Carbonyl–molybdenum complexes of the hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate ligand

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Abstract

The reaction of KBH_4 with 3 equiv. of 3,5-dimethyl-1,2,4-triazole at ca. 230°C yielded potassium hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate, $K\{HB(Me_2tz)_3\}$. The reaction of $Mo(CO)_6$ and $K\{HB(Me_2tz)_3\}$ in N,N-dimethylformamide at 110°C gave $[\{HB(Me_2tz)_3\}Mo(CO)_3]^-$, which was isolated as the salt $NEt_4[\{HB(Me_2tz)_3\}Mo(CO)_3]$ (1). Crystallographic characterisation of 1 revealed a six-coordinate, distorted octahedral anion composed of a facial, tridentate $HB(Me_2tz)_3^-$ ligand and three mutually *cis* (facial) carbonyl ligands. Spectroscopic data were consistent with greater electron-withdrawal by the triazolylborate ligand than by the related hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand. Reaction of 1 with iodine gave $\{HB(Me_2tz)_3\}Mo(CO)_3I$, which was spectroscopically characterised as a seven-coordinate 3:3:1 face-capped octahedral complex.

Keywords: Molybdenum; Triazolylborate; Tricarbonyl; Crystal structure; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

There is wealth of coordination and organometallic chemistry involving use of the scorpionate N_3-donor hydrotrispyrazolylborate ligands [1–3]. The first ligands of this type, hydrotris(pyrazol-1-yl)borate, $HBpz_3^-$ [4,5], and hydrotris(3,5-dimethylpyrazol-1-yl)borate, $HB(Me_2pz)_3^-$ [6], were reported by Trofimenko in 1966–67. Soon afterwards, he reported the first organometallic complexes of these ligands, including the tricarbonyl-metallate salts $NEt_4[LM(CO)_3]$ (M = Cr, Mo and W) [7]. Over the years, these compounds have proved indispensable precursors for more elaborate organometallic species [1–3]. In the late 1980s, Thompson, Trofimenko and co-workers reported the first of a 'second generation' of hydrotrispyrazolylborate ligands [8–10] and these are now finding important applications in organometallic chemistry [11–13]. In contrast, although a cobalt complex of hydrotris(1,2,4-triazol-1-yl)borate, $HBtz_3^-$, was reported by Trofimenko in 1967 [5], the chemistry of triazolylborate ligands has remained unde-

veloped for many decades. Two features of triazole-based ligands make them attractive candidates for further examination. Firstly, they should be electron-withdrawing relative to their pyrazole-based counterparts and the properties of metal complexes should differ accordingly. For example, $[Mo^VO_2]^+$ complexes of the hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate ligand, $HB(Me_2tz)_3^-$, are easier to prepare and more stable than those of pyrazole-based ligands and this has facilitated the full characterisation of such species [14]. Secondly, the *exo* ring-nitrogen atoms of triazole-based ligands may function as donors or participate in hydrogen-bond interactions leading to supramolecular structures. Recent work by Janiak provides some nice examples of this type of behaviour [15].
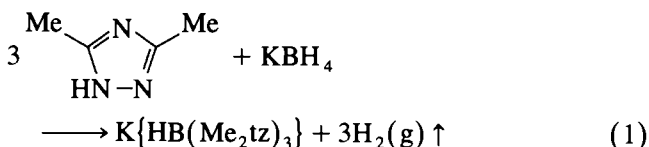
We have developed the high-valent oxo- and thio-molybdenum chemistry of pyrazole- and triazole-based ligands in a quest to model pterin-containing molybdenum enzymes [14,16,17]. We have also initiated a programme of organometallic chemistry aimed at the selective stabilisation or activation of small molecules through changes in N_3-donor coligands. We report here the synthesis and characterisation of $K\{HB(Me_2tz)_3\}$ and the first organometallic compounds of this ligand,

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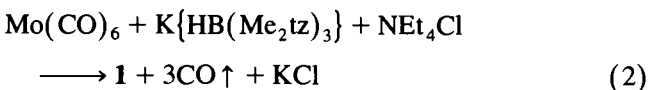viz. $NEt_4[\{HB(Me_2tz)_3\}Mo(CO)_3]$ (1) and $\{HB-(Me_2tz)_3\}Mo(CO)_3I$ (2), along with the crystal structure of 1. During the course of this work, the synthesis and crystal structure of $[N(PPh_3)_2][(HBtz_3)Mo(CO)_3]$ was reported by Shiu et al. [18].

