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Synthesis and structure of the first η^6-pyrazine complex $[V(\eta^6\text{-Me}_4\text{pyrazine})_2]$ and related studies *

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Abstract

The synthesis of vanadium and molybdenum complexes derived from nitrogen-containing heterocyclic aromatic ligands are described. The first η-pyrazine sandwich complex, $[V(\eta^6\text{-Me}_4\text{pyrazine})_2]$, has been prepared by metal vapour synthesis and crystallographically characterized. The synthesis of $[Mo(\eta^6\text{-2,6-lutidine})_2]$ has been substantially improved, and provides a convenient starting material for the preparation of the new half-sandwich compounds $[Mo(\eta^6\text{-2,6-lutidine})(PMe_3)_3]$ and $[Mo(\eta^6\text{-2,6-lutidine})(\eta^3\text{-allyl})Cl]_2$.

1. Introduction

Wucherer and Muetterties reported the synthesis of [M(2,6-lutidine)$_2$] complexes (M = Ti, V, Cr, Mo) using metal vapour synthesis techniques [1]. Here we describe some reactions of the molybdenum compound $[Mo(\eta^6\text{-2,6-lutidine})_2]$ and the synthesis of the first example of an η^6-Me$_4$pyrazine derivative, namely the sandwich compound $[V(\eta^6\text{-Me}_4\text{pyrazine})_2]$.

2. Results and discussion

Co-condensation of Me$_4$pyrazine with vanadium atoms at −196°C gave a dark yellow matrix which darkened upon warming to room temperature. After careful separation of the excess Me$_4$-pyrazine ligand from the reaction mixture, crystallization of the remaining material gave moderately air-sensitive crystals of $[(\eta^6\text{-Me}_4\text{pyrazine})_2V]$ (**1**) in a 4% yield.

Elemental analysis supports the proposed formulation of **1** as $[V(\eta^6\text{-Me}_4\text{pyrazine})_2]$ and the mass spectrum of **1** showed clean peaks for $(\text{Me}_4\text{pyr})_2V^+ (m/e = 323)$; and $\text{Me}_4\text{pyr}^+ (m/e = 136)$. This 17-electron complex gave an ESR spectrum in toluene with the expected eight-line pattern (^{51}V, $I = 7/2$, 100%). To confirm the solid state structure of **1** a single crystal X-ray diffraction study was carried out. Suitable crystals were grown by slow cooling of a solution of **1** in light petroleum ether.

The compound **1** crystallizes in the noncentrosymmetric monoclinic crystal system with space group $P2_1$. The molecular structure together with atomic labelling scheme is shown in Fig. 1 and selected bond lengths and angles are given in Tables 1 and 2, and the positional parameters are given in Table 3. The results of the X-ray analysis confirm the molecular composition proposed on the basis on the elemental microanalytical and spectroscopic data.

The X-ray structure shows that the tetramethylpyrazine ligand is bonded to the vanadium in an η^6-fashion. The V–C distances range from 2.191(5) to 2.211(4) Å with a mean of 2.200(4) Å. The V–N distances are shorter ranging from 2.110(4) to 2.118(4) with a mean of 2.112(4) Å. The differing V–C and V–N bond lengths results in a significant folding of the six-membered ring along the N(1)–N(2) and N(3)–N(4) vectors, respectively. The angles between the normals to the the least square planes defined by N(1), C(1), C(2),

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* Dedicated to Professor E.O. Fischer on the occasion of his 75th birthday.

