMe$_3$ in CH$_2$Cl$_2$ gave [MoCl$_2$(NNPh$_2$)$_2$(PMe$_3$)$_2$] **2**. Treatment of Na$_2$[MoO$_4$] with 2 molar equivalents of Ph$_2$NNH$_2$·HCl in the presence of NEt$_3$ and SiMe$_3$Cl in refluxing dme afforded the salt [NHEt$_3$][MoCl$_4$(NNPh$_2$)(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$_\alpha$–N$_\beta$ 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] tungsten[2] and rhenium.[3] The four-co-ordinate molybdenum complexes [Mo(NC$_6$H$_3$Pr$^i_2$-2,6)(CHCMe$_2$Ph)(OR)$_2$] [R = CMe$_3$, CMe$_2$(CF$_3$) or CMe(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 isoelectronic relationship between the hydrazide(2−) ligand and the imido (NR) group, we have embarked upon a programme of study aimed at exploring the potential of hydrazide 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 [MoCl$_2$(NBu^t)$_2$(dme)] (dme = 1,2-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 [MoCl$_2$(NBu^t)$_2$(dme)] with Ph$_2$NNH$_2$·HCl (2 equivalents) in refluxing dme (*ca.* 2 h) readily gives multigram quantities of [MoCl$_2$(NNPh$_2$)$_2$(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 hydrazide(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(NNR$_2$)$_2$} 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.

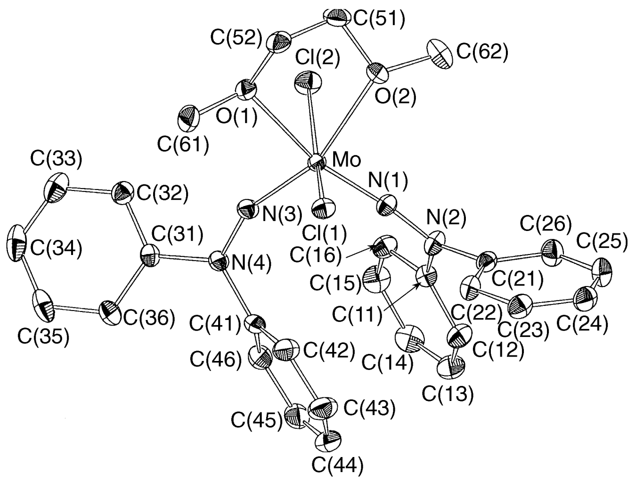

Fig. 1 Molecular structure of complex **1**, without H atoms and with key atoms labelled

Treatment of complex **1** with 1 equivalent of magnesium in thf in the presence of an excess of trimethylphosphine afforded orange crystalline [MoCl$_2$(NNPh$_2$)$_2$(PMe$_3$)$_2$] **2**. Room-temperature NMR data reveal a virtually coupled triplet centred at δ 1.55 in the ^{1}H NMR spectrum and a singlet in the ^{31}P 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$_2$Cl$_2$ 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 Na$_2$[MoO$_4$] with Ph$_2$NNH$_2$·HCl in the presence of NEt$_3$ and SiMe$_3$Cl 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 ^{1}H 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^{I})	103.6(2)	P–Mo–Cl	90.42(4)
N(1)–Mo–P	92.59(9)	Cl^{I}–Mo–Cl	76.76(5)
N(1)–Mo–P^{I}	93.02(9)	N(2)–N(1)–Mo	175.2(2)
P–Mo–P^{I}	170.92(5)	N(1)–N(2)–C(11)	121.4(3)
N(1)–Mo–Cl^{I}	165.80(9)	N(1)–N(2)–C(21)	119.7(3)
P–Mo–Cl^{I}	82.45(4)	C(11)–N(2)–C(21)	118.8(3)
N(1)–Mo–Cl	90.03(9)		

Symmetry relation: I $-x, y, -z + \frac{1}{2}$.