2. Results and discussion

The synthesis of $K\{HB(Me_2tz)_3\}$ uses the strategy employed in the synthesis of potassium hydrotris(1,2,4-triazol-1-yl)borate [5,18] and related pyrazole-based ligands [4–6]. The major difficulty encountered in the synthesis was in the preparation of 3,5-dimethyl-1,2,4-triazole [19–21]. The method described by Jones and Rees [21] was the most convenient of the reported methods but its reproducibility was very poor; the reported yield of 63% was never achieved in our successful syntheses (yields of 0% to 23% were usual). The reaction of 3,5-dimethyl-1,2,4-triazole with potassium borohydride resulted in the stepwise production of 3 equiv. of hydrogen gas and the conversion of BH_4^- to mono-, bis- and ultimately tris-(triazolyl)borates [Eq. (1)].

$$3 \quad \underset{\substack{| \\ HN-N}}{Me \diagdown_N \diagup Me} + KBH_4$$

$$\longrightarrow K\{HB(Me_2tz)_3\} + 3H_2(g)\uparrow \qquad (1)$$

The reaction of $Mo(CO)_6$ with $K\{HB(Me_2tz)_3\}$ in hot N,N-dimethylformamide resulted in decarbonylation and the formation of $K[\{HB(Me_2tz)_3\}Mo(CO)_3]$. Metathesis with NEt_4Cl produced yellow 1 which was recrystallised as a pale yellow, air- and water-stable, diamagnetic, crystalline solid. The overall reaction is shown in Eq. (2). The reaction of $K\{HB(Me_2tz)_3\}$ with $Mo(CO)_3(CH_3CN)_3$ in tetrahydrofuran was slow and did not produce $[\{HB(Me_2tz)_3\}Mo(CO)_3]^-$ in significant amounts. Compound 1 was soluble in acetonitrile, dichloromethane, chloroform, methanol and ethanol, but insoluble in diethyl ether, hexane, tetrahydrofuran, toluene and acetone.

$$Mo(CO)_6 + K\{HB(Me_2tz)_3\} + NEt_4Cl$$

$$\longrightarrow 1 + 3CO\uparrow + KCl \qquad (2)$$

Compound 1 is oxidised by elemental iodine to form the tricarbonyliodo–Mo^{II} complex $\{HB(Me_2tz)_3\}Mo(CO)_3I$, (2) according to Eq. (3):

$$NEt_4[\{HB(Me_2tz)_3\}Mo(CO)_3] + I_2$$

$$\longrightarrow \{HB(Me_2tz)_3\}Mo(CO)_3I + NEt_4I \qquad (3)$$
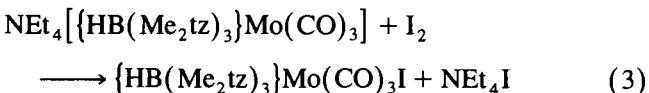
When the reaction was performed in acetonitrile, the product separated and was filtered off. The brown, microcrystalline solid was diamagnetic, moderately air-
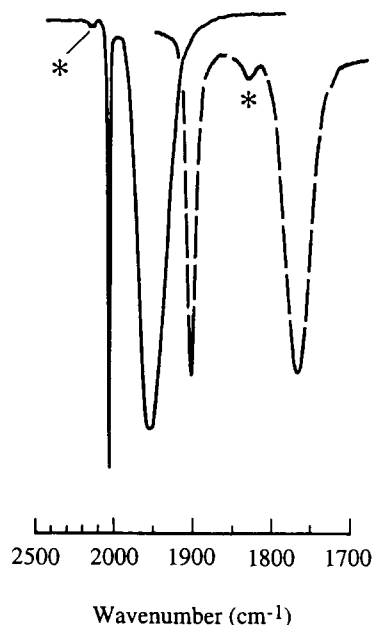

Fig. 1. Solution infrared spectra of 1 (CH_3CN, dashed line) and 2 (CH_2Cl_2, full line). The asterisks indicate solvent peaks.

stable, soluble in dichloromethane and acetonitrile, but insoluble in diethyl ether, hexane and toluene. Gas evolution and decomposition accompanied dissolution of the complex in hot methanol, hot ethanol, acetone and tetrahydrofuran.