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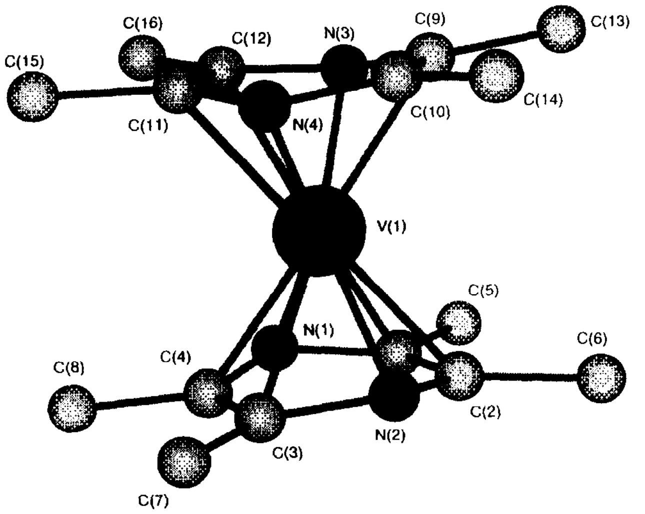


Fig. 1. Molecular structure of 1.

TABLE 1. Selected intramolecular distances for $[V(\eta\text{-}N_2C_4(Me)_4)_2]$ (1); e.s.d. s are given in parentheses

V(1)-N(1)	2.110(4)	N(3)-C(9)	1.394(6)
V(1)-N(2)	2.110(4)	N(3)-C(12)	1.379(6)
V(1)-N(3)	2.118(4)	N(4)-C(10)	1.390(5)
V(1)-N(4)	2.113(4)	N(4)-C(11)	1.391(6)
V(1)-C(1)	2.191(5)	C(1)-C(2)	1.372(7)
V(1)-C(2)	2.198(5)	C(1)-C(5)	1.522(6)
V(1)-C(3)	2.202(4)	C(2)-C(6)	1.490(7)
V(1)-C(4)	2.199(4)	C(3)-C(4)	1.381(6)
V(1)-C(9)	2.205(3)	C(3)-C(7)	1.516(6)
V(1)-C(10)	2.211(4)	C(4)-C(8)	1.529(7)
V(1)-C(11)	2.203(5)	C(9)-C(10)	1.389(8)
V(1)-C(12)	2.194(4)	C(9)-C(13)	1.495(7)
N(1)-C(1)	1.394(7)	C(10)-C(14)	1.515(6)
N(1)-C(4)	1.389(6)	C(11)-C(12)	1.394(8)
N(2)-C(2)	1.413(6)	C(11)-C(15)	1.500(7)
N(2)-C(3)	1.390(6)	C(12)-C(16)	1.523(6)

TABLE 2. Selected intramolecular angles for $[V(\eta\text{-}N_2C_4(Me)_4)_2]$ (1); e.s.d. are given in parentheses

