

Preliminary communication

Severe distortion of π -allyl orientation in a Molybdenum complex containing a sterically demanding ligand: Crystal structure of Hydrotris(3,5-dimethylpyrazolyl)borato-(π -cinnamyl)-dicarbonyl molybdenum(II) ^{*}

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Received 23 March 1994; in revised form 29 June 1994

Abstract

Steric interaction between a terminal allyl substituent and the proximal 3-methyl group of the pyrazole can result in a severe distortion of the π -allyl orientation, as diagnosed by the downfield chemical shift of the central proton of the allyl group and confirmed by the X-ray crystal structure of a π -cinnamyl complex of molybdenum containing hydrotris-(3,5-dimethylpyrazolyl)borate ligand.

Keywords: Molybdenum; Allyl; Pyrazole; Crystal structure; Nuclear magnetic resonance

1. Introduction

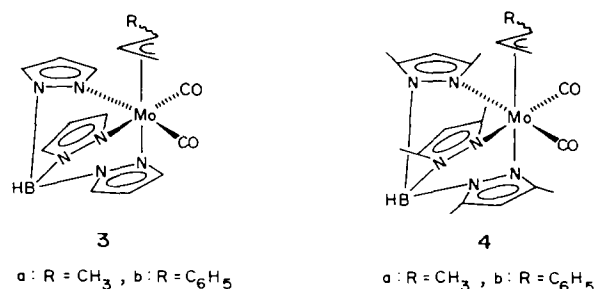
Molybdenum π -allyl complexes containing polypyrazolyl ligands have been well-studied [1]. The complexes usually featured unsubstituted or centrally substituted allyl groups presumably for simplicity of analysis of structural data. However, in the context of possible utilisation in organic synthesis, it is also important to investigate the conformation of complexes containing terminal allyl substituents [2]. In this report, we describe the preparation, characterisation and conformational study of a set of structurally related molybdenum π -allyl complexes containing tripyrazolylborate **1** and tris(3,5-dimethylpyrazolyl) borate **2** ligands. It is observed that the terminal substituents of the allyl ligand can have severe unfavourable steric interaction with the 3-methyl group of pyrazole, resulting in considerable distortion of the π -allyl orientation from normal position. This paper describes the first structural char-

acterisation of Mo(II) complexes containing a distorted π -allyl group.

2. Discussion

Using crotyl chloride and cinnamyl chloride, four complexes were prepared [1a] (Scheme 1) and characterised.

The complexes were purified by chromatography followed by crystallisation, and isolated as yellow to

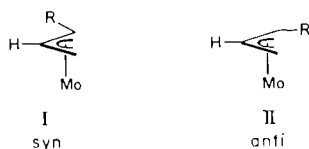


Scheme 1.

^{*} NCL Communication no. 5971.

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orange-red, air-stable, crystalline solids soluble in common organic solvents. Their IR spectra were consistent with two *cis* CO ligands, and a B–H stretch. For complexes **4a** and **4b**, derived from **2**, the typical C=N absorption was observed. Since **1** and **2** are symmetrical, only two conformations are to be considered.



For complexes **3a** and **4a**, these two conformations can be significant, but, the *anti*-CH₃ (conformation-II) is destabilised by an allylic strain. For complexes **3b** and **4b**, only conformation I is significant. Conformation II is substantially destabilised on account of severe allylic strain.

In the absence of any substituent on the 3-position of pyrazole, steric interaction between the ligand and the allyl group is minimal. Thus, for complex **3a**, the only conformer observed in solution had a *syn*-methyl group (conformation I). It appeared as a doublet at 2.05 ppm and the corresponding methine proton appeared at 2.25 ppm.

The ¹H NMR spectrum of complex **3b** displayed peaks corresponding to a single conformer in which the phenyl group is oriented *syn* to the central proton of the allyl group (conformation I). The two *anti* protons appeared at 1.40 ppm and 3.25 ppm, while the central allyl proton multiplet appeared at 4.30 ppm. The broadening of the pyrazole signals indicated a slow *trigonal twist* involving the tridentate ligand [1g].

