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Allyl complexes of molybdenum with Schiff base ligands. The crystal structures of $[MoCl(CO)_2\{N(C_6H_4\text{-}2\text{-}OMe){=}C(Me)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ and $[MoCl(CO)_2\{N(Me){=}C(Ph)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ are described

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Abstract

Treatment of the molybdenum tetracarbonyl complexes of $[Mo(CO)_4L_2]$ (L_2 = pyridyl amine Schiff base ligands) with allyl chloride in refluxing THF afforded η^3-allyl complexes $[MoCl(CO)_2L_2(\eta^3\text{-allyl})]$ (**1**–**9**). These complexes have been characterised by various techniques including ^{1}H-NMR, IR and FABMS spectroscopies and the single crystal X-ray structure determinations of the complexes $[MoCl(CO)_2\{N(C_6H_4\text{-}2\text{-}OMe){=}C(Me)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ (**3**) and $[MoCl(CO)_2\{N(Me){=}C(Ph)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ (**4**).

Keywords: Allyl; Carbonyl; Molybdenum; Pyridyl amine; Schiff base; X-ray structure

1. Introduction

The reactions of $[Mo(CO)_4L_2]$ (L_2 = phosphine and nitrogen donor ligands) with allyl halides are well known [1–11]. We have reported previously the preparation of $[M(CO)_4L_2]$ (M = Mo or W; L = pyridyl amine Schiff base). The *cis*-$[Mo(CO)_4L_2]$ complexes are prepared by treatment of *cis*-$[Mo(CO)_4(pip)_2]$ (pip = piperidine) with 2-acetyl or 2-benzoyl pyridine and the appropriate imine in refluxing *i*-PrOH [12,13].

2. Results and discussion

Allyl complexes of the type $[MoCl(CO)_2L_2(\eta^3\text{-R-allyl})]$, (**1**–**9**), ($L_2$ = pyridyl amine Schiff base, R = H, **1**-Me or **2**-Me) can be prepared successfully by the treatment of $[Mo(CO)_4L_2]$ (L_2 = pyridyl amine Schiff base) with an excess of the appropriate allyl halide in refluxing THF (Scheme 1). These complexes have been characterised by various techniques including ^{1}H-NMR, IR and FABMS spectroscopies and the single crystal X-ray structure determinations of the complexes **3** and **4**. Analogous reactions of $[W(CO)_4L_2]$ (L_2 = pyridyl amine Schiff base) with allyl halides were unsuccessful.

Treatment of complex $[MoCl(CO)_2(\{N(Me){=}C(Me)C_5H_4N\})(\eta^3\text{-}C_3H_5)]$ (**1**) with one equivalent of triphenylphosphine in the presence of potassium hexafluorophosphate in refluxing acetonitrile afforded the cationic complex $[Mo(CO)_2\{N(Me){=}C(Me)C_5H_4N\}(PPh_3)(\eta^3\text{-}C_3H_5)][PF_6]$ (**10**). Complex **10** is less soluble in common organic solvents and was characterised by IR, ^{1}H-NMR, ^{31}P-$\{^1$H$\}$ and FABMS spectroscopy. Complex **1** also reacted with potassium thiocyanate in acetone to form $[Mo(NCS)(CO)_2\{N(Me){=}C(Me)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ (**11**). The brown insoluble solid was characterised by IR, ^{1}H-NMR and FABMS spectroscopy.

The crystal structures of complexes **3** and **4** have been determined. The molecular structure of the complexes **3**

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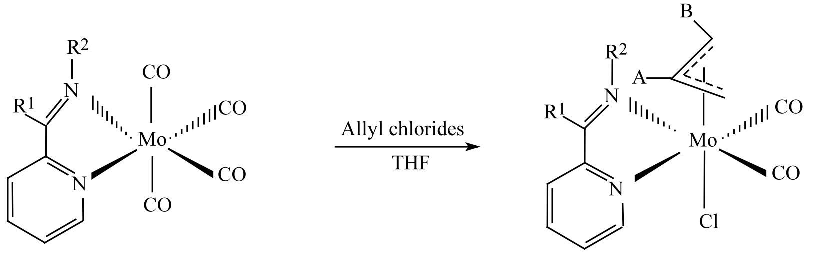

(1) -(9)

Complex No	R^1	R^2	A	B
(1)	Me	Me	H	H
(2)	Me	Ph	H	H
(3)	Me	Ph-2-OMe	H	H
(4)	Ph	Me	H	H
(5)	Ph	Ph	H	H
(6)	Me	Me	H	Me
(7)	Ph	Me	H	Me
(8)	Me	Me	Me	H
(9)	Ph	Me	Me	H