N(2)-V(1)-N(1)	84.1(2)	C(10)-V(1)-C(4)	109.4(2)
N(3)-V(1)-N(1)	151.2(2)	C(10)-V(1)-C(9)	36.7(2)
N(3)-V(1)-N(2)	104.1(2)	C(11)-V(1)-C(3)	152.7(2)
N(4)-V(1)-N(1)	102.8(2)	C(11)-V(1)-C(4)	120.4(2)
N(4)-V(1)-N(2)	151.1(1)	C(11)-V(1)-C(9)	77.3(2)
N(4)-V(1)-N(3)	83.4(2)	C(11)-V(1)-C(10)	64.9(2)
C(1)-V(1)-N(1)	37.8(2)	C(12)-V(1)-C(3)	169.8(2)
C(1)-V(1)-N(2)	68.1(2)	C(12)-V(1)-C(4)	153.0(2)
C(1)-V(1)-N(3)	119.5(2)	C(12)-V(1)-C(9)	65.0(1)
C(1)-V(1)-N(4)	132.6(2)	C(12)-V(1)-C(10)	76.8(2)
C(2)-V(1)-N(1)	68.6(2)	C(12)-V(1)-C(11)	37.0(2)
C(2)-V(1)-N(2)	38.2(2)	C(1)-N(1)-V(1)	74.3(3)
C(2)-V(1)-N(3)	100.7(2)	C(4)-N(1)-V(1)	74.7(2)
C(2)-V(1)-N(4)	168.7(2)	C(4)-N(1)-C(1)	115.5(4)
C(2)-V(1)-C(1)	36.4(2)	C(2)-N(2)-V(1)	74.2(2)
C(3)-V(1)-N(1)	68.1(2)	C(3)-N(2)-V(1)	74.8(2)
C(3)-V(1)-N(2)	37.5(2)	C(3)-N(2)-C(2)	116.5(4)
C(3)-V(1)-N(3)	133.4(2)	C(9)-N(3)-V(1)	74.6(2)
C(3)-V(1)-N(4)	119.0(2)	C(12)-N(3)-V(1)	74.3(2)
C(3)-V(1)-C(1)	76.7(2)	C(12)-N(3)-C(9)	116.9(5)
C(3)-V(1)-C(2)	65.6(2)	C(10)-N(4)-V(1)	75.1(2)
C(4)-V(1)-N(1)	37.5(2)	C(11)-N(4)-V(1)	74.7(2)
C(4)-V(1)-N(2)	68.1(2)	C(11)-N(4)-C(10)	116.8(4)
C(4)-V(1)-N(3)	169.7(2)	N(1)-C(1)-V(1)	68.0(3)
C(4)-V(1)-N(4)	100.2(2)	C(2)-C(1)-V(1)	72.0(3)
C(4)-V(1)-C(1)	64.8(2)	C(2)-C(1)-N(1)	122.7(4)
C(4)-V(1)-C(2)	77.6(2)	C(5)-C(1)-V(1)	131.9(4)
C(9)-V(1)-N(1)	168.8(2)	C(5)-C(1)-N(1)	113.1(5)
C(9)-V(1)-N(2)	100.8(2)	C(5)-C(1)-C(2)	124.1(5)
C(9)-V(1)-N(3)	37.5(2)	N(2)-C(2)-V(1)	67.5(2)
C(9)-V(1)-N(4)	68.1(2)	C(1)-C(2)-V(1)	71.5(3)
C(9)-V(1)-C(1)	153.5(2)	C(1)-C(2)-N(2)	119.7(4)
C(9)-V(1)-C(2)	121.3(3)	C(6)-C(2)-V(1)	130.8(4)
C(10)-V(1)-N(1)	132.3(2)	C(6)-C(2)-N(2)	114.9(4)
C(10)-V(1)-N(2)	119.4(2)	C(6)-C(2)-C(1)	125.3(4)
C(10)-V(1)-N(3)	67.8(2)	N(2)-C(3)-V(1)	67.6(2)

N(2) and N(1), C(3), C(4), N(2) is 14.5° and between the planes defined by N(3), C(9), C(10), N(4) and N(3), C(11), C(12), N(4) is 13.9°. The vanadium–nitrogen bond distances are comparable to those in $[(\eta^6\text{-lutidine})_2V]$ (2) [1]. The $V\text{–}N_2C_4(Me)_{4(centroid)}$ distances are 1.67(4) and 1.68(4) Å. The angle between the normals to these planes {N(1), N(2), C(1), C(2), C(3), C(4) and N(3), N(4), C(9), C(10), C(11), C(12)} is 179.2°. The rings are twisted by 43.0° relative to each other. The internal mean C–C bond length and C–N bond lengths are 1.384(7)(6) Å and 1.392(6) Å, respectively. The average C–Me bond length is 1.511(8) Å.

