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Synthesis and reactions of [Mo(2,6-lutidine)(phosphine)] derivatives [1]

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Abstract

The syntheses of the η-lutidine(phosphine)molybdenum compounds $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)L_3]$ (L = PMe_3 **1**, PPh_2H **2**, $PPhMe_2$ **3**), $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2PPh_2]_3)]$ **4**, $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)L_3][BF_4]$ (L = PMe_3 **5**, PPh_2H **6**, $PPhMe_2$ **7**), $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2PPh_2]_3)]$ $[BF_4]$ **8** and $[Mo(\eta^6\text{-}H_3BNC_5H_3Me_2\text{-}2,6)L_3]$ (L = PPh_2H **9**, $PPhMe_2$ **10**) are described. The crystal structures of complex **2** and **5** have been determined. © 1998 Elsevier Science S.A.

Keywords: Molybdenum; η-arene; Phosphine; Crystal structure; Metal vapour synthesis

1. Introduction

Over the last three decades the chemistry of bis(η-arene)metal sandwich compounds has been well established [1–3]. Although analogous sandwich complexes which incorporate a heteroatom such as N, P or As into the arene ring [4–6] have been prepared their chemistry is virtually unexplored. Treatment of the well known bis-η-arene molybdenum compound $[Mo(\eta\text{-arene})_2]$ with tertiary phosphines or phosphites gives the half sandwich compounds $[Mo(\eta\text{-arene})(PR)_3]$, which exhibit an extensive chemistry of the Mo(η-arene) moiety [1–3,9–15]. The complex $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$, first prepared by Wucherer and Muetterties using metal vapour synthesis techniques [7] has been fully characterised [8] but no reaction chemistry was reported. Recently, we described the improved synthesis of $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$ using our bell-jar reactor [17] and a modified work-up procedure, which enabled us to produce the lutidine arene complex on a scale of 3–4 g [16]. We showed trimethylphosphine reacted with $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$ to give the complex $[Mo(\eta\text{-}2,6\text{-lutidine})(PMe_3)_3]$ **1** [16]. Here we describe further the chemistry of $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$ **1**.

2. Results and discussion

Treatment of $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$ **1** with the neat phosphine ligands PPh_2H and $PPhMe_2$ at room temperature gives the complexes $[Mo(\eta\text{-}2,6\text{-lutidine})(PPh_2H)_3]$ **2** and $[Mo(\eta\text{-}2,6\text{-lutidine})(PPhMe_2)_3]$ **3**, respectively. Warming a toluene solution of $[Mo(\eta\text{-}2,6\text{-lutidine})_2]$ with the tridentate phosphine ligand $CH_3C[CH_2PPh_2]_3$ to 80°C gives $[Mo(\eta\text{-}2,6\text{-lutidine})(CH_3C[CH_2PPh_2]_3)]$ **4**. The complexes **2**–**4** were purified by column chromatography on alumina at low temperature (−20°C). The compounds **2**–**4** are bright red, moderately air stable microcrystalline solids and very soluble in THF and toluene, sparingly soluble in Et_2O and virtually insoluble in pentane. The solids **2**–**4** melt in a sealed capillary without decomposition at 123°C, 139°C, and 275°C, respectively.

Treatment of the neutral half-sandwich complexes **1**–**4** with one equivalent of $HBF_4 \cdot Et_2O$ at −30°C in a Et_2O solution causes an immediate protonation and the complexes $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)L_3][BF_4]$ (L = PMe_3 **5**, PPh_2H **6**, $PhMe_2$ **7**) and $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2PPh_2]_3)][BF_4]$ **8** can be isolated in almost quantitative yields. The complexes **6** and **7** melt without decomposition at 96°C and 153°C, respectively. The compound **8** decomposes at ca. 250°C. The complexes **5**–**8** are soluble in THF and acetone, but insoluble in Et_2O and pentane. Although the complexes **6**–**8** are stable in air after several hours but complex **5** decomposes immediately on exposure to air.

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[1] Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

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Table 1
Analytical and spectroscopic data