The situation was distinctly different for complexes **4a** and **4b**, in which the pyrazoles contained 3- and 5-methyl substituents. In particular, the 3-methyl substituents which shield the metal against kinetic decomposition, also reside close to the terminal substituents on the allyl group. In the case of complex **4a**, an equilibrium was observed in solution because of inter-conversion of conformers I and II. In the latter, the steric interaction between the 3-methyl group on the pyrazole and the methyl group of the crotyl moiety is absent, but an allylic 1,3-strain is present. The ¹H NMR spectra (Fig. 1) reveal that the relative conformational population varied as the solution of the sample was allowed to age over a period of time (15 days). The product obtained from chromatography in the form of a yellow powder clearly had the conformer I as the predominant one. On heating this sample in benzene under reflux for 12 h, the conformer I could be observed as the major component in a 1:2 mixture. The doublet at 2.25 ppm (*J* = 6 Hz) was attributed to the *syn*-methyl (conformer I) and the doublet emerging at 1.20 ppm was assigned to the *anti*-methyl (conformer II) of the crotyl group. The corresponding me-

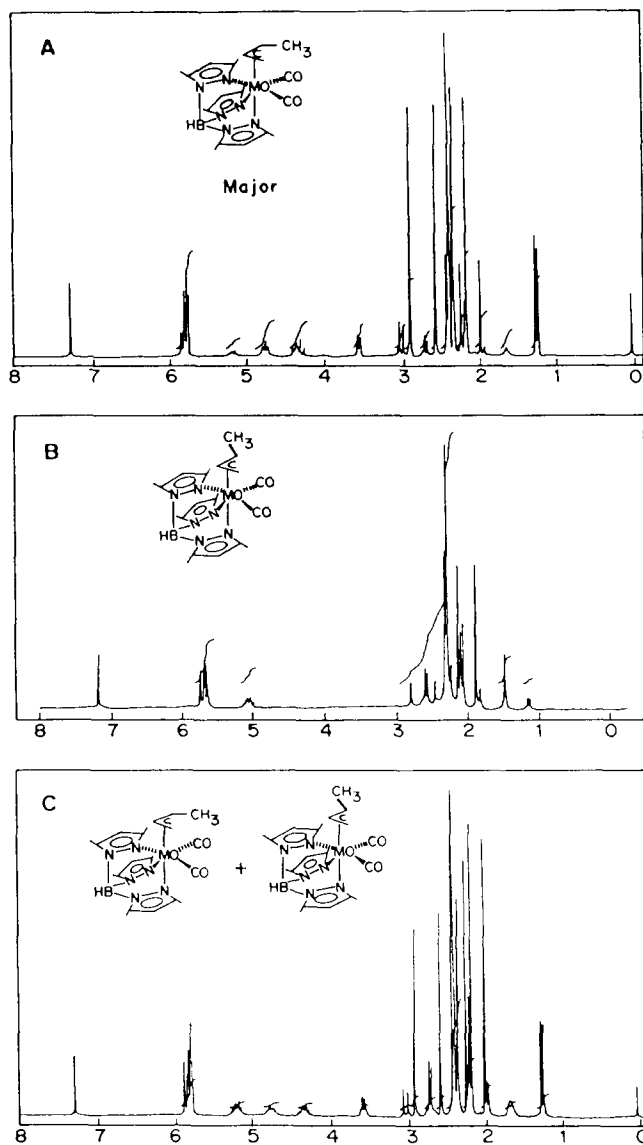
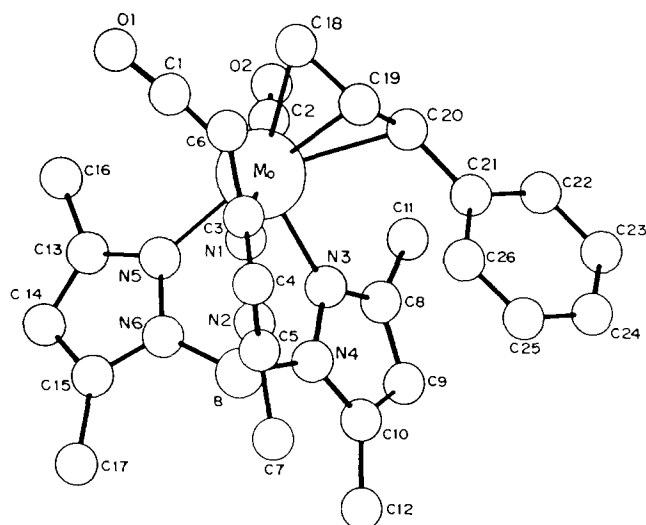


Fig. 1. ¹H NMR spectrum of complex **4a**: (A) crystallised sample; (B) isolated after chromatography; and, (C) sample after 15 days.