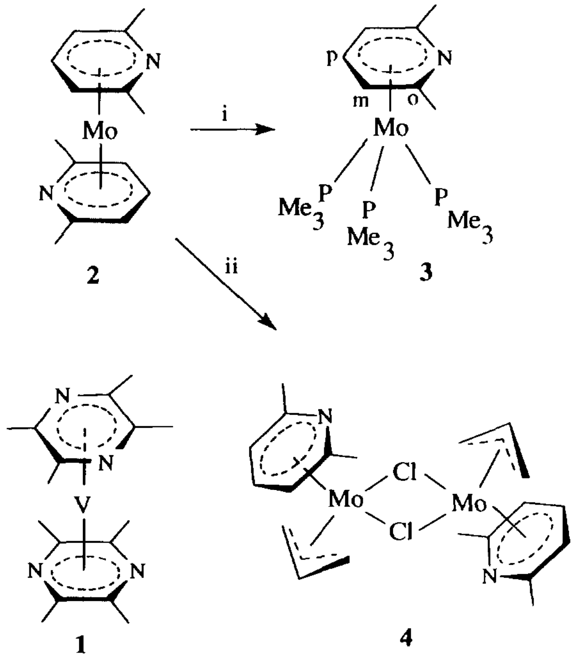
The π-bonding of the η^6-Me_4pyrazine ligand in **1** is unique since in all other cases reported the Me_4pyrazine ligand has been shown to bind through the nitrogen atoms. For example, the Me_4pyrazine ligand has played an important role in linking mixed-valence "Creutz-Taube" type complexes [2]. Attempts to obtain a cyclic voltammogram of **1** in THF using $Bu_4N^+PF_6^-$ as a supporting electrolyte were unsuccessful and chemical oxidation using $AgBF_4$ in THF led to decomposition and release of the Me_4pyrazine ligand. Compound **1** is inert towards ligand displacement by neat PMe_3 at ambient temperatures.

The original preparation of $[Mo(\eta^6\text{-2,6-lutidine})_2]$ (**2**) *via* co-condensation of molybdenum atoms with an excess of 2,6-lutidine reported a yield of 8%. We repeated this reaction using our bell-jar reactor [3] supported by a turbomolecular pump and co-condensed molybdenum atoms (2.9 g) with 2,6-lutidine over a period of 6 h. The reaction mixture was extracted with light petroleum ether, filtered over Celite at −50°C and, after removal of volatiles under reduced pressure, the residue was extracted with light petroleum ether giving $[Mo(\eta^6\text{-2,6-lutidine})_2]$ (**2**) in 39% yield (3.7 g). In the light of this substantially improved yield, we have made preliminary studies of the chemistry of $[Mo(\eta^6\text{-2,6-lutidine})_2]$ (**2**).

Treatment of $[Mo(\eta^6\text{-2,6-lutidine})_2]$ (**2**) with neat trimethylphosphine at room temperature gave orange, air-sensitive $[Mo(\eta^6\text{-2,6-lutidine})(PMe_3)_3]$ (**3**) in 88% yield crystallization. Spectroscopic data for **3** (see

TABLE 2 (*continued*)

