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DIRECT PROOF OF THE REGIOSPECIFIC NATURE OF THE REACTION BETWEEN 1-*H*-3(5)-METHYLPYRAZOLE AND THE TETRAHYDROBORATE(–1) ANION: THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAETHYLAMMONIUM HYDROTRIS(3-METHYLPYRAZOLYL)BORATOTRICARBONYLMOLYBDENUM(0) $[NEt_4][Mo(CO)_3HB(C_4H_5N_2)_3]$

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Summary

Reaction of KBH_4 with three equivalents of 1-*H*-3(5)-methylpyrazole proceeds smoothly at 195–200°C to give a hydrotris(methylpyrazolyl)borate anion (III). The crystal and molecular structure of the tetraethylammonium salt of the tricarbonylmolybdenum complex of III, i.e. $[NEt_4][Mo(CO)_3HB(C_4H_5N_2)_3]$ (IV) has been determined. Crystals of IV are monoclinic, space group $P2_1$ with two molecules in a cell of dimensions a 9.092(2), b 16.265(3), c 9.871(2) Å, β 109.43(2)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0.029$ for 1813 observed reflections. The molybdenum atom has octahedral geometry with the three carbonyl groups *trans* to the three N atoms of the tridentate ligand with principal dimensions: Mo–N 2.281–2.290(5), and Mo–C 1.916–1.934(6) Å. The methyl substituents are located at the 3-positions of the ligand pyrazolyl groups, thus establishing unequivocally the regiospecific nature of the reactions of BH_4^- with 1-*H*-3(5)-methylpyrazole.

Introduction

We have recently demonstrated that the course of the reaction of arenediazonium cations with the hydrotris(pyrazolyl)boratotricarbonylmolybdenum(0) anions, $[Mo(CO)_3HB(C_3H_3N_2)_3]^-$ (I) ($C_3H_3N_2 \equiv$ 1-pyrazolyl), is dramatically altered by the introduction of methyl substituents at the 3- and 5-positions of the ligand pyrazolyl groups [1,2]. In connection with our work in this area we needed to

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prepare an analogue of I with methyl groups on the pyrazolyl 3-carbons only. Recent ^1H NMR and chemical studies [3,4] suggest that BH_4^- reacts at 110°C with 1-*H*-3(5)-methylpyrazole (a tautomeric mixture of 1-*H*-3- and 1-*H*-5-methylpyrazoles) in a regiospecific manner to yield $[H_2B(C_4H_5N_2)_2]^-$ (II) ($C_4H_5N_2 \equiv$ 3-methyl-1-pyrazolyl) as the sole product with no evidence for the formation of the 5-methyl isomer. This conclusion has been rationalised in terms of the avoidance of unfavourable non-bonded interactions in the transition state which would lead to formation of the isomer 5-methyl compound [3]. It seemed likely that a higher reaction temperature would result in the formation of $[HB(C_4H_5N_2)_3]^-$ (III) with the desired orientation of the ligand methyl substituents. Because of the importance of a definite knowledge of the ligand structure in the context of our other work it was considered essential to verify this assumption by X-ray crystallographic methods.

Results and discussion

Gradual heating of a mixture of KBH_4 and 1-*H*-3(5)-methylpyrazole to 195–200°C resulted in the evolution of three moles of H_2 and work-up of the reaction mixture yielded a white microcrystalline solid which analyzed correctly for the potassium salt of anion III. The ^1H NMR spectrum of III (DMSO-d_6, Experimental) shows that the three ligand methylpyrazolyl groups are equivalent but does not in itself establish the ligand structure conclusively. Crystals of the potassium salt were too small for an X-ray crystallographic investigation. The anion was converted into the corresponding tricarbonylmolybdenum complex which was isolated as its tetraethylammonium salt $[NEt_4][Mo(CO)_3HB(C_4H_5N_2)_3]$ (IV). Suitable crystals of this material proved to be readily obtainable. Crystals of IV contain $[NEt_4]^+$ cations and $[Mo(CO)_3HB(C_4H_5N_2)_3]^-$ anions separated by normal Van der Waals distances. A view of the anion with the crystallographic numbering scheme is shown in Fig. 1. The metal atom is six-coordinated by the tridentate $[HB(C_4H_5H_2)_3]^-$ ligand and three carbonyl groups in a distorted octahedral environment. The ligand methyl groups all occupy the 3-positions on the pyrazolyl rings and therefore the regiospecific nature of the reaction of 1-*H*-3(5)-methylpyrazole with BH_4^- is established unambiguously.