The solid state (KBr) infrared spectrum of 1 exhibited a strong, sharp band at 1890 cm^{-1} and a broader, even stronger band at 1745 cm^{-1} which was split by lattice effects. The solution infrared spectrum of 1 showed a similar pattern with bands at 1900 and 1765 cm^{-1}, the latter being broader than the former but not split in the manner observed in the solid-state spectrum (Fig. 1). The two ν(CO) bands are assigned to the a_1 and e modes of the *facial* tricarbonyl–Mo fragment in a C_{3v} anion. Bands characteristic of the $HB(Me_2tz)_3^-$ ligand also featured in the infrared spectra of 1; a medium intensity band at 2520 cm^{-1} and a strong intensity band at 1500 cm^{-1} were assigned to ν(BH) and ν(CN) modes, respectively. The infrared spectrum of $NEt_4[\{HB(Me_2pz)_3\}Mo(CO)_3]$ in acetonitrile exhibited a_1 and e ν(CO) bands at 1891 and 1751 cm^{-1}, respectively. These are lower in energy compared to the ν(CO) bands of 1, consistent with reduced π backbonding in 1 relative to that in $NEt_4[\{HB(Me_2pz)_3\}Mo(CO)_3]$ and the greater electron-withdrawing ability of $HB(Me_2tz)_3^-$ relative to $HB(Me_2pz)_3^-$. The ^1H NMR spectrum of 1 exhibited two methyl resonances assignable to the $HB(Me_2tz)_3^-$ ligand as well as resonances due to the NEt_4^+ cation; the spectrum confirmed the molecular C_{3v} symmetry of the anion (cf. IR analysis). The fast atom bombardment mass spectrum of 1 revealed peak clusters at m/z 742, 613 and 483, which correspond to the $[1 + NEt_4]^+$, $[1 + H]^+$ and $[1 - NEt_4$

+ H]$^+$ cations, respectively. The experimental isotope patterns for these peaks were matched by those calculated for the formulae above.

The solution infrared spectrum of **2** exhibited two ν(CO) bands at 2025 and 1955 cm^{-1} (Fig. 1). These may be attributed to the a_1 and e modes of a tricarbonyl fragment in a complex of C_{3v} symmetry. A structure based on a 3 : 3 : 1 face-capped octahedral geometry is therefore implied. According to the treatment described by Burdett [22], the relative intensities of these bands are related to the γ angle (Fig. 2) by Eq. (4), where I_s and I_a are the intensities of the symmetric and asymmetric ν(CO) modes, respectively.