C(10)–V(1)–C(2)	153.8(2)	C(7)–C(3)–V(1)	132.2(3)
C(11)–V(1)–N(1)	99.7(2)	C(7)–C(3)–N(2)	114.0(4)
C(11)–V(1)–N(2)	169.7(2)	C(7)–C(3)–C(4)	124.7(4)
C(11)–V(1)–N(3)	68.1(2)	N(1)–C(4)–V(1)	67.8(2)
C(11)–V(1)–N(4)	37.5(2)	C(3)–C(4)–V(1)	71.8(3)
C(11)–V(1)–C(1)	109.2(2)	C(3)–C(4)–N(1)	121.4(4)
C(11)–V(1)–C(2)	134.5(2)	C(8)–C(4)–V(1)	129.6(3)
C(12)–V(1)–N(1)	118.9(2)	C(8)–C(4)–N(1)	115.0(4)
C(12)–V(1)–N(2)	133.0(2)	C(8)–C(4)–C(3)	123.3(4)
C(12)–V(1)–N(3)	37.2(2)	N(3)–C(9)–V(1)	67.8(2)
C(12)–V(1)–N(4)	68.1(2)	C(10)–C(9)–V(1)	71.9(2)
C(12)–V(1)–C(1)	104.2(2)	C(10)–C(9)–N(3)	120.5(4)
C(12)–V(1)–C(2)	108.9(2)	C(13)–C(9)–V(1)	130.7(4)
C(4)–V(1)–C(3)	36.6(2)	C(13)–C(9)–N(3)	115.1(6)
C(9)–V(1)–C(3)	109.7(2)	C(13)–C(9)–C(10)	124.3(4)
C(9)–V(1)–C(4)	135.2(2)	N(4)–C(10)–V(1)	67.5(2)
C(10)–V(1)–C(3)	104.4(2)	C(9)–C(10)–V(1)	71.5(2)
C(9)–C(10)–N(4)	121.2(4)		
C(14)–C(10)–V(1)	132.6(3)		
C(14)–C(10)–N(4)	114.9(4)		
C(14)–C(10)–C(9)	123.8(4)		
N(4)–C(11)–V(1)	67.7(2)		
C(12)–C(11)–V(1)	71.2(3)		
C(12)–C(11)–N(4)	120.2(4)		
C(15)–C(11)–V(1)	131.6(3)		
C(15)–C(11)–N(4)	114.9(4)		
C(15)–C(11)–C(12)	124.9(4)		
N(3)–C(12)–V(1)	68.4(2)		
C(11)–C(12)–V(1)	71.9(2)		
C(11)–C(12)–N(3)	121.6(4)		
C(16)–C(12)–V(1)	132.3(4)		
C(16)–C(12)–N(3)	115.0(5)		
C(16)–C(12)–C(11)	123.4(5)		



Scheme 1. (i) Pure PMe_3 at room temperature for 12 h, 88%. (ii) Allyl chloride in toluene, 0°C, for 30 min, then room temperature 12 h, 52%.

Experimental section) are supportive of the structure shown in Scheme 1. The ^1H NMR spectrum of **3** shows that the resonances assignable to the aromatic protons on the coordinated lutidine ligand are shifted substantially upfield from those in the free ligand (δ 3.81 (m) and 3.68 (m) ppm in **2**; δ 7.00 (t, $J(HH) = 7.6Hz$) and 6.56 (d, $J(HH) = 7.6Hz$) for free 2,6-lutidine in C_6D_6). This upfield shift is also apparent in the $^{13}C(^1H)$ NMR; δ 103.0, 73.0 and 68.2 ppm in **2**; δ 157.5, 136.3 and 120.0 ppm for free 2,6-lutidine in C_6D_6 Complex **3** is analogous to other known $[Mo(\eta^6\text{-arene})(PR_3)_3]$ complexes [4]. However, we note that $[Mo(\eta^6\text{-benzene})_2]$ does not react readily with PMe_3 in contrast to the mild conditions required for the formation of **3** from **2**. The compound **3** is thermally stable towards substitution of the η^6-2,6-lutidine ligand, however, photolysis of a solution of **2** in C_6D_6 in a sealed NMR tube showed the appearance of free 2,6-lutidine, and addition of PMe_3 to **2** in benzene gives $[Mo(PMe_3)_6]$ after irradiation at room temperature. Treatment of **2** with carbon monoxide causes rapid displacement of both lutidine ligands giving molybdenum hexacarbonyl in essentially quantitative yield.

Treatment of **2** in toluene at 0°C with allyl chloride gave an immediate colour change from deep brown-orange to purple, from which a dark purple crystalline compound was isolated in 52% yield. The latter is formulated as the dimer $[Mo(\eta^6\text{-}2,6\text{-lutidine})(\eta^3\text{-allyl})Cl]_2$ (**4**) on the basis of the ^1H NMR spectrum and microanalytical results (see Experimental section), and by analogy with $[Mo(\eta^6\text{-benzene})(\eta^3\text{-allyl})Cl]_2$ [5].