Bond distances and bond angles within the anion of IV are listed in Table 1. The Mo–N distances (2.281(5)–2.290(5), mean 2.285(5) Å) are longer than the corre-

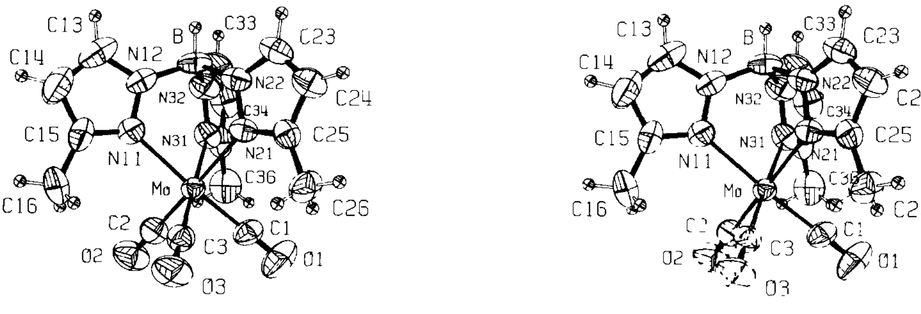

Fig. 1. Stereoview of the anion $[Mo(CO)_3HB(C_4H_5N_2)_3]^-$ with the crystallographic numbering scheme.

TABLE 1

MOLECULAR DIMENSIONS

Bond distances (Å)

Mo–C(1)	1.934(7)	N(1)–C(4)	1.455(13)
Mo–C(2)	1.916(6)	N(1)–C(6)	1.484(12)
Mo–C(3)	1.934(6)	N(1)–C(8)	1.518(12)
C(1)–O(1)	1.155(9)	N(1)–C(10)	1.557(14)
C(2)–O(2)	1.182(7)	C(4)–C(5)	1.617(19)
C(3)–O(3)	1.166(7)	C(6)–C(7)	1.589(19)
		C(8)–C(9)	1.506(18)
		C(10)–C(11)	1.463(19)

	n = 1	*n* = 2	*n* = 3
Mo–N(*n*1)	2.281(5)	2.284(4)	2.290(5)
B–N(*n*2)	1.534(11)	1.523(10)	1.538(10)
N(n1)–N(*n*2)	1.360(7)	1.361(8)	1.369(7)
N(n1)–C(*n*5)	1.340(8)	1.329(9)	1.336(8)
N(n2)–C(*n*3)	1.359(10)	1.352(8)	1.327(9)
C(n3)–C(*n*4)	1.374(13)	1.358(10)	1.335(12)
C(n4)–C(*n*5)	1.377(11)	1.390(9)	1.407(11)
C(n5)–C(*n*6)	1.497(11)	1.480(9)	1.446(12)

Bond angles (°)