Scheme 1.

and **4** are shown in Figs. 1 and 2, which also give the crystallographic numbering scheme. Selected bond distances and angles are given in Tables 1 and 2. The complexes have a distorted octahedral arrangement of ligands around molybdenum. The central carbon of the allyl group is trans to the carbonyl ligands. The angles between the allyl group planes and the $Mo(CO)_2$ planes are 6.9 and 6.7°, respectively for **3** and **4**. The pyridyl amine Schiff base ligand planes lie 16.5 and 17.9° below the horizontal $Mo(CO)_2$ planes for the complexes **3** and **4**, respectively.

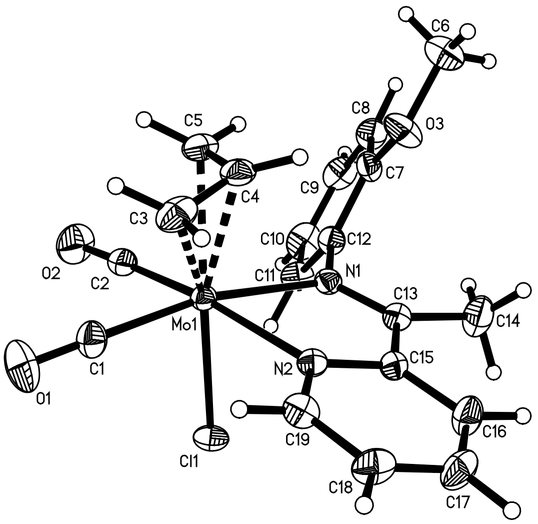

Fig. 1. Molecular structure of **3** showing the atom numbering scheme. Displacement parameters are shown at the 30% level.

The Mo–N(1) and Mo–N(2) [2.258(4) Å, 2.240(3) Å] distances in complex **3** are similar to those of the literature complexes $[Mo(NCS)(CO)_2(bipy)(\eta^3\text{-}C_3H_5)]$ (**12**) [2.256(7) Å, 2.189(7) Å] and $[Mo(NCS)(CO)_2(phen)(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]$ (**13**) [2.252(8) Å, 2.255(8) Å], respectively [8,9]. The Mo–N(1) and Mo–N(2) [2.243(3) Å, 2.233(3) Å] distances in complex **4** are similar to those of the literature complex $[Mo(CO)_4\{N(Me){=}C(Ph)C_5H_4N\}]$ [2.228(2) Å, 2.241(2) Å], respectively [12]. The central allyl carbon atom [2.203(5) Å] and [2.205(4) Å] is closer to the molybdenum atom than the two terminal carbon atoms [2.318(5) Å, 2.313(5) Å] and [2.320(5) Å, 2.319(4) Å] for the complexes **3** and **4**, respectively. The allylic inter-carbon angle **3** [115.4(5)°] and **4** [116.5(5)°] compare well with those of the complexes **12** [115.7(11)°] and **13** [111.5(1)°].

The room temperature ^{1}H-NMR spectra of all complexes are consistent with the structure. The ^{1}H-NMR spectrum of a typical η^3-allyl complex shows three signals for the allyl group from three sets of protons, central (H_c), *syn* (H_s) and *anti* (H_a). The *anti* protons appear as a doublet in the region 1.10–1.52 ppm ($J =$ 6.9–11.2 Hz), while the doublet due to the *syn* protons occur between 2.29 and 3.90 ppm ($J = 3.3$–6.6 Hz). The multiplet assigned to the central allylic proton appears in the range 2.93–3.84 ppm. However, complexes **1**, **3** and **4** show two sets of signals indicating the presence of