Compound[a]	Spectroscopic data[b1]
1. Dark red	H[c]: 1.19 [27, m, $\mathrm{PC}H_3$], 2.35 [6, s, $\mathrm{C_0C}H_3$], 3.68 [2, m, H_m], 3.81 [1, m, H_p]
C, 44.1 (44.55)	
H, 8.3 (8.4)	^{13}C[c]: 23.9 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 26.9 [9, m, $\mathrm{P}C\mathrm{H_3}$], 68.0 [2, s, C_m], 73.1 [1, s, C_p], 103.1 [2, s, C_0]
N, 3.25 (3.25)	
M/e 428 P^+ (EI)	^{31}P[c]: 6.33 [3, s, $P\mathrm{CH_3}$]
2. Bright red	^{1}H[c]: 2.10 [6, s, $\mathrm{C_0C}H_3$], 4.09 [2, m, H_m], 5.10 [1, m, H_p], 6.90 [3, d ($J = 322.7$)PH], 6.97 [18, m, $\mathrm{P(C_6}H_5)$], 7.33 [12, m, $\mathrm{P(C_6}H_5)$]
C, 47.8 (47.5)	
H, 5.8 (5.65)	^{13}C[c]: 22.7 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 71.8 [2, s, C_m], 76.6 [1, s, C_p], 108.7 [2, s, C_0], 127.9, 128.2, 133.3 [s, $\mathrm{P}(C_6\mathrm{H_5})$], 139.9 [6, m, C_i]
N, 4.6 (4.6)	
M/e 763 P^+ (FAB)	^{31}P[c]: 48.34 [3, d ($J = 324.2$) PH]
3. Bright red	^{1}H[c]: 1.42 [18, s, $\mathrm{PC}H_3$], 2.17 [6, s, $\mathrm{C_0C}H_3$], 3.76 [2, m, H_m], 4.48 [1, m, H_p], 7.15 [9, m, $\mathrm{P(C_6}H_5)$], 7.67 [6, m, $\mathrm{P(C_6}H_5)$]
C, 60.4 (60.3)	
H, 6.8 (6.85)	^{13}C[c]: 23.2 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 25.9 [6, s, $\mathrm{P}C\mathrm{H_3}$], 69.4 [2, s, C_m], 74.4 [1, s, C_p], 105.0 [2, s, C_0], 127.6, 128.2, 131.7 [s, $\mathrm{P}(C_6\mathrm{H_5})$], 145.7 [3, m, C_i]
N, 2.4 (2.3)	
M/e 619 P^+ (FAB)	^{31}P[c]: 16.51 [3, s]
4. Bright red	^{1}H[c]: 1.13 [3, s, $\mathrm{C}H_3\mathrm{C}$], 2.17 [6, s, $\mathrm{CC}H_2$], 2.35 [6, s, $\mathrm{C_0C}H_3$], 4.02 [2, m, H_m], 5.02 [1, m, H_p], 6.89 [18, m, $\mathrm{P(C_6}H_5)$], 7.26 [12, m, $\mathrm{P(C_6}H_5)$]
C, 69.5 (69.65)	
H, 6.0 (5.8)	^{13}C[c]: 24.5 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 38.8 [1, s, $C\mathrm{H_3C}$], 40.2 [3, s, $\mathrm{C}C\mathrm{H_2}$], 74.7 [2, s, C_m], 78.3 [1, s, C_p], 110.8 [2, s, C_0], 127.4, 132.5 [m, $\mathrm{P}(C_6\mathrm{H_5})_2$], 144.6 [6, m, C_i]
N, 1.8 (1.7)	
M/e 829 P^+ (FAB)	^{31}P[c]: 42.41 [3, s]
5. Red	^{1}H[d]: 1.42 [27, m, $\mathrm{PC}H_3$], 2.40 [6, s, $\mathrm{C_0C}H_3$], 3.81 [2, m, H_m], 4.39 [1, m, H_m]
C, 36.9 (37.0)	
H, 7.1 (7.2)	^{13}C[d]: 18.9 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 24.7 [9, m, $\mathrm{P}C\mathrm{H_3}$], 64.6 [2, s, C_m], 73.1 [1, s, C_p], 92.3 [2, s, C_0]
N, 2.65 (2.7)	
M/e 428 [P-BF$_4$]$^+$ (FAB)	^{31}P[d]: 0.48 [3, s]
	IR: 3246vs[e]
6. Red	^{1}H[d]: 1.98 [6, s, $\mathrm{C_0C}H_3$], 4.49 [2, m, H_m], 5.81 [1, m, H_p], 6.73 [3, d ($J = 316.6$) PH], 7.24 [18, m, $\mathrm{P(C_6}H_5)$], 7.31 [12, m, $\mathrm{P(C_6}H_5)$]
C, 60.8 (60.8)	
H, 5.2 (5.1)	^{13}C[d]: 23.0 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 72.7 [2, s, C_m], 77.4 [1, s, C_p], 102.0 [2, s, C_0], 134.0, 134.9, 138.3 [s, $\mathrm{P}(C_6\mathrm{H_5})$], 140.6 [6, m, C_i]
N, 1.6 (1.65)	
M/e 763 [P-BF$_4$]$^+$ (FAB)	^{31}P[d]: 29.20 [3, s]
	IR: 3194vs[e]
7. Red	^{1}H[d]: 1.63 [18, s, $\mathrm{PC}H_3$], 2.08 [6, s, $\mathrm{C_0C}H_3$], 4.11 [2, m, H_m], 5.29 [1, m, H_p], 7.44 [9, m, $\mathrm{P(C_6}H_5)$], 7.65 [6, m, $\mathrm{P(C_6}H_5)$]
C, 52.8 (52.8)	
H, 6.3 (6.1)	^{13}C[d]: 18.4 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 24.0 [6, s, $\mathrm{P}C\mathrm{H_3}$], 66.2 [2, s, C_m], 73.4 [1, s, C_p], 93.3 [2, s, C_0], 129.2, 130.2, 132.0 [s, $\mathrm{P}(C_6\mathrm{H_5})$], 142.4 [3, m, C_i]
N, 2.2 (2.0)	
M/e 619 [P-BF$_4$]$^+$ (FAB)	^{31}P[d]: 8.34 [3, s]
	IR: 3219vs[e]
8. Pink	^{1}H[d]: 1.64 [3, s, $\mathrm{C}H_3\mathrm{C}$], 2.30 [6, s, $\mathrm{C_0C}H_3$], 2.45 [6, s, $\mathrm{CC}H_2$], 4.34 [2, m, H_m], 5.38 [1, m, H_p], 7.11 [18, m, $\mathrm{P(C_6}H_5)$], 7.21 [12, m, $\mathrm{P(C_6}H_5)$]
C, 62.5 (63.0)	
H, 5.6 (5.4)	^{13}C[d]: 15.6 [1, s, $C\mathrm{H_3C}$], 19.7 [2, s, $\mathrm{C_0}C\mathrm{H_3}$], 38.7 [3, s, $\mathrm{C}C\mathrm{H_2}$], 70.5 [2, s, C_m], 74.5 [1, s, C_p], 128.7, 132.9 [m, $\mathrm{P}(C_6\mathrm{H_5})$]
N, 1.4 (1.5)	
M/e 829 [P-BF$_4$]$^+$ (FAB)	^{31}P[d]: 32.79 [3, s]
	IR: 3208vs[e]