C(1)–Mo–C(2)	85.4(4)	Mo–C(1)–O(1)	178.6(7)
C(1)–Mo–C(3)	84.3(3)	Mo–C(2)–O(2)	178.7(9)
C(1)–Mo–N(11)	175.9(3)	Mo–C(3)–O(3)	178.0(5)
C(1)–Mo–N(21)	96.2(3)	N(12)–B–N(22)	109.6(5)
C(1)–Mo–N(31)	96.1(2)	N(12)–B–N(32)	108.2(6)
C(2)–Mo–C(3)	86.2(2)	N(22)–B–N(32)	109.1(6)
C(2)–Mo–N(11)	98.5(3)		
C(2)–Mo–N(21)	176.1(3)	C(4)–N(1)–C(6)	113.3(9)
C(2)–Mo–N(31)	95.1(2)	C(4)–N(1)–C(8)	106.5(8)
C(3)–Mo–N(11)	97.4(2)	C(4)–N(1)–C(10)	113.6(10)
C(3)–Mo–N(21)	97.5(2)	C(6)–N(1)–C(8)	111.0(9)
C(3)–Mo–N(31)	178.6(2)	C(6)–N(1)–C(10)	104.7(8)
N(11)–Mo–N(21)	79.8(3)	C(8)–N(1)–C(10)	107.6(8)
N(11)–Mo–N(31)	82.1(2)	N(1)–C(4)–C(5)	112.2(10)
N(21)–Mo–N(31)	81.2(2)	N(1)–C(6)–C(7)	107.4(11)
		N(1)–C(8)–C(9)	114.1(9)
		N(1)–C(10)–C(11)	117.4(11)

	n = 1	*n* = 2	*n* = 3
Mo–N(*n*1)–N(*n*2)	119.3(4)	119.6(4)	120.3(3)
Mo–N(*n*1)–C(*n*5)	133.6(4)	133.0(5)	132.3(5)
N(*n*2)–N(*n*1)–C(*n*5)	107.1(5)	107.0(4)	107.4(5)
B–N(*n*2)–N(*n*1)	122.2(5)	121.8(5)	120.5(4)
B–N(*n*2)–C(*n*3)	129.4(6)	129.4(5)	130.3(6)
N(*n*1)–N(*n*2)–C(*n*3)	108.3(6)	108.6(5)	108.8(6)
N(*n*2)–C(*n*3)–C(*n*4)	109.1(7)	109.1(5)	109.6(7)
C(*n*3)–C(*n*4)–C(*n*5)	104.8(7)	105.1(6)	106.4(6)
N(*n*1)–C(*n*5)–C(*n*4)	110.7(7)	110.2(6)	107.8(7)
N(*n*1)–C(*n*5)–C(*n*6)	120.7(6)	121.8(5)	122.0(6)
C(*n*4)–C(*n*5)–C(*n*6)	128.5(7)	128.0(6)	130.1(6)

sponding distances reported for the closely related anion $[Mo(CO)_3HB(C_5H_7N_2)_3]^-$ (V) ($C_5H_7N_2 \equiv$ 3,5-dimethyl-1-pyrazolyl) (mean 2.263(6) Å) [5] and for the radical $[Mo(CO)_3HB(C_3H_3N_2)_3]^{\cdot}$ (VI) ($C_3H_3N_2 \equiv$ 1-pyrazolyl) (mean 2.207(7) Å) [6] while the Mo–C distances in the anion of IV (1.916(7)–1.934(6), mean 1.928(6) Å) are shorter than the corresponding distances in the above-mentioned complexes (mean 1.941(8) (V) and 2.013(11) Å (VI)); the mean *trans* N ··· C separation in all the three complexes is, however, identical (4.21(1) Å). In a related but seven-coordinate complex $MoBr(CO)_3HB(C_5H_7N_2)_3$ (VII) [7], wherein Br occupies the seventh coordination site, the Mo–N distances are significantly shortened (range 2.213(5)–2.231(5) Å) with concomitant Mo–C distance lengthening (range 1.957(7)–2.000(8) Å), although the *trans* C ··· N separation is unaffected (mean 4.20(1) Å). Similar effects have been observed in $Mo(\eta^3\text{-COR})(CO)_2HB(C_5H_7N_2)_3$ ($R = C_6H_5CH_3$-*p* or C_6H_{11}) [1] where the sixth coordination site is occupied by the mid-point of the η^2-COR ligand (mean N ··· C 4.19(1) and 4.20(1) Å). The C–O distances and Mo–C–O angles in the anion of IV (1.155–1.182(7), mean 1.168(8) Å and 178.0–178.7(9), mean 178.4(7)°) are comparable to those found in V (mean 1.167(5) Å and 176.6(7)°) [5].