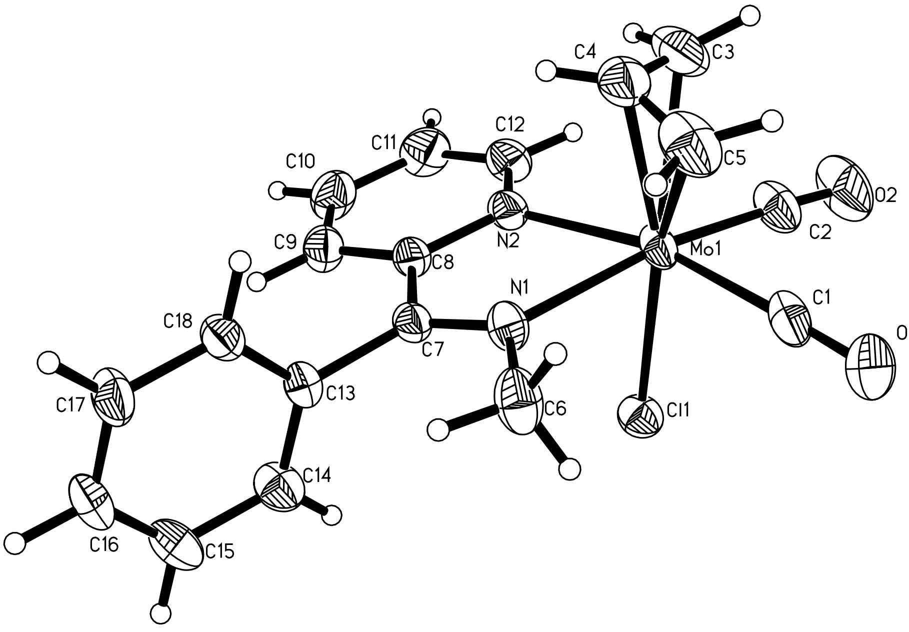

Fig. 2. Molecular structure of **4** showing the atom numbering scheme. Displacement parameters are shown at the 30% level.

Table 1
Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parenthesis for **3**

Bond lengths			
Mo–C(1)	1.959(5)	N(1)–C(13)	1.285(5)
Mo–C(2)	1.947(5)	N(2)–C(15)	1.367(5)
Mo–C(3)	2.318(5)	N(2)–C(19)	1.326(5)
Mo–C(4)	2.203(5)	C(1)–O(1)	1.148(6)
Mo–C(5)	2.313(5)	C(2)–O(2)	1.158(5)
Mo–N(1)	2.258(4)	C(3)–C(4)	1.408(7)
Mo–N(2)	2.240(3)	C(4)–C(5)	1.394(6)
Mo–Cl	2.4835(13)	O(3)–C(6)	1.420(6)
N(1)–C(12)	1.441(6)	O(3)–C(7)	1.372(5)
Bond angles			
C(2)–Mo–C(1)	80.0(2)	C(3)–C(4)–C(5)	115.4(5)
C(1)–Mo–C(4)	104.3(2)	C(1)–Mo–Cl	87.4(2)
C(2)–Mo–C(4)	104.2(2)	C(2)–Mo–Cl	89.0(1)
C(1)–Mo–N(1)	168.2(2)	C(4)–Mo–Cl	163.6(1)
C(1)–Mo–N(2)	103.2(2)	N(1)–Mo–Cl	81.38(10)
C(2)–Mo–N(1)	103.2(2)	N(2)–Mo–Cl	80.68(10)
C(2)–Mo–N(2)	169.1(2)	N(1)–Mo–N(2)	71.73(13)
O(1)–C(1)–Mo	177.2(5)	C(7)–O(3)–C(6)	118.2(4)
O(2)–C(2)–Mo	178.3(5)	O(3)–C(7)–C(8)	124.8(5)

Table 2
Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parenthesis for **4**

Bond lengths			
Mo–C(1)	1.962(5)	N(1)–C(6)	1.462(5)
Mo–C(2)	1.954(3)	N(1)–C(7)	1.286(4)
Mo–C(3)	2.320(5)	N(2)–C(8)	1.370(4)
Mo–C(4)	2.205(4)	N(2)–C(12)	1.337(5)
Mo–C(5)	2.319(4)	C(1)–O(1)	1.147(5)
Mo–N(1)	2.243(3)	C(2)–O(2)	1.148(4)
Mo–N(2)	2.233(3)	C(3)–C(4)	1.385(7)
Mo–Cl	2.4874(9)	C(4)–C(5)	1.394(7)
Bond angles			
C(2)–Mo–C(1)	81.0(2)	O(2)–C(2)–Mo	177.5(5)
C(1)–Mo–C(4)	104.3(2)	C(3)–C(4)–C(5)	116.5(5)
C(2)–Mo–C(4)	103.7(2)	C(1)–Mo–Cl	88.4(1)
C(1)–Mo–N(1)	99.6(1)	C(2)–Mo–Cl	87.2(1)
C(1)–Mo–N(2)	166.9(1)	C(4)–Mo–Cl	164.4(1)
C(2)–Mo–N(1)	168.6(1)	N(1)–Mo–Cl	81.5(1)
C(2)–Mo–N(2)	104.8(2)	N(2)–Mo–Cl	80.2(1)
O(1)–C(1)–Mo	177.9(4)	N(1)–Mo–N(2)	72.5(1)