Table 1 (continued)

Compound[a]	Spectroscopic data[b]
9. Orange	$^{1}H^{f}$: 1.97 [6, s, C_0CH_3], 3.99 [2, m, H_m], 5.39 [1, m, H_p], 6.57 [3, d ($J = 333.3$) P*H*], 7.11 [30, m, $P(C_6H_5)$]
C, 66.7 (66.6)	
H, 5.7 (5.85)	$^{13}C^{f}$: 22.9 [2, s, C_0CH_3], 71.0 [2, s, C_m], 72.3 [1, s, C_p], 106.1 [2, s, C_0], 128.1, 128.8, 132.9 [s, $P(C_6H_5)$], 140.9 [6, s, C_i]
N, 1.9 (1.8)	
	$^{31}P^{f}$: 43.72 [3, d ($J = 333.3$) *P*H]
	$^{11}B^{f}$: −14.0 [1, s]
10. Orange	$^{1}H^{f}$: 1.51 [18, s, PCH_3], 2.47 [6, s, C_0CH_3], 3.68 [2, m, H_m], 4.70 [1, m, H_p], 7.34 [9, m, $P(C_6H_5)$], 7.54 [6, m, $P(C_6H_5)$]
C, 57.8 (59.0)	
H, 7.1 (7.2)	$^{13}C^{c}$: 22.1 [2, s, C_0CH_3], 24.1 [6, s, PCH_3], 68.6 [2, s, C_m], 72.4 [1, s, C_p], 103.8 [2, s, C_0], 127.9, 129.0, 131.2 [s, $P(C_6H_5)$], 143.2 [3, m, C_i]
N, 2.2 (2.2)	
M/e 619 $[P\text{-}BH_3]^+$ (FAB)	$^{31}P^{f}$: 11.45 [3, s]
	$^{11}B^{f}$: −18.6 [1, s]

[a] Analytical data given as: found (calculated) %.

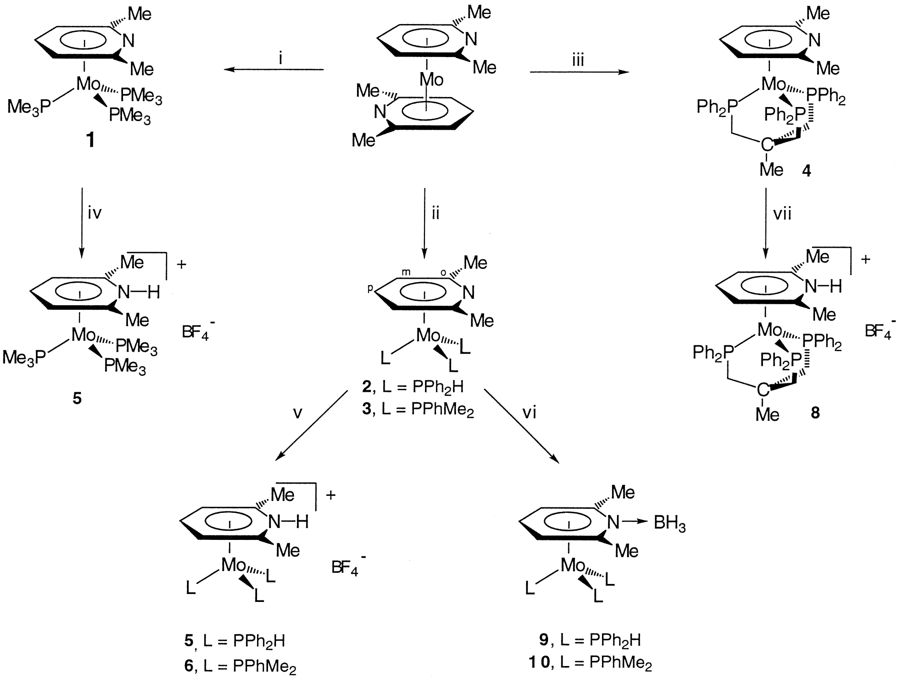
[b] ^1H at 300.13 MHz, ^{13}C at 75.5 MHz and ^{31}P at 121.6 MHz. NMR data given as: chemical shift (δ), relative intensity, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (in Hz) and assignment. The labelling of atoms is given in the structure of **2** in the Scheme 1. Infrared data in Nujol mulls (cm^{-1}). The M/e values refer to the ^{98}Mo isotope.