$$\tan^2\gamma = I_s/I_a \qquad (4)$$

For **2**, a γ angle of 22° was calculated using this treatment. This is consistent with a face-capped octahedral structure in which the carbonyl ligands are splayed away from the C_3 axis by the capping iodo ligand. For six-coordinate [{HB(Me$_2$tz)$_3$}Mo(CO)$_3$]$^-$, the γ angle determined by Eq. (4) was 33°; this value compares well with γ ca. 35° in the solid-state structure of **1**. The solid-state infrared spectrum exhibited several bands at 2050, 1960, 1940 and 1920 cm^{-1}. It is unclear whether this signifies the presence of several isomers or results from solid-state effects. Bands at 2560 cm^{-1} and 1502 cm^{-1} were assigned to the ν(BH) and ν(CN) modes of HB(Me$_2$tz)$_3^-$, respectively. The ^{1}H NMR spectrum of **2** exhibited two singlet resonances consistent with effective C_{3v} symmetry and a 3 : 3 : 1 face-capped octahedral geometry. We have been unable to grow crystals suitable for the X-ray diffraction study needed to define the solid-state structure. Related molybdenum complexes have been synthesised but only (HBpz$_3$)Mo(CO)$_3$Br has been structurally characterised [23]. It exhibits a 3 : 4 piano stool or capped trigonal prismatic structure having C_s symmetry; in solution, three ν(CO) infrared bands consistent with the maintenance of C_s symmetry are
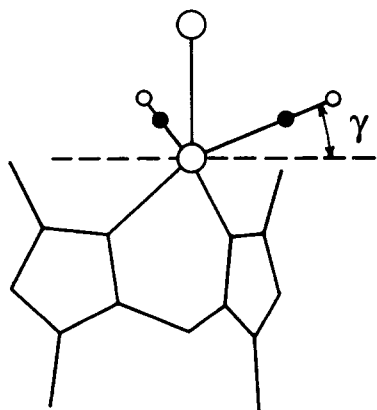
Fig. 2. Definition of the angle γ in **2**. Only the skeleton of the pyrazolylborate ligand is shown in a view perpendicular to a molecular mirror plane containing γ.
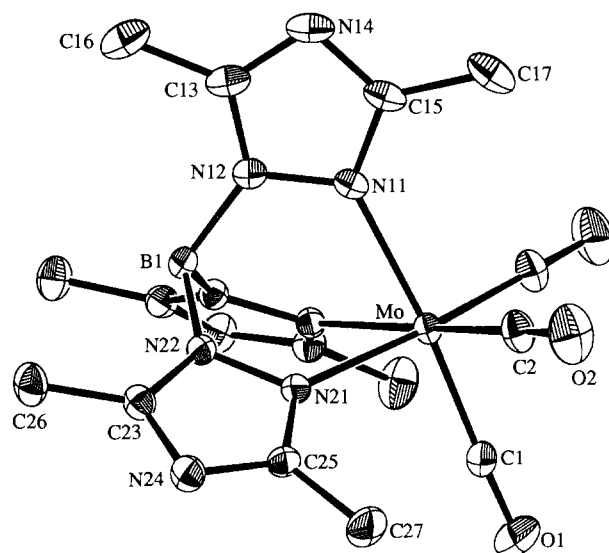
Fig. 3. ORTEP [31] diagram of the anion of **1** showing the numbering scheme employed; the anion possesses crystallographic mirror symmetry.

observed, but fluxionality on the NMR time scale leads to a spectrum typical of a C_{3v} species. The solution infrared spectra of this and related complexes [23] are quite different from that of **2**. Recent work has demonstrated that a 3 : 3 : 1 face-capped octahedral geometry pertains to [{HB(Me$_2$pz)$_3$}W(CO)$_3$(PMe$_3$)]$^+$ and related phosphine complexes [24], but this geometry is still rare in seven-coordinate tricarbonyl species.

A view of the anion of **1** is shown in Fig. 3. Positional parameters and selected interatomic distances and angles are given in Tables 1 and 2, respectively. The crystal is comprised of discrete [{HB(Me$_2$tz$_3$)}Mo(CO)$_3$]$^-$ anions and NEt$_4^+$ cations; the closest non-hydrogen contact in the lattice occurs between the N11 and C6c atoms (3.377(7) Å, symmetry operation: 0.5 + X, − Y, 0.5 + Z). The six-coordinate complex exhibits crystallographically imposed mirror symmetry and a distorted octahedral structure. The coordination sphere is comprised of a facially tridentate HB(Me$_2$tz)$_3^-$ ligand and three mutually *cis* carbonyl groups; indeed, the anion approaches C_{3v} symmetry. The structure is typical of tricarbonyl–molybdenum(0) complexes in general [25], and is exactly analogous to the structures established for NEt$_4$[{HB(Me$_2$pz)$_3$}Mo(CO)$_3$] [26], NEt$_4$[{HB(Mepz)$_3$}Mo(CO)$_3$] [27] [HB(Mepz)$_3^-$ = hydrotris(3-methylpyrazol-1-yl)borate], NEt$_4$[(HBpz$_3$)-Mo(CO)$_3$] [18] and [N(PPh$_3$)$_2$][(HBtz$_3$)Mo(CO)$_3$] [18]. The Mo—C and Mo—N distances in **1** are equal within experimental error to related distances in the aforementioned HBtz$_3^-$ and HB(Me$_2$pz)$_3^-$ complexes. This indicates that any effects of differences in the electronic properties of these tridentate ligands are not observable crystallographically. Further, there appears to be no significant structural differences imposed by the pre-