two isomers in a 3:1 ratio. The two isomers are due to the allyl group taking up different orientations which are slow to interconvert on the NMR timescale at room temperature. Solubility problems inhibited a study of the low temperature ^{1}H-NMR spectra. The ^{1}H-NMR spectra of complexes **6** and **7**, where the allyl group is the 1-methyl substituted allyl, are much more complex. This is due to the complexes being unsymmetrical, hence making all the protons inequivalent in the molecules. The ^{1}H-NMR spectra of complexes **8** and **9**, containing a 2-methyl substituted allyl group, are less complicated than those for the η^3-C_3H_5 complexes. This is due to the replacement of the central proton by a methyl group, therefore removing coupling to the terminal protons. The methyl groups appear in the range 1.22–1.43 ppm with the *anti* protons 1.31–1.34 ppm and the *syn* protons appearing between 2.69 and 2.96 ppm.

The nitrogen donor ligands and phenyl group all have multiplets in the aromatic region of the spectra between 6.68 and 9.38 ppm. The methyl group bonded to nitrogen appears as a singlet between 3.38 and 4.18 ppm. The methyl group bonded to carbon also appears as a singlet between 2.23 and 2.54 ppm. The spectrum of complex **3** also showed a singlet at 3.92 ppm for the OMe which is bonded to the two-position of the phenyl group.

The infrared spectra of the complexes [MoCl(CO)$_2$L$_2$-(η^3-allyl)] exhibited two bands of approximately equal intensity in the carbonyl stretching region between 1945 and 1840 cm^{-1} as expected for a *cis* geometry of carbonyl groups around the metal. The complexes also showed ν(C=N) stretching frequencies in the region of 1580–1600 cm^{-1}.

The FABMS spectra show parent ions and fragmentation due to loss of the chloride and successive carbonyl ligands.

3. Experimental

All reactions were performed under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen just prior to use. Light petroleum ether refers to the fraction that boils in the 40–60° range. Microanalysis were carried out by either Butterworth Laboratories Ltd., UK or TUBITAK-Marmara Research Centre, Turkey. The FAB mass spectrum of the solid complexes were obtained on a Kratos Concept double focusing sector mass spectrometer. The ^{1}H-NMR spectra were recorded at room temperature (r.t.) in [^{2}H$_1$]chloroform on a Bruker AM300 spectrometer operating at 300.13 MHz with SiMe$_4$ (0.0 ppm) as internal reference. The ^{31}P–{^{1}H}-NMR were recorded at r.t. in dicholoromethane on a JEOL JNM-FX90 spectrometer operating at 36.2 MHz with [P(OH)$_4$]$^+$ in [^{2}H$_2$]-water (0.0 ppm) as external reference. The quoted IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer in Nujol mulls between NaCl plates in the range 3000–600 cm^{-1}.

Allyl chloride, 3-chloro-2-methyl-1-propene and 1-chloro-3-methyl-1-propene were used as supplied from Aldrich. The complexes [Mo(CO)$_4$L$_2$] (L$_2$ = pyridyl amine Schiff base ligands), were prepared as described in the literature [12,13].

3.1. Preparation of [MoCl(CO)$_2${N(Me)=C(Me)C$_5$H$_4$N}(η^3-C$_3$H$_5$)] (1)

A mixture of [Mo(CO)$_4${N(Me)=C(Me)C$_5$H$_4$N}] (0.648 g, 2 mmol) and excess allyl chloride (0.940 g, 0.012 mol) was refluxed in THF (10 cm^3) for 3 h. The resulting dark purple solution was cooled to r.t. and the addition of light petroleum ether precipitated a dark purple solid which was filtered, washed with light petroleum ether and dried in vacuo. Recrystallisation from dichloromethane/diethyl ether yielded the title complex **1**. Yield 0.42 g (58% based on Mo). Anal. Found: C, 42.41; H, 4.29; N, 7.16. C$_{13}$H$_{15}$ClMoN$_2$O$_2$ Calc.: C, 42.85; H, 4.12; N, 7.69%. IR: 1940, 1840 ν(CO), 1598 ν(N=C) cm^{-1}. Mass spectrum: [MH]$^+$ at *m/z* 364, [MH−Cl]$^+$ 329, [MH−2CO]$^+$ 308. ^{1}H-NMR: isomer a: 8.78–7.26 (4H, m, Arom.), 4.18 (3H, s, N–C*H$_3$*), 2.54 (3H, s, C–C*H$_3$*), 1.30 (2H, d, J = 11.2 Hz, *anti*-C*H*), 3.20 (2H, br, *syn*-C*H*), 3.84 (1H, m, central C*H*). isomer b: 8.78–7.26 (4H, m, Arom.), 3.68 (3H, s, N–C*H$_3$*), 2.39 (3H, s, C–C*H$_3$*), 1.48 (2H, d, J = 8.2 Hz, *anti*-C*H*), 2.98 (2H, br, *syn*-C*H*), 3.77 (1H, m, central C*H*).