[c] In $[^2H_6]$ benzene.

[d] In $[^2H_6]$ acetone.

[e] Assigned to ν(NH) frequency.

[f] In $[^2H_2]$ dichloromethane.



Scheme 1. (i) Neat PMe_3 at room temperature for 12 h, yield 79%. (ii) For L = PPh_2H, neat PPh_2H at room temperature for 24 h, yield 78%. For L = $PPhMe_2$, neat $PPhMe_2$ at room temperature for 18 h, yield 59%. (iii) Triphos in toluene at 80°C for 15 h, yield 55%. (iv) Addition of $HBF_4 \cdot Et_2O$ to Et_2O solution at −78°C, yield 75%. (v) For L = PPh_2H, addition of $HBF_4 \cdot Et_2O$ to Et_2O solution at −30°C, yield 96%. For L = $PPhMe_2$, addition of $HBF_4 \cdot Et_2O$ to Et_2O solution at −30°C, yield 94%. (vi) For L = PPh_2H, addition of $BH_3 \cdot THF$ to Et_2O solution at −10°C, yield 80%. For L = $PPhMe_2$, addition of $BH_3 \cdot THF$ to Et_2O solution at room temperature, yield 92%. (vii) Addition of $HBF_4 \cdot Et_2O$ to Et_2O solution at −30°C, yield 96%.

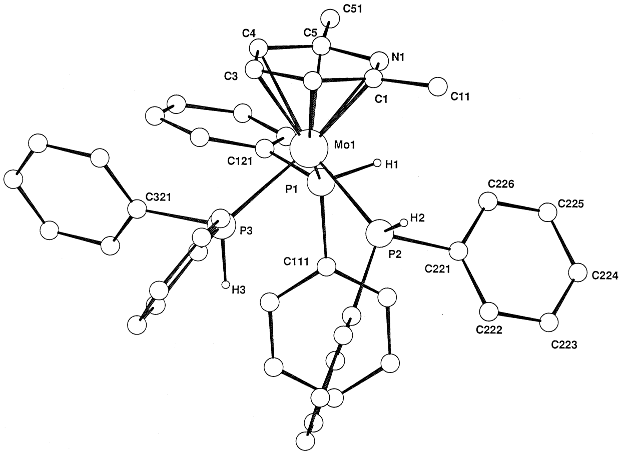


Fig. 1. Perspective view of molecule **2**.

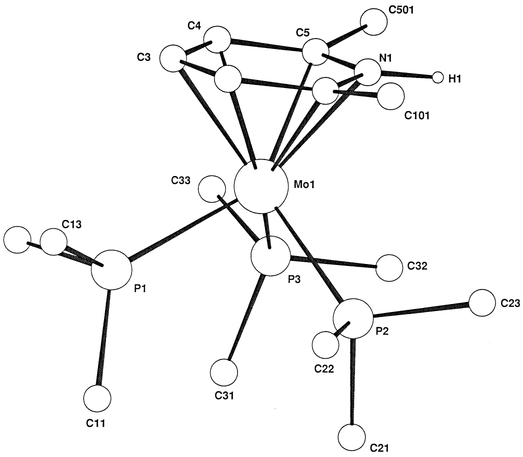


Fig. 2. Perspective view of molecule **5**.

Treatment of a diethyl ether solution of complexes **2** and **3** with one equivalent of the Lewis acid, complex $BH_3 \cdot THF$ at low temperature results in the formation of orange solids, which have been identified as the Lewis-acid–base adducts $[Mo(\eta^6\text{-}H_3BNC_5H_3Me_2\text{-}2,6)L_3]$ (L = PPh_2H **9**, $PPhMe_2$ **10**) in almost quantitative yield. They are soluble in benzene and CH_2Cl_2, but insoluble in Et_2O and pentane. In solution, an equilibrium between the starting materials and the products, **9** and **10**, is observed by proton NMR. The addition of an excess of $BH_3 \cdot THF$ to solutions of **9** and **10** in deuterated benzene shifts the equilibrium towards product formation. Reactions between other Lewis acids like BF_3 and $B(C_6F_5)_3$ and **6** or **7** resulted in the decomposition of **1**.

The analytical and spectroscopic data characterising the compounds **1**–**10** are given in Table 1. A summary of the reactions and the conditions is shown in Scheme 1.