Table 1
Fractional atomic coordinates for 1

Atom	x	y	z
Mo [a]	0	−0.13898(6)	0.2360
O1 [a]	0	−0.3922(8)	0.3842(3)
O2	−0.1911(4)	0.0539(6)	0.3320(3)
N1c [a]	0	−0.0570(8)	−0.4134(4)
N11 [a]	0	0.0271(6)	0.1217(4)
N12 [a]	0	−0.0384(7)	0.0424(3)
N14 [a]	0	0.2398(8)	0.0285(4)
N21	−0.1277(3)	−0.2831(4)	0.1550(2)
N22	−0.1081(3)	−0.3081(4)	0.0710(2)
N24	−0.2715(3)	−0.4383(5)	0.1000(2)
C1 [a]	0	−0.2989(9)	0.3271(4)
C1c [a]	0	0.1327(11)	−0.4245(7)
C2c [a]	0	0.2014(15)	−0.5104(7)
C2	−0.1181(5)	−0.0173(7)	0.2965(3)
C3c [a]	0	−0.0898(13)	−0.3220(6)
C4c [a]	0	−0.2778(14)	−0.2984(7)
C5c	−0.1035(4)	−0.1398(7)	−0.4557(4)
C6c	−0.2169(5)	−0.0722(11)	−0.4236(7)
C13 [a]	0	0.0904(10)	−0.0113(5)
C15 [a]	0	0.1943(8)	0.1104(5)
C16 [a]	0	0.0721(14)	−0.1035(7)
C17 [a]	0	0.3159(9)	0.1796(6)
C23	−0.1957(4)	−0.4008(6)	0.0407(3)
C25	−0.2255(4)	−0.3625(6)	0.1689(3)
C26	−0.2064(5)	−0.4560(7)	−0.0472(3)
C27	−0.2790(5)	−0.3739(7)	0.2529(3)
B1 [a]	0	−0.2337(10)	0.0291(4)

[a] Atom located on crystallographic mirror plane with site occupancy factor = 0.5.

sumably greater steric requirements of $HB(Me_2tz)_3^-$ relative to $HBtz_3^-$. The charge balance in the structure of 1 is provided by an NEt_4^+ cation, also disposed about a crystallographic mirror plane; there are no abnormal features associated with the cation.

In conclusion, the synthesis and characterisation of 1 and 2 provides an important platform for the develop-

ment of the organometallic chemistry of the hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate ligand. These compounds are likely to constitute important starting materials for future work in this field of chemistry.

3. Experimental details

Unless otherwise stated, all manipulations were performed under purified dinitrogen using standard Schlenk techniques. Solvents were dried, distilled and deoxygenated before use. All other chemicals were obtained from Aldrich Chemical Co. and were laboratory grade or above. Infrared spectra were recorded using Perkin-Elmer 983G or Shimadzu IR-408 spectrophotometers calibrated with polystyrene. ^1H NMR spectra were obtained using a Varian 300 MHz FT NMR spectrometer. Electron-impact (70 eV) and fast atom bombardment mass spectra were obtained on a JEOL JMS-AX505H mass spectrometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA, USA.

3.1. Synthesis of 3,5-dimethyl-1,2,4-triazole

The method used by Jones and Rees [21] was adapted for this synthesis. Under a slow flow of nitrogen, a mixture of acetamide (150 g, 2.54 mol) and hydrazine hydrate (80 g, 1.6 mol) was gently heated at 100°C overnight until ammonia evolution had ceased, and then at 220°C for 4 h during which water distilled from the reaction mixture. Crude 3,5-dimethyl-1,2,4-triazole (b.p. 250–260°C) was obtained as a pale pink liquid by short-path distillation. The solid formed upon cooling was recrystallised from acetone as white crystals in a yield of ca. 28 g, 23%. M.p. 142°C (lit. values: 142°C