3.2. Preparation of [MoCl(CO)$_2${N(Ph)=C(Me)C$_5$H$_4$N}((η^3-C$_3$H$_5$)] (2)

Using the same procedure as for **1** a mixture of [Mo(CO)$_4${N(Ph)=C(Me)C$_5$H$_4$N}] (0.3 g, 0.74 mmol) and excess allyl chloride (0.940 g, 0.012 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **2**. Yield 0.120 g (38% based on Mo). Anal. Found: C, 50.83; H, 3.81; N, 6.74. C$_{18}$H$_{17}$ClMoN$_2$O$_2$ Calc.: C, 50.59; H, 3.98; N, 6.54%. IR: 1930, 1850, ν(CO), 1600 ν(N=C) cm^{-1}. Mass spectrum: [MH]$^+$ at *m/z* 426, [MH−Cl]$^+$ 389, [MH−2CO]$^+$ 370. ^{1}H-NMR: 9.22–7.07 (9H, m, Arom.), 2.23 (3H, s, C–C*H$_3$*), 1.38 (1H, d, J = 9.1 Hz, *anti*-C*H*), 1.08 (1H, d, J = 9.3 Hz, *anti*-C*H*), 3.10 (2H, br, *syn*-C*H*), 3.54 (1H, m, central CH).

3.3. Preparation of [MoCl(CO)$_2${N(C$_6$H$_4$-2-OMe)=C(Me)C$_5$H$_4$N}(η^3-C$_3$H$_5$)] (3)

Using the same procedure as for **1** a mixture of [Mo(CO)$_4${N(C$_6$H$_4$-2-OMe)=C(Me)C$_5$H$_4$N}] (0.4 g, 0.92 mmol) and excess allyl chloride (0.940 g, 0.012 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **3**. Yield 0.260 g (62% based on Mo). Anal. Found: C, 49.88; H, 4.24; N, 6.02. C$_{19}$H$_{19}$ClMoN$_2$O$_3$ Calc.: C, 50.11; H, 4.18; N, 6.15%. IR: 1940, 1840, ν(CO), 1590 ν(N=C) cm^{-1}. Mass spectrum: [MH]$^+$ at *m/z* 456, [MH−Cl]$^+$ 421, [MH−2CO]$^+$ 400. ^{1}H-NMR: isomer a: 9.37–6.68 (8H, m, Arom.), 3.92 (3H, s, O–C*H$_3$*), 2.24 (3H, s, C–C*H$_3$*), 1.40 (2H, d, J = 9.7 Hz, *anti*-C*H*), 3.13 (2H, br, *syn*-C*H*), 3.66 (1H, m, central C*H*). Isomer b: 9.37–6.68 (8H, m, Arom.), 3.88 (3H, s, O–C*H$_3$*), 2.16 (3H, s, C–C*H$_3$*), 1.10 (2H, d, J = 9.5 Hz, *anti*-C*H*), 2.29 (2H, br, *syn*-C*H*), 2.93 (1H, m, central C*H*).