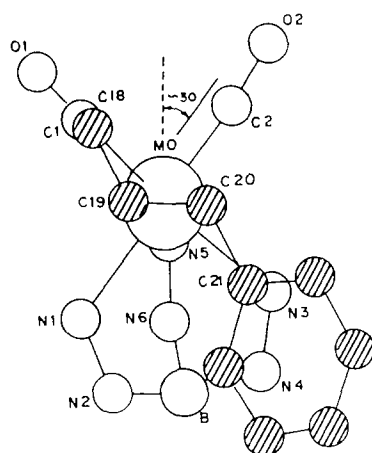
thine multiplets were located at 2.70 ppm and 4.70 ppm respectively. The assignment of peaks to individual conformers was confirmed by a 2D COSY spectrum.

Attention must be drawn to an important feature which concerned the chemical shift of the central allyl proton in the two conformers of **4a**. For conformer I, it appeared at 5.20 ppm, while for conformer II the signal appeared at 4.30 ppm. The difference was considerable. The central allyl proton of the *syn* conformer was significantly deshielded compared to corresponding signals in other complexes of this series.

While the ¹H NMR signals of **4b** [3] were sharp and revealed the presence of only one conformer, the downfield shift of the central allyl proton (5.40 ppm) was immediately noticed. Though Templeton reported



(a)



(b)

Fig. 2. (a) PLUTO diagram of complex **4b**. (b) Distortion of the allyl group.

the NMR data for this complex earlier [3], nothing unusual about the chemical shift of the central allyl proton was mentioned. With this set of compounds and other known complexes [1], it is now possible to define the normal region of central allyl proton absorption as 3.70–4.30 ppm, compared to which, a chemical shift greater than 5.40 ppm is a significant deviation. To ascertain the structural integrity of **4a** and **4b** which featured unusually deshielded central allyl proton, X-ray structure determination of complex **4b** was undertaken. The PLUTO diagram is displayed in Fig. 2. The positional parameters, bond lengths and bond angles are given in Tables 1–3 respectively. The overall structure was indeed as expected.

Table 1
Atomic coordinates

Atom	x	y	z
MO	0.24535(6)	0.84866(4)	0.11283(4)
B	0.3077(8)	0.6604(5)	0.1317(4)
O1	0.4843(5)	0.9638(3)	0.0969(3)
O2	0.1901(6)	0.9695(3)	0.2409(4)
N1	0.2979(5)	0.7596(3)	0.0168(3)
N2	0.2916(5)	0.6837(3)	0.0376(3)
N3	0.1377(5)	0.7553(3)	0.1743(3)
N4	0.1737(5)	0.6802(3)	0.1634(3)
N5	0.4207(5)	0.7877(3)	0.1948(3)
N6	0.4286(5)	0.7089(3)	0.1847(3)
C1	0.3953(7)	0.9217(4)	0.0998(4)
C2	0.2083(7)	0.9219(4)	0.1937(4)
C3	0.3130(7)	0.7602(5)	-0.0632(4)
C4	0.3115(8)	0.6872(5)	-0.0924(4)
C5	0.2991(7)	0.6390(4)	-0.0295(4)
C6	0.3378(9)	0.8334(5)	-0.1059(4)
C7	0.2886(9)	0.5539(5)	-0.0281(5)
C8	0.0356(7)	0.7532(4)	0.2181(4)
C9	0.0027(7)	0.6776(4)	0.2311(4)
C10	0.0911(7)	0.6332(4)	0.1986(4)
C11	-0.0279(8)	0.8217(4)	0.2477(5)
C12	0.1039(9)	0.5474(5)	0.1978(6)
C13	0.5331(6)	0.8078(4)	0.2525(4)
C14	0.6134(7)	0.7444(4)	0.2793(4)
C15	0.5458(7)	0.6833(4)	0.2365(4)
C16	0.5613(8)	0.8881(4)	0.2834(5)
C17	0.5856(8)	0.5998(5)	0.2426(6)
C18	0.1829(8)	0.9465(4)	0.0114(5)
C19	0.0837(8)	0.8859(4)	-0.0057(4)
C20	-0.0064(7)	0.8747(5)	0.0454(4)
C21	-0.1066(7)	0.8077(5)	0.0326(4)
C22	-0.2342(8)	0.8170(5)	0.0551(5)
C23	-0.3304(8)	0.7568(6)	0.0454(5)
C24	-0.2992(9)	0.6885(6)	0.0139(5)
C25	-0.1743(8)	0.6781(5)	-0.0079(5)
C26	-0.0799(8)	0.7366(5)	0.0005(4)