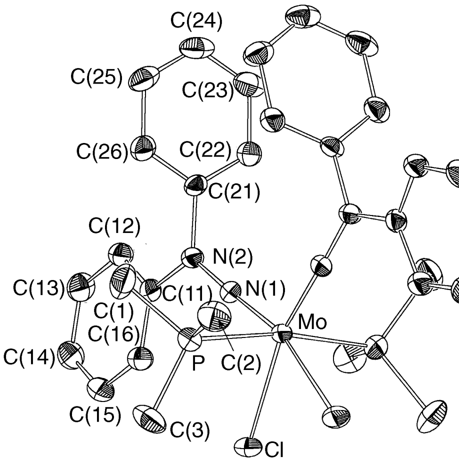

Fig. 2 Molecular structure of complex **2**, without H atoms and with key atoms labelled

were consistent with the stoichiometry [NHEt$_3$][MoCl$_4$(NNPh$_2$)(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* NNPh$_2$ 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-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).

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)		

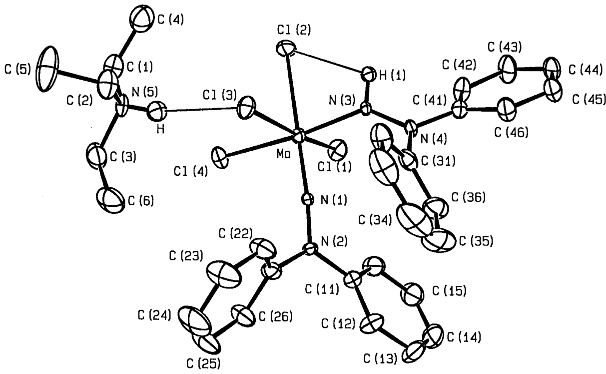

Fig. 3 Molecular structure of complex **3**, without H atoms and with key atoms labelled

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 NNPh$_2$ 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 $\cdots$ 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$_\alpha$N$_\beta$Ph$_2$ units in complexes **1**–**3** and in many other complexes of this type, supports the suggestion[7] that these ligands are described more accurately as 'isodiazene' than as 'hydrazido(2–)'. The coplanarity of the three bonds to N$_\beta$ is a constant theme, pointing to N$_\beta$ being conjugated. The N$_\alpha$–N$_\beta$ bond distances are intermediate between those for single and double bonds[8] (single bond, 1.40–1.46; double bond, 1.22–1.26 Å). Even in the protonated ligand of **3**, N$_\beta$ 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	$C_{28}H_{30}Cl_2MoN_4O_2$	$C_{15}H_{19}ClMo_{0.5}N_2P$	$C_{30}H_{37}Cl_4MoN_5$
M	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	$P2_1/n$	*Pbcn*	$P2_1/n$
a/Å	15.981(5)	9.278(3)	12.1775(36)
b/Å	9.984(2)	21.692(7)	10.6011(9)
c/Å	17.688(5)	16.097(9)	26.4756(97)
β/°	97.78(2)		99.44(2)
U/Å^3	2796.1(13)	3240(2)	3371.5(1.6)
Z	4	8	4
D_c/g cm^{-3}	1.476	1.401	1.390
μ(Mo-Kα)/mm^{-1}	0.692	0.694	0.725
F(000)	1272	1408	1448
T/K	291	291	291
2θ Range/°	1.61–25.02	1.88–24.98	1.5–25.0
hkl 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 (R_{int})	4910 (0.0121)	2827 (0.0414)	6305 (0.013)
Reflections observed	4004 [$I > 2\sigma(I)$]	2240 [$I > 2\sigma(I)$]	5016 [$I > 1.5\sigma(I)$]
Absorption correction T_{max}, T_{min}	1.00, 0.92	1.00, 0.857	1.00, 0.93
Weighting scheme, w	$1/[\sigma^2(F_o^2) + (0.0299P)^2 + 1.4945P]$, $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.9756P]$, $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o) + (0.02F_o)^2]$
Data, restraints, parameters	4910, 0, 454	2827, 0, 177	5016, 0, 361
$R1$, $wR2$[a]	0.0267, 0.0678	0.0475, 0.1033	0.034, 0.046[b]
S[c]	1.193	1.251	1.80[d]