3.4. Preparation of [MoCl(CO)$_2${N(Me)=C(Ph)C$_5$H$_4$N}(η^3-C$_3$H$_5$)] (4)

Using the same procedure as for **1** a mixture of [Mo(CO)$_4${N(Me)=C(Ph)C$_5$H$_4$N}] (0.2 g, 0.5 mmol) and excess allyl chloride (0.940 g, 0.012 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **4**. Yield 0.1 g (50% based on Mo). Anal. Found: C, 49.88; H, 3.90; N, 6.45. $C_{18}H_{17}ClMoN_2O_2$ Calc.: C, 50.58; H, 3.98; N, 6.56%. IR: 1935, 1850, ν(CO), 1580 ν(N=C) cm^{-1}. Mass spectrum: $[MH]^+$ at *m/z* 426, $[MH-Cl]^+$ 391, $[MH-2CO]^+$ 370. ^1H-NMR: isomer a: 9.15–7.11 (9H, m, Arom.), 3.96 (3H, s, N–C*H₃*), 1.36 (2H, d, $J = 6.9$ Hz, *anti*-C*H*), 3.90 (2H, d, $J = 3.3$ Hz, *syn*-C*H*), 3.20 (1H, m, central C*H*). Isomer b: 9.15–7.11 (9H, m, Arom.), 3.45 (3H, s, N–C*H₃*), 1.52 (2H, d, $J = 8.8$ Hz, *anti*-C*H*), 3.30 (2H, d, $J = 3.4$ Hz, *syn*-C*H*), 3.10 (1H, m, central C*H*).

3.5. Preparation of $[MoCl(CO)_2\{N(Ph)=C(Ph)C_5H_4N\}(\eta^3\text{-}C_3H_5)]$ (**5**)

Using the same procedure as for **1** a mixture of $[Mo(CO)_4\{N(Ph)=C(Ph)C_5H_4N\}]$ (0.3 g, 0.64 mmol) and excess allyl chloride (0.940 g, 0.012 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **5**. Yield 0.06 g (20% based on Mo). Anal. Found: C, 56.55; H, 4.05; N, 5.33. $C_{23}H_{19}ClMoN_2O_2$ Calc.: C, 56.67; H, 3.90; N, 5.75%. IR: 1945, 1850, ν(CO), 1585 ν(N=C) cm^{-1}. Mass spectrum: $[MH]^+$ at *m/z* 488 $[MH-Cl]^+$ 453, $[MH-2CO]^+$ 432. ^1H-NMR: 9.28–7.04 (14H, m, Arom.), 1.45 (2H, d, $J = 9.3$ Hz, *anti*-C*H*), 3.65 (2H, d, $J = 6.6$ Hz, *syn*-C*H*), 3.13 (1H, m, central C*H*).

3.6. Preparation of $[MoCl(CO)_2\{N(Me)=C(Me)C_5H_4N\}(\eta^3\text{-}1\text{-}MeC_3H_4)]$ (**6**)

Using the same procedure as for **1** a mixture of $[Mo(CO)_4\{N(Me)=C(Me)C_5H_4N\}]$ (0.4 g, 1.16 mmol) and excess crotyl chloride (0.930 g, 0.010 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **6**. Yield 0.07 g (16% based on Mo). Anal. Found: C, 44.16; H, 4.15; N, 5.88. $C_{14}H_{17}ClMoN_2O_2$ Calc.: C, 44.33; H, 3.85; N, 6.35%. IR: 1925, 1840, ν(CO), 1590 ν(N=C) cm^{-1}. Mass spectrum: $[MH]^+$ at *m/z* 378, $[MH-Cl]^+$ 343, $[MH-2CO]^+$ 322. ^1H-NMR: 8.73–7.64 (4H, m, Arom.), 3.36 (3H, s, N–C*H₃*), 2.35 (3H, s, C–C*H₃*), 1.55 (d, $J = 4.7$ Hz, C*H₃*), 1.65 (d, $J = 5$ Hz, C*H₃*), 2.34 (s), 2.98 (s), 4.14 (m, central C*H*).

3.7. Preparation of $[MoCl(CO)_2\{N(Me)=C(Ph)C_5H_4N\}(\eta^3\text{-}1\text{-}MeC_3H_4)]$ (7)

Using the same procedure as for **1** a mixture of $[Mo(CO)_4\{N(Me)=C(Ph)C_5H_4N\}]$ (0.3 g, 0.74 mmol) and excess crotyl chloride (0.930 g, 0.010 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **7**. Yield 0.150 g (46% based on Mo). Anal. Found: C, 51.69; H, 4.26; N, 6.25. $C_{19}H_{19}ClMoN_2O_2$ Calc.: C, 51.70; H, 4.31; N, 6.35%. IR: 1930, 1845, ν(CO), 1600 ν(N=C) cm^{-1}. Mass spectrum: $[MH]^+$ at *m/z* 441, $[MH-Cl]^+$ 405, $[MH-2CO]^+$ 384. ^1H-NMR: 8.94–7.16 (9H, m, Arom.), 3.38 (3H, s, N–C*H₃*), 1.55 (m), 1.67 (m), 2.35 (m), 2.97 (s), 3.60(m).