Table 2
Bond distances

Mo–N(1)	2.327(5)	C(3)–C(4)	1.352(11)
Mo–N(3)	2.275(5)	C(3)–C(6)	1.492(11)
Mo–N(5)	2.207(5)	C(4)–C(5)	1.344(11)
Mo–C(1)	1.986(7)	C(5)–C(7)	1.481(12)
Mo–C(2)	1.915(7)	C(8)–C(9)	1.377(10)
Mo–C(18)	2.353(7)	C(8)–C(11)	1.469(10)
Mo–C(19)	2.309(7)	C(9)–C(10)	1.347(10)
Mo–C(20)	2.518(7)	C(10)–C(12)	1.495(11)
B–N(2)	1.554(9)	C(13)–C(14)	1.370(9)
B–N(4)	1.546(9)	C(13)–C(16)	1.486(10)
B–N(6)	1.556(9)	C(14)–C(15)	1.360(10)
O(1)–C(1)	1.145(8)	C(15)–C(17)	1.499(10)
O(2)–C(2)	1.165(8)	C(18)–C(19)	1.419(11)
N(1)–N(2)	1.365(8)	C(19)–C(20)	1.347(11)
N(1)–C(3)	1.336(8)	C(20)–C(21)	1.508(11)
N(2)–C(5)	1.351(8)	C(21)–C(22)	1.385(11)
N(3)–N(4)	1.371(7)	C(21)–C(26)	1.385(12)
N(3)–C(8)	1.344(8)	C(22)–C(23)	1.394(13)
N(4)–C(10)	1.357(8)	C(23)–C(24)	1.352(15)
N(5)–N(6)	1.380(7)	C(24)–C(25)	1.356(13)
N(5)–C(13)	1.332(8)	C(25)–C(26)	1.360(11)
N(6)–C(15)	1.346(8)		

Table 3
Bond angles

N(3)–Mo–N(5)	76.59(18)	N(1)–C(3)–C(6)	121.3(7)
N(3)–Mo–C(1)	157.44(23)	C(4)–C(3)–C(6)	128.8(6)
N(3)–Mo–C(2)	90.06(23)	C(3)–C(4)–C(5)	108.3(6)
N(3)–Mo–C(19)	105.34(24)	N(2)–C(5)–C(4)	106.4(7)
N(5)–Mo–C(1)	82.63(23)	N(2)–C(5)–C(7)	123.0(7)
N(5)–Mo–C(2)	98.19(24)	C(4)–C(5)–C(7)	130.6(7)
N(5)–Mo–C(19)	160.85(23)	N(3)–C(8)–C(9)	109.4(6)
C(1)–Mo–C(2)	84.3(3)	N(3)–C(8)–C(11)	124.3(6)
C(1)–Mo–C(19)	97.2(3)	C(9)–C(8)–C(11)	126.3(6)
C(2)–Mo–C(19)	100.8(3)	C(8)–C(9)–C(10)	107.1(6)
N(2)–B–N(4)	110.6(5)	N(4)–C(10)–C(9)	108.1(6)
N(2)–B–N(6)	108.0(6)	N(4)–C(10)–C(12)	122.4(6)
N(4)–B–N(6)	107.2(5)	C(9)–C(10)–C(12)	129.5(6)
N(2)–N(1)–C(3)	105.5(5)	N(5)–C(13)–C(14)	110.2(6)
B–N(2)–N(1)	119.5(5)	N(5)–C(13)–C(16)	123.4(6)
B–N(2)–C(5)	129.0(6)	C(14)–C(13)–C(16)	126.4(6)
N(1)–N(2)–C(5)	110.1(5)	C(13)–C(14)–C(15)	106.2(6)
Mo–N(3)–N(4)	117.8(4)	N(6)–C(15)–C(14)	108.7(6)
Mo–N(3)–C(8)	135.8(4)	N(6)–C(15)–C(17)	122.4(6)
N(4)–N(3)–C(8)	106.3(5)	C(14)–C(15)–C(17)	128.9(6)
B–N(4)–N(3)	120.9(5)	Mo–C(19)–C(18)	74.0(4)
B–N(4)–C(10)	129.0(6)	Mo–C(19)–C(20)	82.5(4)
N(3)–N(4)–C(10)	109.0(5)	C(18)–C(19)–C(20)	119.8(7)
Mo–N(5)–N(6)	117.4(3)	C(19)–C(20)–C(21)	121.2(7)
Mo–N(5)–C(13)	136.0(4)	C(20)–C(21)–C(22)	118.1(7)
N(6)–N(5)–C(13)	106.5(5)	C(20)–C(21)–C(26)	124.8(7)
B–N(6)–N(5)	123.1(5)	C(22)–C(21)–C(26)	117.1(7)
B–N(6)–C(15)	127.9(5)	C(21)–C(22)–C(23)	120.6(8)
N(5)–N(6)–C(15)	108.4(5)	C(22)–C(23)–C(24)	119.9(8)
Mo–C(1)–O(1)	176.3(6)	C(23)–C(24)–C(25)	120.2(8)
Mo–C(2)–O(2)	176.2(6)	C(24)–C(25)–C(26)	120.4(8)
N(1)–C(3)–C(4)	109.8(6)	C(21)–C(26)–C(25)	121.6(7)