Table 2
Selected bond distances (Å) and angles (°) for the anion of 1 [a]

Bond distances					
Mo–C1	1.932(7)	Mo–C2	1.933(5)	Mo–N11	2.256(6)
Mo–N21	2.274(4)	C1–O1	1.176(8)	C2–O2	1.164(6)
N11–N12	1.374(8)	N11–C15	1.333(8)	N12–C13	1.332(9)
N12–B1	1.557(9)	N14–C13	1.34(1)	N14–C15	1.36(1)
N21–N22	1.383(5)	N21–C25	1.314(6)	N22–C23	1.342(6)
N22–B1	1.537(5)	N24–C23	1.329(6)	N24–C25	1.365(6)
C13–C16	1.49(1)	C15–C17	1.47(1)	C23–C26	1.483(7)
C25–C27	1.487(6)				

Bond angles				
C1–Mo–C2′	86.8(2)		C2–Mo–C2′	90.1(3)
C1–Mo–N11	174.7(3)		C1–Mo–N21	96.1(2)
C2–Mo–N11	96.9(2)		C2–Mo–N21	94.3(2)
C2–Mo–N21′	174.8(2)		N11–Mo–N21	80.0(1)
N21–Mo–N21′	81.1(2)		Mo–C1–O1	178.0(6)
Mo–C2–O2	178.5(5)			

[a] The primed atoms are related by mirror symmetry to the atoms labelled in Fig. 3.

[19] and 140°C [21]). IR (KBr) (cm^{-1}): 3300 (s); 3070 (s); 3000–2500 (br); 1605 (m); 1525 (m); 1500 (m); 1460 (s); 1420 (s); 1390 (w); 1380 (w); 1320 (s); 1140 (w); 1075 (s); 1005 (w); 995 (w); 900 (m); 750 (m); 700 (w). ^{1}H NMR (CDCl$_3$)δ: 2.43 (s, 6H, 2 CH$_3$); 9.80 (br, 1H, NH).

3.2. Synthesis of potassium hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borate

3,5-Dimethyl-1,2,4-triazole (41 g, 0.42 mol) and potassium borohydride (4.92 g, 0.091 mol) were finely ground and intimately mixed. The mixture was heated gradually and melted at ca. 140°C with rapid evolution of hydrogen gas. The temperature of the mixture was increased slowly to 230–250°C, and maintained there for 2.5 h with occasional stirring. The melt partly solidified during heating. The mixture was then allowed to cool with stirring sufficient to prevent the formation of a solid mass. The light brown solid was finely ground and the excess of triazole was removed by sublimation for 5 h at 130°C under high vacuum. The yield of cream coloured product was 24.7 g, 79%. IR (KBr) (cm^{-1}): ν(BH): 2500; 1560 (s); 1512 (s); 1410 (br); 1370 (w); 1335 (s); 1220 (s); 1195 (m); 1075 (m), 1040 (m); 1005 (w); 978 (w); 950 (w); 820 (s); 708 (m), 702 (m); 670 (m). ^{1}H NMR (D$_2$O)δ: 1.94 (s, 9H, 3 CH$_3$); 2.09 (s, 9H, 3 CH$_3$).

3.3. Synthesis of tetraethylammonium tricarbonyl{hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borato}molybdate(0) (1)