3.8. Preparation of $[MoCl(CO)_2\{N(Me)=C(Me)C_5H_4N\}(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (**8**)

Using the same procedure as for **1** a mixture of $[Mo(CO)_4\{N(Me)=C(Me)C_5H_4N\}]$ (0.205 g, 0.6 mmol) and excess 3-chloro-2-methyl-propene (0.920 g, 0.010 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **8**. Yield 0.150 g (66% based on Mo). Anal. Found: C, 44.12; H, 4.42; N, 7.23. $C_{14}H_{17}ClMoN_2O_2$ Calc.: C, 44.39; H, 4.49; N, 7.39%. IR: 1928, 1850, ν(CO), 1590 ν(N=C) cm^{-1}. Mass spectrum: $[MH]^+$ at *m/z* 378, $[MH-Cl]^+$ 343, $[MH-2CO]^+$ 322. ^1H-NMR: 8.77–7.25 (4H, m, Arom.), 3.68 (3H, s, N–C*H₃*), 2.43 (3H, s, C–C*H₃*), 1.22 (3H, s, C*H₃*), 1.31 (1H, s, *anti*-C*H*), 1.34 (1H, s, *anti*-C*H*), 2.69 (1H, s, *syn*-C*H*), 2.86 (1H, s, *syn*-C*H*).

3.9. Preparation of $[MoCl(CO)_2\{N(Me)=C(Ph)C_5H_4N\}(\eta^3\text{-}2\text{-}MeC_3H_4)]$ (**9**)

Using the same procedure as for **1** a mixture of $[Mo(CO)_4\{N(Me)=C(Ph)C_5H_4N\}]$ (0.2 g, 0.5 mmol) and excess 3-chloro-2-methyl-propene (0.920 g, 0.010 mol) was refluxed in THF (10 cm^3) for 3 h to afford the title complex as a dark purple solid **9**. Yield 0.180 g (82% based on Mo). Anal. Found: C, 51.23; H, 4.45; N, 6.30. $C_{19}H_{19}ClMoN_2O_2$ Calc.: C, 51.70; H, 4.31; N, 6.35%. IR: 1930, 1855, ν(CO), 1590 ν(N=C) cm^{-1}. Mass spectrum: $[M]^+$ at *m/z* 440, $[M-Cl]^+$ 405, $[M-2CO]^+$ 384. ^1H-NMR: 8.80–7.15 (9H, m, Arom.), 3.44 (3H, s, N–C*H₃*), 1.32 (2H, s, *anti*-C*H*), 1.43 (3H, s, C*H₃*), 2.81 (1H, s, *syn*-C*H*), 2.96 (1H, s, *syn*-C*H*).

3.10. Preparation of $[Mo(CO)_2\{N(Me)=C(Me)C_5H_4N\}(PPh_3)(\eta^3\text{-}C_3H_5)]PF_6$ (**10**)

A mixture of $[MoCl(CO)_2\{N(Me)=C(Me)C_5H_4N\}\text{-}(\eta^3\text{-}C_3H_5)]$ (**1**) (0.217 g, 0.6 mmol) and triphenylphosphine (0.152 g, 0.6 mmol) and KPF_6 (0.110 g, 0.6 mmol) was refluxed in acetonitrile (20 cm^3) for 3 h. After cooling to r.t. the reaction mixture was rotary evaporated to dryness to yield a red oil. This oil was dissolved in dichloromethane, filtered to remove potassium chloride and a red solid **10** was precipitated by addition of diethyl ether. Yield 0.3 g (60%). Anal. Found: C, 50.80; H, 4.23; N, 3.61. $C_{31}H_{30}F_6MoN_2O_2P_2$ Calc.: C, 50.68; H, 4.09; N, 3.81%. IR: 1940, 1855 ν(CO), 1730 ν(N=C) cm^{-1}. ^{31}P–$\{^1H\}$-NMR (CH_2Cl_2): 20.79, 157.7 ppm. Mass spectrum: $[M-PF_6]^+$ at *m/z* 591. ^1H-NMR ($(CD_3)_2CO$): 8.87–6.72 (19H, m, Arom.), 3.27 (3H, s, N–C*H₃*), 2.69 (3H, s, C–C*H₃*), 2.15 (2H, d, *anti*-C*H*), 2.58 (2H, br, *syn*-C*H*), 3.50 (1H, m, central C*H*).