The structure of the molecule is a distorted octahedron with one pyrazole ligand *trans* to the π -cinnamyl group. Significantly, the phenyl ring is twisted away from the π -allyl plane by about 30°. The π -allyl group itself is distorted in two ways. The benzylic carbon C(20) is more distant from the metal {2.518(7) Å} compared to the other two allyl carbon atoms {distances being Mo–C(19): 2.309(7) Å and Mo–C(18): 2.353(7) Å for C(19) and C(18)}. The bond between C(18) and C(19) is longer {1.419(11) Å} than the bond between C(19) and C(20) {1.347(11) Å}.

A close look at the structure also revealed that the orientation of the π -allyl group was considerably deviated from its usual position. In all the structures of Mo(CO)₂- π -allyl complexes reported to date, the π -allyl group is aligned almost parallel to the CO–Mo–CO fragment [4]. In **4b**, the allyl group was twisted by about 30° around the Mo–allyl axis and the phenyl ring was accommodated between two pyrazole groups. This brought the central allyl proton close to the deshielding region of pyrazole ring anisotropy, which could explain its downfield shift. However, the bond lengths and the distances of the three allyl carbons from the molybdenum atom did not indicate that a π -allyl group was being transformed into a σ -allyl group. It is un-

clear why the phenyl ring moved into a more restrictive environment while a similar twist of the allyl group in the opposite direction would have also alleviated steric strain, and there would not have been any congestion around the phenyl group. The phenyl ring is no longer coplanar with the π -allyl group (the angle between the two planes is about 31°) as is usually observed. Thus, a slippage to η^3 -benzyl from a η^3 -allyl also seems unlikely.

In summary, we have shown that a 3-methyl substituent on the pyrazole of tripyrazolylborate ligands can have substantial steric interaction with the terminal substituent on the allyl group in molybdenum π -allyl complexes leading to a considerable deviation from normal allyl orientation. Such structural distortion in this class of complexes have been unambiguously characterised with the help of X-ray crystal structure for the first time.

3. Experimental details

All experiments were done under argon atmosphere with degassed solvents. Melting points were recorded on Thermonic Campbell melting-point apparatus and are uncorrected. The ¹H and ¹³C NMR spectra in CDCl₃ were recorded on a Bruker AC-200 spectrometer. Elemental analyses were carried out with Carlo-Erba CHNS Analyser (Model EA-1108) by Dr. S.Y. Kulkarni and his group at NCL. Crotyl chloride, cinnamyl chloride [1h] and ligands **1** and **2** [5] were prepared by reported procedures.

3.1. Preparation of complexes **3** and **4**

A typical procedure for the preparation of **3a** is as follows:

Molybdenum hexacarbonyl (0.528 g, 2 mmol) and crotyl chloride (1 ml, excess) were heated under reflux in acetonitrile (20 ml) for 5 h. After cooling the reaction mixture to room temperature, a solution of **1** (0.8 g, 2.5 mmol) in acetonitrile (10 ml) was added with a syringe. Immediate precipitation of the salt was observed. After stirring at room temperature for 5 min, solvent was removed and the residue was chromatographed over flash silica gel under argon with dichloromethane as eluent. A yellow-coloured band was collected. After evaporation of the solvent, **3a** was obtained as a yellow powder which afforded analytically pure, yellow crystals from toluene-hexane.