The dimensions of the tridentate hydrotris(3-methylpyrazolyl)borato ligand are unexceptional with mean bond lengths: B–N 1.532(11), N–N 1.363(7), N–C 1.405(9), C_{sp^2}–C_{sp^2} 1.374(11) and C_{sp^3}–C_{sp^2} 1.474(11) Å. The cation, $[NEt_4]^+$ has a fully staggered conformation with mean N–C and C–C bond lengths 1.504(13) and 1.544(19) Å, respectively.

Experimental

Reagents and solvents were commercial samples and were used as received. IR spectra were recorded on a Perkin–Elmer 257 spectrometer calibrated with respect to a standard polystyrene film. ^{1}H NMR spectra were obtained on a Perkin–Elmer Hitachi R20A instrument operating at 60 MHz. Microanalyses were carried out by the staff of the Microanalytical Laboratory of University College, Cork.

Potassium hydrotris(3-methylpyrazolyl)borate (III)

A mixture of 1-*H*-3(5)-methylpyrazole [8] (8.2 g, 0.1 mol) and KBH_4 (1.35 g, 0.025 mol) was heated slowly to 195–200°C and maintained at that temperature until 1.69 l (0.075 mol) of hydrogen had evolved (wet test meter). The mixture was worked up as described by Trofimenko [9] to yield 3.69 g (50.2%) of white microcrystalline $K[HB(C_4H_5N_2)_3]$ (III).

Microanalysis: Found: C, 48.76; H, 5.61; N, 28.29. $C_{12}H_{16}BKN_6$ calcd.: C, 48.97; H, 5.48; N, 28.58%. ^{1}H NMR (DMSO-d_6, Me_4Si); δ 7.22 (doublet, J 1.8 Hz, 3H, 5-(H)); δ 5.77 (doublet, J 1.8 Hz, 3H, 4-(H)); δ 2.09 (singlet, 9H, 3-(CH_3)) ppm (Assignments inferred from data on $K[H_2B(C_4H_5N_2)_2]$ in ref. 3.

Tetraethylammonium hydrotris(3-methylpyrazolyl)boratotricarbonylmolybdenum(0), $[NEt_4][Mo(CO)_3HB(C_4H_5N_2)_3]$ (IV)

The complex was prepared in 91% yield from III and $Mo(CO)_6$ by the general method described by Trofimenko [10]. Microanalysis: Found: C, 48.37; H, 6.33; N, 17.63. $C_{23}H_{36}BMoN_7O_3$ calcd.: C, 48.86; H, 6.42; N, 17.34%. IR (CH_3CN) ν(CO); 1892, 1753 cm^{-1}.

Collection and reduction of X-ray data

Crystals of $[NEt_4][Mo(CO)_3HB(C_4H_5N_2)_3]$ (IV) were grown as pale-yellow prisms from hot acetonitrile. The crystal used for cell constant determination and for intensity data collection had approximate dimensions 0.37 × 0.30 × 0.28 mm. Following machine location and centring of 25 reflections with $10 < \theta < 25°$ on an Enraf Nonius CAD4 diffractometer using monochromatized Mo-K_α radiation, accurate cell parameters and the orientation matrix were obtained by a least-squares refinement. Data were collected to a maximum θ of 22.5° by the $\omega/2\theta$ scan technique. A total of 1869 unique reflections were collected of which 1813 had intensities greater than $3\sigma(I)$ and were used in structure solution and refinement. The intensities of three standard reflections monitored at regular intervals did not change significantly over the period of data collection. The data were corrected for