3.11. Preparation of [Mo(NCS)(CO)$_2${N(Me)=C(Me)C$_5$H$_4$N}(η^3-C$_3$H$_5$)] (**11**)

A mixture of [MoCl(CO)$_2${N(Me)=C(Me)C$_5$H$_4$N}-(η^3-C$_3$H$_5$)] (**1**) (0.150 g, 0.412 mmol) and potassium thiocyanate (0.04 g, 0.412 mmol) was refluxed in acetone (10 cm^3) for 2 h. After cooling to r.t. the reaction mixture was rotary evaporated to dryness to yield a brown oil. This oil was dissolved in dichloromethane, filtered to remove potassium chloride and a brown solid was precipitated by addition of diethyl ether. Yield 0.030 g (19%). Anal. Found: C, 44.03; H, 3.84; N, 11.16. $C_{14}H_{15}MoN_3O_2S$ Calc.: C, 43.64; H, 3.90; N, 10.91%. IR: 2083 ν(N≡C), 1935, 1855 ν(CO), 1597 ν(N=C), cm^{-1}. Mass spectrum [MH]$^+$ at *m*/*z* 387. ^{1}H-NMR ((CD$_3$)$_2$SO): 8.75–7.50 (4H, m, *Arom*.), 3.58 (3H, s, N–C*H$_3$*), 2.30 (3H, s, C–C*H$_3$*), 1.25 (2H, d, *anti*-C*H*), 3.32 (2H, br, *syn*-C*H*), 3.97 (1H, m, central C*H*).

4. Crystal data

4.1. $C_{19}H_{19}ClMoN_2O_3$ (**3**)

$M = 454.75$, monoclinic, space group $P2_1/n$, $a = 9.971(1)$, $b = 11.906(2)$, $c = 16.249(2)$ Å, $\beta = 93.70\ (1)°$, $U = 1925.0(4)$ Å^3, $Z = 4$, $\mu = 0.841$ mm^{-1}, λ(Mo–K$_\alpha$) = 0.71073 Å, $F(000) = 920$, $D_{calc} = 1.569$ Mg m^{-3}.

A purple crystal was used for data collection with approximate dimensions $0.35 \times 0.23 \times 0.04$ mm^3 and was glued to the end of a thin glass fibre using epoxy resin. Intensity data were measured on a Siemens P4 diffractometer at 290(2) K, using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å), and a ω-scan method. A total of 4425 reflections were measured over the range $2.51 < \theta < 25.00°$ with $-1 \le h \le 19$, $-1 \le k \le 13$ and $-19 \le l \le 19$. A semi empirical absorption correction was applied to the data based on psi scans (max., min. transmission factors 0.89 and 0.75). The reflections were corrected for Lorentz and polarisation effects and merged to give 3382 independent reflections ($R_{int} = 0.0315$).

The structures were solved by direct methods and refined with full-matrix least-squares on F^2 using the program SHELXTL-PC [14]. The ratio of data:parameters was 3382:235. All non-hydrogen atoms were refined with anisotropic displacement parameters. Final cycles of refinement gave $R_1 = 0.0413$, $wR_2 = 0.0830$ for all data, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.00P]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The maximum and minimum electron densities in the final ΔF map were 0.37 and -0.38 e Å^{-3}, respectively.

The geometry of the molecule is shown in Fig. 1. Selected bond distances and bond angles are listed in Table 1.

4.2. $C_{18}H_{17}ClMoN_2O_2$ (**4**)

$M = 424.73$, orthorhombic, space group $P2_12_12_1$, $a = 8.066(1)$, $b = 12.696(1)$, $c = 18.036(1)$ Å, $U = 1847.0(3)$ Å^3, $Z = 4$, $\mu = 0.866$ mm^{-1}, λ(Mo–K$_\alpha$) = 0.71073 Å, $F(000) = 856$, $D_{calc} = 1.527$ Mg m^{-3}.

Conditions were as for **3** except for the following: crystal size $0.52 \times 0.42 \times 0.40$ mm^3; intensity data were collected in the range $2.77 < \theta < 26.49°$ for 2866 reflection. Absorption correction max. and min. transmission factors were 0.88 and 0.83, respectively. Final cycles of refinement gave $R_1 = 0.0241$, $wR_2 = 0.0620$ for all data, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.41P]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The maximum and minimum electron densities in the final ΔF map were 0.24 and -0.26 e Å^{-3}, respectively.

The geometry of the molecule is shown in Fig. 2. Selected bond lengths and angles are given in Table 2.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 181457 and 181458 for compounds **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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