TABLE 3. Fractional atomic coordinates for $[V(\eta\text{-}N_2C_4(Me)_4)_2]$ (**1**); e.s.d. are given in parentheses

Atom	x	y	z	U_{eq} [a]
V(1)	0.69794(6)	0.0994(2)	0.30291(7)	0.0326
N(1)	0.8512(4)	0.1353(3)	0.5236(5)	0.0466
N(2)	0.6367(4)	−0.0389(3)	0.4470(5)	0.0420
N(3)	0.6488(4)	0.0428(3)	0.0476(4)	0.0444
N(4)	0.6556(4)	0.2619(3)	0.1922(4)	0.0394
C(1)	0.8900(5)	0.0279(4)	0.4697(6)	0.0440
C(2)	0.7876(5)	−0.0576(4)	0.4295(6)	0.0445
C(3)	0.6066(5)	0.0577(4)	0.5369(5)	0.0418
C(4)	0.7114(5)	0.1430(4)	0.5738(5)	0.0412
C(5)	1.0539(5)	0.0184(6)	0.4507(8)	0.0670
C(6)	0.8193(6)	−0.1706(5)	0.3580(8)	0.0638
C(7)	0.4496(5)	0.0618(5)	0.5803(7)	0.0583
C(8)	0.6790(6)	0.2559(5)	0.6566(6)	0.0594
C(9)	0.5184(4)	0.0943(6)	0.0826(4)	0.0410
C(10)	0.5221(5)	0.2030(4)	0.1520(5)	0.0387
C(11)	0.7775(5)	0.2201(4)	0.1244(5)	0.0405
C(12)	0.7729(4)	0.1114(6)	0.0537(5)	0.0443
C(13)	0.3816(6)	0.0219(5)	0.0488(7)	0.0588
C(14)	0.3861(5)	0.2639(5)	0.1972(6)	0.0546
C(15)	0.9103(6)	0.2977(5)	0.1429(7)	0.0635
C(16)	0.9035(6)	0.0578(5)	−0.0174(7)	0.0653

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

3. Experimental details

All manipulations and reactions were carried out using either standard Schlenk-vessel and vacuum-line techniques under an atmosphere of dinitrogen, which had been purified by passage over MnO (or a BASF catalyst) and 4-Å molecular sieves, or in a dry-box containing dinitrogen.

Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentoxide (dichloromethane) potassium (tetrahydrofuran), sodium (toluene, triglyme), sodium–potassium alloy (1:3 w/w) (light petroleum (b.p. 40–60°C) diethyl ether pentane). Deuterated solvents (Aldrich) for NMR studies were stored in Young's ampoules under an atmosphere of dinitrogen over sodium/potassium alloy ([^{2}H$_6$] benzene) or dried using calcium hydride (CD_2Cl_2) and transfered by vacuum distillation.

Proton, ^{13}C and ^{31}P spectra were recorded using a Brüker AM 300 (^{1}H 300 MHz, ^{13}C 75.5 MHz, ^{31}P 121.6 MHz). Spectra were referenced internally using residual protio solvent resonances (^{1}H and ^{13}C) relative to tetramethylsilane ($\delta = 0$ ppm) or externally using trimethylphosphate in D$_2$O(^{31}P). All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t-triplet, m = multiplet), coupling constant, relative integration and assignment).

Elemental analyses were performed by the Microanalytical Department of this laboratory and are expressed as found (required) in % w/w/.