Crystals of **2** and **5** suitable for X-ray diffraction were made and their structures have been determined. The perspective views of the two molecules are shown in Figs. 1 and 2, respectively. Selected bond angles and distances are listed in Tables 2 and 3, and the fractional atomic coordinated are given in Tables 4 and 5. The distances between the coordinated lutidine and the molybdenum centre range from 2.267(3) to 2.310(3) Å. In the compound **2** the carbon atoms C(1), C(3) and C(5) are slightly drawn out of the ring plane and towards the metal atom and give the lutidine a chair-like conformation. The methyl groups of the ring in *ortho* positions are slightly bent out of the plane and away from the molybdenum. The intra-ring distances of N(1)–C(1) and N(1)–C(5) in the coordinated lutidine range from 1.386(4) and 1.396(4) Å, respectively. These bond distances are shorter than the remaining carbon–carbon bond lengths in the ring which are found between 1.412(5) and 1.419(5) Å. Similar observations have been made for other related complexes [8].

Table 2
Selected interatomic distances (Å) and angles (°) for **2**

Mo	–P(1)	2.421(8)	P(1)	–Mo	–P(2)	93.43(3)
Mo	–P(2)	2.413(9)	P(1)	–Mo	–P(3)	91.10(3)
Mo	–P(3)	2.395(8)	P(2)	–Mo	–P(3)	85.60(3)
Mo	–N	2.298(2)	P(1)	–Mo	–N(1)	94.99(7)
Mo	–C(1)	2.269(3)	P(2)	–Mo	–N(1)	102.46(7)
Mo	–C(2)	2.310(3)	P(3)	–Mo	–N(1)	169.56(7)
Mo	–C(3)	2.267(3)	Mo	–P(1)	–C(111)	126.5(1)
Mo	–C(4)	2.310(3)	Mo	–P(1)	–C(121)	119.1(1)
Mo	–C(5)	2.280(3)	C(111)	–P(111)	–C(121)	99.2(1)
Mo	–CEN	1.805	C(1)	–N(1)	–C(5)	116.6(3)
N	–C(1)	1.386(4)	C(1)	–C(2)	–C(3)	119.0(3)
N	–C(5)	1.396(4)	C(3)	–C(4)	–C(5)	118.6(3)
C(1)	–C(2)	1.417(4)	N(1)	–C(5)	–C(4)	123.1(3)
C(2)	–C(3)	1.412(5)	CEN	–Mo	–P(1)	121.3
C(3)	–C(4)	1.419(5)	CEN	–Mo	–P(2)	123.47
C(4)	–C(5)	1.418(5)	CEN	–Mo	–P(3)	131.03

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

Table 3
Selected interatomic distances (Å) and angles (°) for **5**

Mo	–P(1)	2.451(7)	P(1)	–Mo	–P(2)	92.44(2)
Mo	–P(2)	2.466(7)	P(1)	–Mo	–P(3)	88.32(2)
Mo	–P(3)	2.458(7)	P(2)	–Mo	–P(3)	89.66(2)
Mo	–N	2.245(2)	P(1)	–Mo	–N(1)	156.77(6)
Mo	–C(1)	2.259(3)	P(2)	–Mo	–N(1)	98.35(6)
Mo	–C(2)	2.304(3)	P(3)	–Mo	–N(1)	112.13(6)
Mo	–C(3)	2.269(3)	Mo	–P(1)	–C(11)	125.2(1)
Mo	–C(4)	2.300(3)	Mo	–P(1)	–C(12)	115.7(1)
Mo	–C(5)	2.238(3)	Mo	–P(1)	–C(13)	113.1(1)
Mo	–CEN	1.777	C(11)	–P(1)	–C(12)	100.3(1)
N	–C(1)	1.411(4)	C(1)	–N(1)	–C(5)	123.2(2)
N	–C(5)	1.405(3)	C(1)	–C(2)	–C(3)	120.6(3)
C(1)	–C(2)	1.406(4)	C(3)	–C(4)	–C(5)	119.9(2)
C(2)	–C(3)	1.415(4)	N(1)	–C(5)	–C(4)	117.8(2)
C(3)	–C(4)	1.414(4)	CEN	–Mo	–P(1)	120.80
C(4)	–C(5)	1.419(4)	CEN	–Mo	–P(2)	127.94
			CEN	–Mo	–P(3)	126.54

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

The molybdenum atom in **5** is not equidistant to all the lutidine ring atoms and the atoms C(3) and N(1) are slightly bent out of the ring plane towards the molybdenum atom. The protonation of the nitrogen atom results in a slight lengthening of the N(1)–C(1) and N(1)–C(5) bonds [$(N–C)_{avg}$ = 1.391 Å for **2**; $(N–C)_{avg}$ = 1.408 Å for **5**].

In conclusion, the new reactions and compounds are shown in the Scheme. Generally it is found that the chemistry is similar to that of [Mo(η-toluene)$_2$], however, the η-lutidine ligands of 1 are more readily displaced.