A suspension of Mo(CO)$_6$ (5.0 g, 18.9 mmol) and K{HB(Me$_2$$^+$2)$_3$} (6.41 g, 18.9 mmol) in N,N-dimethylformamide (100 ml) was heated at 110°C under a flow of nitrogen for 6 h. The solution was evaporated at 60°C under vacuum to ca. 50 ml and then poured into a stirred aqueous solution of NEt$_4$Cl (7 g in 75 ml). The mixture was stirred for 30 min with ice-cooling. The resultant yellow precipitate was filtered off, washed with water (40–50 ml) and dried in vacuo. The crude product was recrystallised from a minimum of hot acetonitrile, filtered off and washed with dichloromethane. The yield was 5.61 g, 49%. Analysis Found: C, 45.15; H, 6.48; N, 23.05%. C$_{23}$H$_{39}$BMoN$_{10}$O$_3$ calc.: C, 45.26; H, 6.44; N, 22.95%. IR (KBr) (cm^{-1}): 2990 (w); 2910 (w); ν(BH): 2520 (m); ν(CO): 1890 (vs) and 1745 (vs); ν(CN): 1500 (m); 1405 (m); 1370 (m); 1350 (w); 1215 (m); 1180 (w); 1060 (m); 820 (w); 790 (w); 715 (w); 705 (w); 660 (w); 640 (w). IR (CH$_3$CN) (cm^{-1}): ν(CO): 1765 and 1900. ^{1}H NMR (CD$_3$OD)δ: 1.28 (tt, 12H, $^3J_{H-H}$ = 7 Hz, $J_{^{14}N-H}$ = 2 Hz, 4 CH$_3$ of NEt$_4^+$); 2.50 (s, 9H, 3 CH$_3$); 2.58 (s, 9H, 3 CH$_3$); 3.29 (q, 8H, $^3J_{H-H}$ = 7 Hz, 4 CH$_2$ of NEt$_4^+$). M.S. m/z (%, most intense peak within cluster): 742 (9.7); 613 (12.3); 483 (40).

3.4. Synthesis of tricarbonyl{hydrotris(3,5-dimethyl-1,2,4-triazol-1-yl)borato}iodomolybdenum(II) (2)

A mixture of 1 (0.5 g, 0.82 mmol) and iodine (0.28 g, 1.64 mmol) in acetonitrile (10 ml) was stirred for 1 h. The precipitate was filtered off, washed with cold methanol and dried under vacuum. The yield of brown crystalline solid was 0.43 g, 88%. Analysis Found: C, 29.81; H, 3.50; N, 19.67%. C$_{16}$H$_{23}$BIMoN$_9$O$_4$ (MeOH solvate) calc.: C, 30.07; H, 3.63; N, 19.73%. IR (KBr) (cm^{-1}): ν(BH): 2560 (m); ν(CO): 2050 (s), 1960 (vs), 1940 (s) and 1920 (s); ν(CN): 1510 (s). IR (CH$_2$Cl$_2$) (cm^{-1}): ν(CO): 2025 and 1955. ^{1}H NMR (CDCl$_3$)δ: 2.39 (s, 9H, 3 CH$_3$); 2.63 (s, 9H, 3 CH$_3$); 3.49 (s, 3H, CH_3OH).

3.5. Crystal structure of 1

Crystals of 1 were grown by slow cooling of a hot saturated solution of the complex in acetonitrile. Intensity data for a pale-yellow crystal (0.11 × 0.19 × 0.48 mm) were collected at room temperature on a Rigaku AFC6R employing Mo K α radiation ($\lambda = 0.71073$ Å) and the ω:2θ scan technique. The 1968 data (θ_{max} 27.5°) were corrected for Lorentz and polarisation effects [28] as well as for absorption employing an empirical procedure [29]; the range of transmission factors was 0.980 to 1.030. A total of 1661 data satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for 1: C$_{23}$H$_{39}$BMoN$_{10}$O$_3$, M = 610.4, orthorhombic, space group Pmn2$_1$, $a = 11.581(5)$, $b = 7.894(3)$, $c = 16.053(8)$ Å; $V = 1467(2)$; $Z = 2$, $D_x = 1.381$ g cm^{-3}, $F(000) = 636$, $\mu = 4.88$ cm^{-1}, $R = 0.031$, $R_w = 0.032$.

The structure was solved by direct methods [30] and refined by a full-matrix least-squares procedure based on F [28]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. The refinement was continued until convergence employing sigma weights [28] with $R = 0.031$ and $R_w = 0.032$. The maximum peak in the final difference map was 0.49 e Å^{-3} and the analysis of variance showed no special features. Fractional atomic coordinates are listed in Table 1, selected interatomic parameters are collected in Table 2 and the crystallographic numbering scheme for the anion in 1 is shown in Fig. 3. Tables of thermal parameters hydrogen atom coordinates, and a complete list of bond distances and angles, have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgment

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