All the other complexes were similarly prepared and isolated.

3a: Yellow crystals. Yield: 0.52 g, (62%); m.p.: 222°C (decomposition). IR: 2500 (B–H), 1920 (CO), 1830 (CO), 1520 (C=N) cm⁻¹. ¹H NMR: 1.20 (dd, 1 H, *J*_{Ha–Hs} = 3 Hz, *J*_{Ha–Hc} = 9 Hz), 2.05 (d, 3H, *J*_{CH3–Ha} = 6

(Hz), 2.25 (m, 1H), 3.30 (dd, 1H, $J_{\text{Hs-Ha}} = 3$ Hz, $J_{\text{Hs-Hc}} = 6$ Hz), 3.80 (m, 1H), 6.10 (bs, 3H), 7.50 (bs, 3H), 7.95 (bs, 3H). ^{13}C NMR: 18.5, 50.1, 69.9, 80.2, 80.9, 105.1, 135.2, 144.1, 228.5, 231.8. Anal. Found: C, 42.9; H, 4.1; N, 19.6. $\text{C}_{15}\text{H}_{17}\text{MoN}_6\text{O}_2\text{B}$ Calc.: C, 42.9; H, 4.0; N, 20.0%.

3b: Orange crystals. Yield: 72.6%; m.p.: 192°C (decomposition). IR: 2500 (B–H), 1910 (CO), 1830 (CO), 1510 (C=N) cm^{-1} . ^1H NMR: 1.40 (dd, 1H, $J_{\text{Ha-Hs}} = 2$ Hz, $J_{\text{Ha-Hc}} = 9$ Hz), 3.25 (d, 1H, $J_{\text{Ha'-Hc}} = 10$ Hz), 3.50 (dd, 1H, $J_{\text{Hs-Ha}} = 2$ Hz, $J_{\text{Hs-Hc}} = 6$ Hz), 4.30 (m, 1H), 6.10 (bs, 3H), 7.50 (bs, 3H), 8.30 (bs, 3H), 7.0–7.20 (m, 6H). ^{13}C NMR: 47.6, 77.8, 86.0, 105.3, 125.2, 126.9, 127.4, 128.1, 128.4, 128.8, 135.4, 135.9, 145.0, 227.7, 238.8. Anal. Found: C, 50.1; H, 3.95; N, 17.1. $\text{C}_{20}\text{H}_{19}\text{MoN}_6\text{O}_2\text{B}$ Calc.: C, 49.8; H, 3.97; N, 17.4%.

4a: Red crystals. Yield: 57.0%. m.p.: 227°C (decomposition). IR: 2540 (B–H), 1930 (CO), 1810 (CO), 1550 (C=N) cm^{-1} . ^1H NMR: Conformer with *anti*- CH_3 : 1.20 (d, 3H, $J_{\text{CH}_3\text{-Ha'}} = 6$ Hz) 3.05 (d, 1H, $J_{\text{Ha-Hc}} = 10$ Hz) 3.60 (d, 1H, $J_{\text{Hs-Hc}} = 6$ Hz) 4.30 (m, 1H) 4.70 (m, 1H). Conformer with *syn*- CH_3 : 2.0 (d, 1H, $J_{\text{Ha-Hc}} = 10$ Hz) 2.25 (d, 3H, $J_{\text{CH}_3\text{-Ha'}} = 6$ Hz), 2.70 (m, 2H), 5.20 (m, 1H), 2.0 (s, 3H), 2.10 (s, 3H), 2.20 (s, 3H), 2.30 (s, 3H), 2.55 (s, 3H), 2.90 (s, 3H); 5.80 (m, 3H). ^{13}C NMR: 12.6, 12.8, 14.0, 14.5, 14.9, 15.2, 19.8, 64.4, 68.1, 88.9, 106.8, 107.2, 144.1, 150.3, 151.0, 233.6, 234.2. Anal. Found: C, 49.9; H, 5.9; N, 16.5. $\text{C}_{21}\text{H}_{29}\text{MoN}_6\text{O}_2\text{B}$ Calc.: C, 50.0; H, 5.7; N, 16.6%.