Table 4
Fractional atomic co-ordinates for compound **2**

Atom	x	y	z
Mo(1)	0.13077(3)	0.35912(3)	0.29935(1)
P(1)	0.36841(8)	0.33924(8)	0.33923(4)
P(2)	0.02706(8)	0.12859(8)	0.30751(4)
P(3)	0.10501(8)	0.27056(8)	0.17178(4)
N(1)	0.1436(3)	0.4765(3)	0.4131(1)
C(1)	0.0033(3)	0.4180(3)	0.3728(2)
C(2)	−0.0588(3)	0.4420(3)	0.3005(2)
C(3)	0.0270(4)	0.5225(3)	0.2652(2)
C(4)	0.1690(4)	0.5897(3)	0.3064(2)
C(5)	0.2239(3)	0.5627(3)	0.3790(2)
C(11)	−0.0840(4)	0.3396(4)	0.4148(2)
C(51)	0.3694(4)	0.6391(3)	0.4282(2)
C(111)	0.4269(3)	0.1897(3)	0.3142(2)
C(112)	0.4647(4)	0.1710(4)	0.2486(2)
C(113)	0.4996(5)	0.0548(4)	0.2274(2)
C(114)	0.4955(4)	−0.0458(4)	0.2705(2)
C(115)	0.4592(4)	−0.0276(4)	0.3356(2)
C(116)	0.4263(3)	0.0903(4)	0.3584(2)
C(121)	0.5129(3)	0.4724(3)	0.3280(2)
C(122)	0.6470(3)	0.5096(3)	0.3800(2)
C(123)	0.7556(3)	0.6067(4)	0.3691(2)
C(124)	0.7317(4)	0.6637(4)	0.3048(2)
C(125)	0.5992(4)	0.6278(4)	0.2534(2)
C(126)	0.4889(3)	0.5334(3)	0.2656(2)
C(211)	−0.0175(3)	−0.0161(3)	0.2313(2)
C(212)	−0.1572(4)	−0.0767(4)	0.1874(2)
C(213)	−0.1890(4)	−0.1842(4)	0.1286(2)
C(214)	−0.0840(4)	−0.2328(4)	0.1126(2)
C(215)	0.0546(4)	−0.1739(4)	0.1557(2)
C(216)	0.0884(4)	−0.0652(3)	0.2133(2)
C(221)	0.1056(3)	0.0587(3)	0.3897(2)
C(222)	0.0895(3)	−0.0791(3)	0.3868(2)
C(223)	0.1480(4)	−0.1279(3)	0.4508(2)
C(224)	0.2227(4)	−0.0387(4)	0.5175(2)
C(225)	0.2404(4)	0.0991(4)	0.5206(2)
C(226)	0.1823(3)	0.1481(3)	0.4573(2)
C(311)	−0.0722(3)	0.1985(3)	0.1027(2)
C(312)	0.1910(4)	0.2196(4)	0.1185(2)
C(313)	−0.3213(4)	0.1689(4)	0.0665(2)
C(314)	−0.3372(4)	0.0950(4)	−0.0036(2)
C(315)	−0.2199(4)	0.0711(4)	−0.0197(2)
C(316)	−0.0876(4)	0.1241(3)	0.0329(2)
C(321)	0.1856(3)	0.3759(3)	0.1132(2)
C(322)	0.1409(4)	0.4875(3)	0.0935(2)
C(323)	0.2068(4)	0.5716(4)	0.0530(2)
C(324)	0.3196(4)	0.5456(4)	0.0327(2)
C(325)	0.3648(4)	0.4349(4)	0.0512(2)
C(326)	0.2968(4)	0.3494(4)	0.0901(2)

Table 5
Fractional atomic co−ordinates for compound **5**

Atom	x	y	z
Mo(1)	0.71036(2)	0.23825(2)	0.33138(1)
P(1)	0.53267(6)	0.28971(5)	0.41491(4)
P(2)	0.86852(7)	0.31789(5)	0.42110(4)
P(3)	0.72529(7)	0.08011(5)	0.40884(4)
C(1)	0.7844(3)	0.3330(2)	0.2303(2)
C(2)	0.6521(3)	0.3485(2)	0.2311(2)
C(3)	0.5675(3)	0.2647(2)	0.2315(2)
C(4)	0.6146(3)	0.1646(2)	0.2223(2)
C(5)	0.7478(3)	0.1470(2)	0.2222(2)
C(11)	0.5440(3)	0.3162(3)	0.5220(2)
C(12)	0.3940(3)	0.2059(2)	0.4123(2)
C(13)	0.4593(3)	0.4102(2)	0.3836(2)
C(21)	0.8897(3)	0.2840(2)	0.5257(2)
C(22)	0.8484(3)	0.4552(3)	0.4298(2)
C(23)	1.0356(3)	0.3060(3)	0.3929(2)
C(31)	0.6870(3)	0.0704(2)	0.5146(2)
C(32)	0.8814(3)	0.0179(2)	0.4114(2)
C(33)	0.6238(3)	−0.0243(2)	0.3729(2)
C(101)	0.8791(3)	0.4157(2)	0.2161(2)
C(501)	0.8111(3)	0.0485(2)	0.2017(2)
N(1)	0.8286(2)	0.2322(2)	0.2217(1)
B(1)	0.7933(3)	−0.2909(3)	0.3156(2)
F(1)	0.9156(2)	−0.3277(1)	0.2987(1)
F(2)	0.7693(2)	−0.2037(2)	0.2717(1)
F(3)	0.7866(2)	−0.2704(2)	0.3960(1)
F(4)	0.7062(2)	−0.3662(2)	0.2948(1)