3.1. Synthesis of [V(η^6-1,4-Me$_4$C$_4$N$_2$)$_2$] (1)

Vanadium metal (1.8 g, 35.3 mmol), 40 g of tetramethylpyrazine and light petroleum ether (b.p. 40–60°C) (50 ml) were co-condensed over 2 h onto the wall of a liquid-nitrogen cooled glass bell-jar. During the co-condensation, a yellow matrix developed. The matrix was allowed to warm to room temperature, after which it was washed from the glass jar into a receiving flask using THF. The washings were filtered through Celite and the filtrate was concentrated. The remaining solid was extracted into light petroleum ether (40–60°C), filtered through Celite, and upon concentration of the filtrate to *ca.* 20 ml white crystals of excess tetramethylpyrazine formed. The solution was decanted from the tetramethylpyrazine and the solvent was removed under reduced pressure. The remaining excess ligand was sublimed from the residue at 40°C at 10^{-1} Torr. The residual dark solid was extracted into petroleum ether (40–60°C) and after filtration the filtrate was cooled slowly to −80°C giving black crystals of **4**. Yield: 415 mg, 1.28 mmol, 4%. Found: C, 58.82; H, 7.91; N. 16,85. Anal. $C_{16}H_{24}N_4V$ calcd.: C, 59.37; H, 7.42; N, 17.3%. Mass spectrum: (*m/e*) 323 (P$^+$ and base); 136 ([P–C$_8$H$_{12}$N$_2$V]$^+$).

3.2. Synthesis of [Mo(η^6-2,6-(CH$_3$)$_2$C$_5$H$_3$N)$_2$] (2)

A modification of the previously published method [1] was used. Molybdenum metal (2.93 g, 30.5 mmol) and pure 2,6-lutidine (200 cm^3) were co-condensed onto the surface of a glass bell-jar which was cooled by liquid nitrogen. A black matrix developed over a 6-h period. The matrix was allowed to warm to room temperature and was then washed from the reaction vessel using petroleum ether (40–60°C) (*ca.* 1.5 l). The extract was filtered through a Celite bed at −50°C and the filtrate was evaporated to dryness *in vacuo*. The residue was extracted with petroleum ether (40–60°C, 2 × 500 cm^3), filtered through a Celite bed at −50°C and the filtrate concentrated to 200 cm^3. The latter was cooled to −80°C giving orange-brown needle crystals which were isolated and dried *in vacuo*. Yield: 3.7 g, 39%.

3.3. Synthesis of [Mo(η^6-2,6-(CH$_3$)$_2$C$_5$H$_3$N)(PMe)$_3$] (3)

The compound [(η^6-2,6-lutidine)$_2$Mo] (**2**) (330 mg, 1.06 mmol) was treated with pure PMe$_3$ (*ca.* 2 cm^3). The dark-orange solution was stirred at room temperature for 12 h, during which time the mixture gradually turned bright-orange. The volatile materials were removed *in vacuo*, leaving an orange solid. This was extracted with petroleum ether (40–60°C, 20 cm^3) and filtered. The filtrate was concentrated and cooled to −80°C giving orange, air-sensitive crystals of **3**. Yield: 400 mg, 0.93 mmol, 88%. ^{1}H NMR data (in ^{2}H$_6$-benzene): δ 1.193 (m, 27H, P*Me* $_3$); 2.35 (s, 6H, ring-*Me*); 3.68 (m, 2H, H_{m}); 3.81 (m. 1H, H_{p}). ^{13}C{^{1}H} NMR (in ^{2}H$_6$-benzene); δ 103.09 (s, C_o); 73.09 (s, C_{p}); 68.04 (s, C_{m}); 26.98 (m, P*Me* $_3$), 23.93 (s, ring-*Me*). ^{31}P{^{1}H} NMR (in ^{2}H$_6$-benzene); δ 6.33. Mass spectrum: *m/e* 432 (P$^+$), 356 ([P–PMe$_3$]$^+$). Found: C, 44.14; H, 8.27; N, 3.25. $C_{16}H_{36}MoNP_3$ calcd. C, 44.55; H, 8.41; N, 3.25%.