TABLE 2

FINAL FRACTIONAL COORDINATES ($\times 10^5$ for Mo; $\times 10^4$ for remainder) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Mo	19288(4)	-25000	21620(3)
C(1)	1757(8)	-1328(4)	2413(8)
O(1)	1625(9)	-629(4)	2543(8)
C(2)	451(7)	-2602(7)	3156(6)
O(2)	-461(6)	-2649(5)	3772(6)
C(3)	145(7)	-2341(4)	446(6)
O(3)	-951(5)	-2233(3)	-565(5)
B	5212(8)	-3597(6)	2678(8)
N(11)	2299(6)	-3864(3)	1843(5)
N(12)	3777(6)	-4160(3)	2182(6)
C(13)	3694(11)	-4982(5)	1926(9)
C(14)	2155(13)	-5215(5)	1400(11)
C(15)	1330(8)	-4501(4)	1373(7)
C(16)	-400(8)	-4378(5)	854(10)
N(21)	3812(5)	-2423(5)	1106(4)
N(22)	5072(5)	-2931(3)	1558(6)
C(23)	6112(7)	-2696(4)	922(8)
C(24)	5510(7)	-2056(5)	24(7)
C(25)	4063(6)	-1904(4)	165(6)
C(26)	2894(8)	-1280(5)	-591(7)
N(31)	4077(6)	-2692(3)	4160(5)
N(32)	5265(6)	-3193(4)	4102(5)
C(33)	6406(8)	-3164(6)	5358(8)
C(34)	5988(8)	-2677(6)	6257(7)
C(35)	4503(7)	-2367(5)	5477(6)
C(36)	3504(10)	-1809(6)	5913(8)
N(1)	2368(7)	-4784(4)	6603(6)
C(4)	3872(13)	-4425(9)	6723(16)
C(5)	5068(18)	-4439(11)	8355(17)
C(6)	2448(17)	-5679(7)	6909(14)
C(7)	3389(22)	-6093(10)	5990(18)
C(8)	1292(14)	-4607(8)	5088(11)
C(9)	-257(15)	-5040(12)	4692(13)
C(10)	1610(16)	-4405(9)	7663(13)
C(11)	1299(18)	-3521(10)	7559(16)

Lorentz, polarization factors and for absorption: maximum and minimum values of the transmission coefficient are 0.895 and 0.862 respectively.

Crystal data. $C_{23}H_{36}BMoN_7O_3$, $M_r = 565.34$, monoclinic, a 9.092(2), b 16.265, c 9.871(2) Å, β 109.43(2)°, V 1376.8 Å^3, D_c 1.36 g cm^{-3}, $Z = 2$, $F(000) = 588$, Mo-K_α radiation, λ 0.70926 Å, μ(Mo-K_α) 5.08 cm^{-1}. Space group $P2_1(C_2^2)$ from systematic absences: $0k0$, $k = 2n + 1$.

Solution and refinement of the structure

The structure was solved by the heavy-atom method. Initial refinement by full-matrix least-squares calculations [11] with isotropic temperature factors for the