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

expected to have two N_α lone pairs in the $N_\alpha N_\beta C_2$ plane (alternatively regarded as a combination of a σ lone pair on the NN vector and a π pair in the NNC_2 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 isodiazene 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 $Mo-N_\alpha-N_\beta$ 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 $Mo-N_\alpha-N_\beta$ 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 microanalytical 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 (^{1}H) and 162.0 MHz (^{31}P, referenced to dilute aqueous H_3PO_4, δ 0) and a Bruker DRX 300 machine at 75.0 MHz (^{13}C); chemical shifts are referenced to the residual protio impurity of the deuteriated solvent. The IR spectra (Nujol mulls, CsI or KBr windows) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. The complex $[Mo(NBu^t)_2Cl_2]\cdot dme$[9] was prepared by the literature method. All other chemicals were obtained commercially and used as received unless stated otherwise.

Syntheses

$[MoCl_2(NNPh_2)_2(dme)]$ 1. The complex $[MoCl_2(NBu^t)_2(dme)]$ (1.0 g, 2.5 mmol) and $Ph_2NNH_2\cdot HCl$ (1.1 g, 5.0 mmol) in dme (30 cm^3) were refluxed for 12 h. After filtration and concentration (to *ca.* 20 cm^3) 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. $C_{28}H_{30}Cl_2MoN_4O_2$ 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 ($CDCl_3$): ^{1}H (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, CH_2) and 3.52 (s, 6 H, CH_3); ^{13}C-{^{1}H} (75 MHz), δ 142.77, 128.39, 125.58, 120.87, 71.01 (s, CH_2 of dme) and 63.86 (s, CH_3 of dme).

$[MoCl_2(NNPh_2)_2(PMe_3)_2]$ 2. Trimethylphosphine (0.21 cm^3, 2.0 mmol) was added to $[MoCl_2(NNPh_2)_2(dme)]$ (0.5 g, 0.8 mmol) and Mg (0.02 g, 0.83 mmol) in thf (30 cm^3). After stirring for 12 h, the volatiles were removed under reduced pressure and the residue was taken up in CH_2Cl_2 (20 cm^3). Diffusion of heptane into CH_2Cl_2 gave orange prisms. Yield 0.4 g, 82% (Found: C, 52.5; H, 5.7; N, 8.0. $C_{30}H_{38}MoN_4P_2\cdot CH_2Cl_2$ 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 ($CDCl_3$): ^{1}H (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, PMe_3); ^{13}C-{^{1}H} (75 MHz), δ 146.39, 131.64, 128.66, 124.29, 17.72 (t, J = 13.0 Hz, PMe_3); ^{31}P (162 MHz), δ 5.92 (s).

$[NHEt_3][MoCl_4(NNPh_2)(NHNPh_2)]$ 3. Triethylamine (13.6 cm^3, 97.6 mmol) and $SiMe_3Cl$ (24.5 cm^3, 193.0 mmol) were added to $Na_2[MoO_4]$ (5.0 g, 24.3 mmol) and $Ph_2NNH_2\cdot HCl$ (10.72 g, 48.5 mmol) in dme (*ca.* 20 cm^3). 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.

$C_{30}H_{37}Cl_4MoN_5$ 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 ($CDCl_3$): ^1H (400 MHz), δ 12.94 (s, 1 H, $NHNPh_2$), 8.29 (br s, 1 H, Et_3NH), 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, CH_2CH_3) and 1.31 (t, 9 H, *J* = 7.2 Hz, CH_2CH_3); ^{13}C-{^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-Kα radiation ($\lambda = 0.710\,73$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $20 < \theta < 25°$ for complex **1**, $20 < \theta < 22°$ for **2** and $22 < \theta < 25°$ 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, *wR2* (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 e $Å^{-3}$. 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 e $Å^{-3}$. 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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