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 4Å molecular sieves and then distilled over sodium (toluene), sodium/potassium alloy and benzophenone (benzene), sodium and benzophenone (diethyl ether, THF), or calcium hydride (pentane, 40/60 petroleum ether, heptane, dichloromethane) under a slow continuous stream of dinitrogen. Perdeuterated solvents for NMR spectroscopy were deoxygenated and then dried over calcium hydride (dichloromethane) or potassium (benzene and toluene). Activated, neutral, Brockmann I, standard grade, ~ 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. NMR spectra were recorded on a Bruker AM (^1H, ^{13}C and ^{31}P NMR spectra were recorded at 300.13, 75.5, and 121.6 MHz, respectively). The spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances and measured relative to TMS (^1H and ^{13}C; $\delta = 0$ ppm), or referenced externally to $BF_3 \cdot Et_2O$ (^{11}B; $\delta = 0$ ppm), $CFCl_3$ (^{19}F; $\delta = 0$ ppm) or 85% H_3PO_4 (^{31}P; $\delta = 0$ ppm). All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hertz. 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 mass spectra were obtained by the EPSRC Mass Spectrometry Service Centre. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer in the range 400 cm^{-1} to 4000 cm^{-1}. Samples were either prepared as Nujol mulls between KBr plates, as KBr discs or as dilute solutions in a solution cell with KBr windows: all data given are in wavenumbers (cm^{-1}). Elemental analyses were performed by the Oxford Analytical Laboratory.

3.1. Synthesis of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PMe_3)_3]$ (**1**)

The complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (210 mg, 0.68 mmol) was stirred for 12 h in 3 mL neat PMe_3 at room temperature. The resulting red–brown solution was evaporated to dryness, extracted into pentane and crystallised at −80°C to give dark red crystals. Yield, 230 mg (79%).

3.2. Synthesis of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPh_2H)_3]$ (**2**)

The complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (830 mg, 2.68 mmol) was dissolved in 5 mL neat PPh_2H and stirred for 24 h at room temperature. The resulting red mixture was brought onto alumina and a column chromatography at −25°C was carried out to separated unreacted PPh_2H ligand from **2**. The free ligand was eluted with light petroleum (b.p. 40/60). Further elution with a mixture of light petroleum (40–60°C)/Et_2O (1/1) afforded a red fraction, from which complex **2** was obtained as a bright red, microcrystalline solid after removal of the solvent in vacuo. Yield, 1.6 g (78%).

3.3. Synthesis of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPhMe_2)_3]$ (**3**)

A solution of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (430 mg, 1.39 mmol) in 5 mL neat $PPhMe_2$ was stirred for 18 h at room temperature. The resulting red mixture was brought onto alumina and separated by column chromatography at −25°C. Excess $PPhMe_2$ was removed with a mixture of light petroleum (40–60°C)/Et_2O (5/1) and further elution with Et_2O/THF (9/1) gave a red fraction from which the volatiles were removed under reduced pressure to leave a red oily residue. Extraction into THF and precipitation with an excess of pentane yielded a bright red, microcrystalline solid. Yield, 510 mg (59%).

3.4. Synthesis of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2P(C_6H_5)_2]_3)]$ (**4**)

A mixture of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (0.4 g, 1.29 mmol) and triphos (1 g, 1.6 mmol) in 10 mL toluene was heated at 80°C for 15 h. The dark red solution was evaporated to dryness and the resulting oily residue was purified by column chromatography on alumina at −25°C. Unreacted triphos was removed with light petroleum (40–60°C)/Et_2O (1/1). Further elution with Et_2O/THF (9/1) afforded a red band, from which complex **4** was isolated as a red oil after evaporation of the solvent in vacuo. The resulting oily residue was triturated with pentane to give an intense bright red, microcrystalline solid. Yield, 590 mg (55%).

3.5. Synthesis of $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(PMe_3)_3][BF_4]$ (**5**)

To a deep red solution of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PMe_3)_3]$ (200 mg, 0.46 mmol) in 50 mL Et_2O a solution of $HBF_4 \cdot Et_2O$ (85%) (0.07 mL, 0.46 mmol) was added at −78°C to give a beige precipitate. After the mixture was warmed to room temperature, the colourless supernatant was decanted off and the resulting residue was dried in vacuo. The solid was washed with Et_2O and crystallisation at −80°C from a concentrated solution of THF yielded dark red crystals. Yield: 180 mg (75%).

3.6. Synthesis of $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(PPh_2H)_3][BF_4]$ (**6**)

The complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPh_2H)_3]$ (66 mg, 0.09 mmol) in 25 mL Et_2O was treated with $HBF_4 \cdot Et_2O$ (85%) (0.015 mL, 0.09 mmol) at −30°C to give an orange precipitate. The mixture was warmed to room temperature, the supernatant decanted off and the resulting residue was dried in vacuo to give a red, microcrystalline solid. Yield, 74 mg (96%).