TABLE 3

THERMAL PARAMETERS [a] ($\times 10^3$) (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	37(1)	40(1)	39(1)	−1(1)	10(1)	2(1)
C(1)	71(4)	51(5)	59(3)	−1(3)	30(3)	12(3)
O(1)	154(6)	52(4)	107(4)	−2(3)	59(4)	18(3)
C(2)	55(3)	66(6)	49(2)	15(4)	16(2)	3(4)
O(2)	71(3)	121(6)	81(3)	20(4)	43(2)	11(3)
C(3)	51(3)	52(5)	52(3)	1(3)	19(3)	1(3)
O(3)	53(2)	105(5)	60(2)	14(2)	−8(2)	13(2)
B	48(4)	70(5)	69(4)	11(4)	11(3)	28(4)
N(11)	54(3)	49(3)	51(3)	0(2)	15(2)	3(3)
N(12)	66(3)	45(3)	69(3)	4(2)	22(3)	16(3)
C(13)	116(7)	56(4)	90(5)	9(4)	40(5)	34(5)
C(14)	126(7)	45(4)	111(6)	−5(4)	55(6)	−4(4)
C(15)	82(4)	42(4)	70(4)	−9(3)	27(3)	−12(3)
C(16)	66(4)	77(5)	117(6)	−17(5)	22(4)	−31(4)
N(21)	39(2)	53(3)	45(2)	0(3)	11(2)	5(3)
N(22)	39(2)	65(3)	60(3)	−4(2)	15(2)	8(2)
C(23)	42(3)	82(6)	72(4)	−9(3)	24(3)	3(3)
C(24)	55(4)	88(5)	58(4)	−1(4)	26(3)	2(3)
C(25)	50(3)	56(3)	47(3)	−5(3)	19(2)	−7(3)
C(26)	80(4)	64(4)	63(4)	22(3)	32(3)	15(3)
N(31)	47(2)	69(5)	42(2)	1(2)	7(2)	−5(2)
N(32)	46(3)	82(4)	51(3)	12(3)	5(2)	9(3)
C(33)	51(4)	114(6)	68(4)	20(5)	−4(3)	6(4)
C(34)	72(4)	109(9)	50(3)	7(4)	−5(3)	−20(5)
C(35)	70(4)	67(5)	39(3)	−4(3)	8(3)	−22(4)
C(36)	103(6)	94(6)	55(4)	−20(4)	18(4)	−14(5)
N(1)	75(3)	59(3)	61(3)	18(3)	31(3)	9(3)
C(4)	108(8)	125(9)	190(13)	70(9)	59(8)	19(7)
C(5)	137(11)	161(14)	162(13)	10(11)	−9(9)	−36(10)
C(6)	167(10)	77(6)	127(8)	19(6)	66(8)	18(7)
C(7)	258(20)	175(15)	167(14)	−46(12)	4(13)	128(16)
C(8)	137(9)	133(10)	89(6)	31(6)	33(6)	25(8)
C(9)	103(10)	225(17)	109(11)	−2(11)	10(8)	−30(11)
C(10)	130(9)	128(10)	100(7)	−11(7)	53(7)	−1(8)
C(11)	215(15)	148(12)	148(11)	−46(9)	62(11)	78(12)

[a] These anisotropic thermal parameters are coefficients in the temperature factor expression: $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^\star b^\star + 2U_{13}hla^\star c^\star + 2U_{23}klb^\star c^\star)]$. The overall U_{iso} values for the hydrogen atoms refined to 0.125(10) for non-methyl and 0.201(15) Å^2 for methyl hydrogen.

non-hydrogen atoms lowered R to 0.057 which further dropped to 0.038 after a further six cycles with the non-hydrogen atoms allowed anisotropic vibration. A difference map calculated at this stage revealed maxima (0.6–0.2 e $Å^{-3}$) at positions expected for H atoms, which were included in the subsequent refinement in geometrically idealized positions (C–H 0.95 Å) and in addition overall isotropic thermal parameters were refined for the various types of hydrogen atoms. The weights used in the refinement were derived from the counting statistics. Scattering factors for H atoms were taken from those of Stewart et al. [12], and for the non-hydrogen atoms from ref. 13. Refinement converged with $R = 0.0287$ and $R_w = [\Sigma w\Delta^2/\Sigma wF_0^2]^{1/2} = 0.0313$ for the 1813 observed reflections. Because the space group is polar we computed a parallel, independent refinement run with the opposite configuration including anomalous dispersion [14], for Mo, and O; this converged with $R = 0.0299$ and $R_w = 0.0328$. A statistical test on the R-factor ratio [15] indicated that the latter configuration could be rejected at the 0.005 significance level as being the configuration present in the crystal. Accordingly, all coordinates reported herein refer to the statistically favoured configuration. A difference map calculated at the conclusion of the refinement was essentially featureless. Final fractional coordinates are given in Table 2 and anisotropic thermal parameters in Table 3. Calculated hydrogen coordinates and listings of the structure factor amplitudes are available from the authors on request.

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