3.4. Synthesis of [Mo(η^6-2,6-lutidine)(η^3-C$_3$H$_5$)Cl]$_2$ (4)

The compound [Mo(η^6-2,6,-lutidine)$_2$] (**2**) (280 mg, 090 mmol) in toluene (*ca.* 30 cm^3) at 0°C was treated with pure allyl chloride (3 cm^3) in a dropwise manner. The initially dark orange solution changed to dark purple. The reaction mixture was allowed to stand at 0°C for 30 min and was then warmed to room temperature. The reaction mixture was kept at room temperature for 12 h after which time purple crystals and brown precipitate had separated. The solution was filtered and the volatiles were removed under reduced pressure. The residue was extracted into toluene and the extract was filtered. The filtrate was cooled to −20°C giving air-stable purple crystals (300 mg). Concentration of the mother liquor followed by cooling to −80°C gave another 30 mg of **3**. Overall yield: 130 mg, 0.23 mmol, 52%. ^1H NMR data (in $^2H_6$-benzene): δ 1.85 (s, 6H, ring-*Me*); 2.27 (d, J(HH) = 6Hz, C_3H_5); 2.71 (*d*, J(HH) = 10.8Hz, C_3H_5); 3.40 (m, 2H, H_p); 4.09 (m, 1H, H_m); 5.12 (m, C_2H_5). Anal. Found: C, 42.98; H, 5.17; Cl, 12.61; N, 4.71. $C_{11}H_{14}MoNCl$ calcd.: C, 42.95; H, 5.06; Cl. 12.68; N. 5.01%.

3.5. *Crystal structure determination*

Crystals of **1** were sealed under nitrogen in Lindemann glass capillaries.

Crystal data: $Vn_4C_{16}H_{24}$, $M = 323.33$, monoclinic, $a = 9.071(3)$, $b = 11.748(5)$, $c = 17.950(2)$ Å, $U = 3837.4$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P2_1$, $Z = 2$, $p_c = 1.28$ g cm^{-3}. Black rectangular air-sensitive tablets. Crystal dimensions $0.3 \times 0.5 \times 1.0$ mm^3, μ(Mo Kα) = 5.72 cm^{-1}, $F(000) = 342$.

Data collection and processing: CAD4 diffractometer, ω–2θ mode with scan width $= 0.8 + 0.35\tan\theta$, scan speed 1.0–6.6° min^{-1}, graphite-monochromated Mo Kα radiation; 2120 unique reflections measured ($1.50 \leq \theta^0 \leq 25$, h, k, ± 1) (merging $R = 0.030$ after absorption correction), giving 1550 with $I \geq 3\sigma(I)$. Linear and approx, isotropic crystal decay, *ca.* 1%, corrected during processing. Correction for Lorentz and polarization effects [6].

Structure analysis and refinement: Direct methods (V atom) followed by normal heavy-atom procedures. Full matrix least-squares refinement with vanadium, nitrogen and carbon atoms with anisotropy thermal parameters. Hydrogens placed in calculated positions (C–H 1.0 Å) and allowed to ride on their attached carbons. Corrections for anomalous dispersion and isotropic extinction [7] were made in the final cycles of refinement. A two term Chebysev weighting scheme [8] was applied with coefficients 2.85, 0.66. Final R and R_w values of 0.039 and 0.0397. Final residual electron density < 2.5 e Å^{-3}. Atomic scattering factors and anomalous dispersion coefficients were taken from ref. 9.

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References

1 E.J. Wucherer and E.L. Muetterties, *Organometallics, 6* (1987) 1691.
2 C. Creutz, *Prog. Inorg. Chem. 30* (1983) 1.
3 F.G.N. Cloko and M.L.H. Green, *Chem. Soc., Dalton Trans.*, (1981) 1938.
4 R.H. Morris and J.M. Ressner *J. Chem. Soc., Chem. Commun.*, (1983) 909.
5 M.L.H. Green and W.E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, (1973) 301.
6 A.C.T. North, D.C. Philips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
7 A.C. Larson, *Acta Crystallogr., 23* (1967) 664.
8 J.R. Carruthers and D.J. Watkin, *Acta Crystallogr., Sect. A, 35*, (1979) 698.
9 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974, p. 99.