3.7. Synthesis of $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(PPhMe_2)_3][BF_4]$ (**7**)

A solution of complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPhMe_2)_3]$ (240 mg, 0.39 mmol) in 50 mL Et_2O was cooled to −30°C and treated with $HBF_4 \cdot Et_2O$ (85%) (0.06 mL, 0.39 mmol) to give a beige precipitate. The suspension was warmed to room temperature, the supernatant decanted off and the residue dried under reduced pressure. The resulting solid was extracted into

THF and pentane was added until the precipitation of **7** was completed. The pale red supernatant was filtered off and the remaining orange, microcrystalline solid was dried in vacuo. Yield, 260 mg (94%).

3.8. Synthesis of $[Mo(\eta^6\text{-}HNC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2P(C_6H_5)_2]_3)][BF_4]$ (**8**)

Complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(CH_3C[CH_2P(C_6H_5)_2]_3)]$ (70 mg, 0.08 mmol) was dissolved in 50 mL Et_2O and treated with $HBF_4 \cdot Et_2O$ (85%) (0.012 mL, 0.08 mmol) at −30°C to give a pink precipitate. The reaction mixture was warmed to room temperature, the colourless supernatant was filtered off and the residue dried under reduced pressure. The resulting filtrate was washed with pentane and dried in vacuo to yield an intense pink, microcrystalline solid. Yield, 70 mg (96%).

3.9. Synthesis of $[Mo(\eta^6\text{-}H_3BNC_5H_3Me_2\text{-}2,6)(PPh_2H)_3]$ (**9**)

To a red solution of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPh_2H)_3]$ (200 mg, 0.26 mmol) in 50 mL Et_2O a THF solution of $BH_3 \cdot THF$ (1M, 0.26 mL, 0.26 mmol) was added at −10°C. The mixture was warmed to room temperature and light petroleum (40–60°C) was added until the precipitation of **9** was completed. The supernatant was decanted off and the resulting orange, microcrystalline solid was dried under reduced pressure. Yield, 160 mg (80%).

3.10. Synthesis of $[Mo(\eta^6\text{-}H_3BNC_5H_3Me_2\text{-}2,6)(PPhMe_2)_3]$ (**10**)

The complex $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(PPhMe_2)_3]$ (150 mg, 0.24 mmol) in 50 mL Et_2O was treated with a THF solution of $BH_3 \cdot THF$ (1M, 0.5 mL, 0.5 mmol) at room temperature to give an orange precipitate. After 2 h of additional stirring light petroleum (40–60°C) was added until the precipitation of **10** was completed. The supernatant was filtered off and the resulting orange, microcrystalline solid dried in vacuo. Yield, 140 mg (92%).

3.11. Crystal structure determination of complex **2** and **5**

Crystal data for **2**: $C_{43}H_{42}MoNP_3$, $M = 761.67$, triclinic, $a = 10.270(2)$, $b = 10.364(3)$, $c = 18.823(1)$ Å, $\alpha = 96.32(2)$, $\beta = 105.34(1)$, $\gamma = 103.72(1)°$, $U = 1844.9$ Å^3, space group $P1$, $Z = 2$, Mo-Kα ($\lambda = 0.71069$ Å), $D_c = 1.37$ g cm^{-3}, $\mu = 5.05$, $F(000) = 788$, $T = 120$ K. Crystal dimensions $0.15 \times 0.20 \times 0.30$ mm^3. Of the 8052 reflections measured, total unique data 5085, 4406 were unique with $I > 3\sigma(I)$. The structure was solved by the Patterson method. Hydrogens were included in the calculation but were not refined. The final $R = 3.95$, $R_w = 4{,}54\%$ for 445 least-square parameters.

Crystal data for **5**: $C_{16}H_{37}BF_4MoNP_3$, $M = 519.1$, monoclinic, $a = 10.513(5)$, $b = 13.133(5)$, $c = 16.879(3)$ Å, $\beta = 90.78(4)$, $U = 2330.2$ Å^3, space group $P2_1/c$, $Z = 4$, Mo-Kα ($\lambda = 0.71069$ Å), $D_c = 1.48$ g cm^{-3}, $\mu = 7.84$, $F(000) = 1072$, $T = 120$ K. Crystal dimensions $0.20 \times 0.20 \times 0.33$ mm^3. Of the 10091 reflections measured, total unique data 3625, 3015 were unique with $I > 3\sigma(I)$. The structure was solved by the Patterson method, to final $R = 3.09$, $R_w = 3.56\%$ for 239 least-square parameters. The H(1) hydrogen was refined in the least squares analysis and the remaining hydrogens were placed geometrically. Corrections for Lorentz and polarization effects as well as empirical correction for absorption [18] were applied. Crystallographic calculations were carried out using the CRYSTALS program package [19] on Micro VAX 3800 computer. Neutral atom scattering factors were taken from the usual sources [20]. Hydrogen atom coordinates, thermal parameters, and complete lists of remaining bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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