4b: Red crystals. Yield: 45%; m.p.: 195°C (decomposition). IR: 2510 (B–H), 1930 (CO), 1820 (CO), 1540 (C=N) cm^{-1} . ^1H NMR: 2.10 (d, 1H, $J_{\text{Ha-Hc}} = 10$ Hz), 2.25–2.55 (Six 3H singlets, 18H), 3.70 (d, 1H, $J_{\text{Hs-Hc}} = 6$ Hz), 4.25 (d, 1H, $J_{\text{Ha'-Hc}} = 9$ Hz), 5.40 (m, 1H), 5.50 (s, 1H), 5.80 (bs, 2H), 6.90–7.10 (m, 5H). ^{13}C NMR: 12.4, 12.5, 12.8, 14.8, 15.4, 15.5, 57.3, 82.3, 89.6, 106.8, 125.9, 127.3, 127.5, 139.2, 144.2, 144.4, 151.9, 230.1, 234.2. Anal. Found: C, 55.1; H, 5.6; N, 14.7. $\text{C}_{26}\text{H}_{31}\text{MoN}_6\text{O}_2\text{B}$ Calc.: C, 55.1; H, 5.4; N, 14.8%.

3.2. Crystal structure determination of **4b**

Dark red crystals of **4b** were grown from toluene-hexane. Data were measured on an Enraf-Nonius CAD-4 diffractometer with Mo– $\text{K}\alpha$ 0.7093 Å radi-

ation at 290 K. $a = 9.794(2)$ Å, $b = 17.360(2)$ Å, $c = 16.213(5)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 102.21^\circ$, $V = 2694.4(1)$ Å³. $Z = 4$, $d_{\text{calc}} = 1.399$ mg/m⁻³, $\mu = 0.51$ mm⁻¹. Crystals were monoclinic, Space group $P2_1/c$. Intensity data were collected for 3865 reflections, ($2\theta_{\text{max}} = 47^\circ$), of which 2457 reflections [$I > 2.5 \sigma(I)$] were significant. The structure was solved by direct method (MULTAN-80) using NRCVAX (PC version) program package for crystal structure solution [6]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealised positions with fixed isotropic temperature factors, and were not refined. Using 325 parameters, $R = 0.045$ and $R_w = 0.040$.

Acknowledgements

The authors wish to thank Dr. S. Rajappa for encouragement and support. The research was funded by the Department of Science and Technology, New Delhi. Two of us (KMS and MN) thank CSIR and UGC, India, for research fellowships.

References

- [1] (a) S. Trofimenko, *J. Am. Chem. Soc.*, **91** (1969) 3183; (b) S. Trofimenko, *Inorg. Chem.*, **9** (1970) 2493; (c) S. Trofimenko, *J. Am. Chem. Soc.*, **92** (1970) 5118. (d) K.R. Breakell, S.J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, **57** (1979) 139; (e) K.B. Shiu, K.S. Liou, C.P. Cheng, B.R. Fang, Y. Wang, G.H. Lee and W.J. Vong, *Organometallics*, **8** (1989) 1219; (f) K.B. Shiu, C.J. Chang, S.L. Wang and F.L. Liao, *J. Organomet. Chem.*, **407** (1991) 225; (g) V.S. Joshi, V.K. Kale, K.M. Sathe, A. Sarkar, S.S. Tavale and C.G. Suresh, *Organometallics*, **10** (1991) 2898; (h) V.S. Joshi, A. Sarkar and P.R. Rajamohanam, *J. Organomet. Chem.*, **409** (1991) 341.
- [2] J.W. Faller, C. Lambert and M.R. Mazzieri, *J. Organomet. Chem.*, **383** (1990) 161.
- [3] C.A. Rusik, M.A. Collins, A.S. Gamble, T.L. Tonker and J.L. Templeton, *J. Am. Chem. Soc.*, **111** (1989) 2550.
- [4] M.D. Curtis and O. Eisenstein, *Organometallics*, **3** (1984) 887.
- [5] (a) S. Trofimenko, *J. Am. Chem. Soc.*, **89** (1967) 3170; (b) S. Trofimenko, *J. Am. Chem. Soc.*, **89** (1967) 6288.
- [6] E.J. Gabe, Y. Le Page, J.P. Charlane and P.S. White, NRCVAX-An interactive program system for structure analysis, *J. Appl. Cryst.*, **22** (1989) 384.