# Syntheses of 4-Benzyl-3,5-dimethylpyrazolylborato Complexes of Molybdenum and Tungsten Nitrosyls: Molecular Structure of $[Mo(CO)_2(NO)\{HB(3,5\text{-}Me_2\text{-}4\text{-}PhCH_2C_3N_2)_3\}]$, a Complex with an 'Inverted' Bowl-like Structure†

**John C. Jeffery, Stefan S. Kurek, Jon A. McCleverty,* Elefteria Psillakis, Rob M. Richardson, Michael D. Ward and Andrzej Wlodarczyk***
*School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK*

Reaction of $[HB(bdmpz)_3]^-$, obtained by reaction of 4-benzyl-3,5-dimethylpyrazole (Hbdmpz) with $KBH_4$, with $[M(CO)_6]$ (M = Mo or W) and $p\text{-}MeC_6H_4SO_2N(NO)Me$ afforded $[M(CO)_2(NO)\{HB(bdmpz)_3\}]$ (M = Mo or W). The molybdenum carbonyl was converted into $[Mo(NO)\{HB(bdmpz)_3\}X(Y)]$ (X = Y = Cl, I or $OC_6H_4Me\text{-}p$; X = Cl, Y = OMe or $OC_6H_4Me\text{-}p$) the spectral and electrochemical properties of which are virtually identical to those of $[Mo(NO)\{HB(dmpz)_3\}X(Y)]$ (Hdmpz = 3,5-dimethylpyrazole), indicating that the addition of a benzyl group has no significant electronic effect in the new species. However, a crystal and molecular structure determination of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ revealed that the molecule has a highly symmetrical structure, the $CH_2$ groups of the benzyl groups in the tris(pyrazolyl)borate ligand being disposed in a star-shaped configuration where the phenyl rings adopt an 'inverted' bowl-like structure with the BH group inside and the $Mo(CO)_2(NO)$ group outside the bowl. The arrangement of the 4-benzyl groups with respect to the pyrazolyl rings and the H–B ··· Mo three-fold axis is strongly reminiscent of an inverted three-legged 'Isle of Man' symbol.

By taking advantage of the tripodal nature of the tris(pyrazolyl)borate ion, and by appropriate functionalisation at the 3 positions in the planar pyrazolyl rings, we have shown that it is possible to construct simple bowl-shaped ligands which can incorporate metal centres. Thus, in $[Mo(CO)_2(NO)\{HB(mppz)_3\}]$ the 3-*p*-methoxyphenylpyrazolyl (mppz) groups form a cavity within which the $Mo(NO)(CO)_2$ group is accommodated (Fig. 1), and we have observed that while it was possible to replace the CO groups by $Cl^-$, substitution of carbonyl by iodide could not be achieved.[1] We think this failure to effect substitution may be a consequence of the protective bowl shape of the ligand. Clearly, replacement of the methoxy and the phenyl groups by other longer-chain alkyl and more extended aromatic rings may produce other interesting steric effects which, by careful design, may have significant effects on the chemical and, particularly, the physical properties of the complexes.

In seeking to explore other potential shapes within this tripodal ligand system we have begun to investigate the effects of substitution at the 4 position in the tris(3,5-dimethylpyrazolyl)borate ion. Incorporation of aromatic groups directly onto the pyrazole ring could lead to the generation of disc-like complexes, whereas benzyl groups could generate oblate, normal or inverted bowl-like structures. In this paper we describe our generation of 4-benzyl complexes, in particular the synthesis of some molybdenum and tungsten nitrosyl derivatives, and the determination of the crystal structure of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ (bdmpz = 4-benzyl-3,5-dimethylpyrazolyl).

Although other metal-containing species of this borate can be prepared (and will be reported in subsequent papers), we initially chose the molybdenum and tungsten nitrosyls to promote our structural interests largely because of our considerable experience with related species $[M(NO)\{HB(dmpz)_3\}X(Y)]$ (dmpz = 3,5-dimethylpyrazolyl) and our intimate knowledge of the physicochemical characteristics of these compounds.[2] From Corey–Pauling–Koltun (CPK) models it is clear that the benzyl groups can adopt a number of

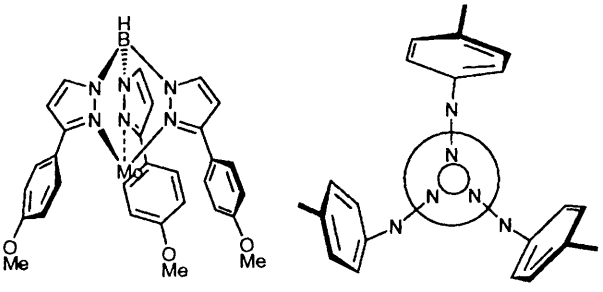

**Fig. 1** Bowl-like arrangement in $[Mo(CO)_2(NO)\{HB(mppz)_3\}]$

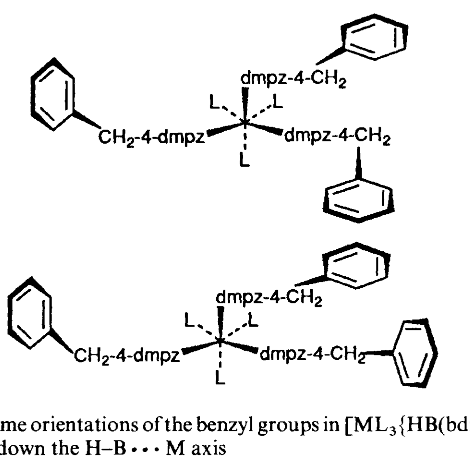

**Fig. 2** Some orientations of the benzyl groups in $[ML_3\{HB(bdmpz)_3\}]$ projected down the H–B ··· M axis

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

conformations, one of which could generate an oblate structure and another could lead to the generation of shallow bowl-like structures. The relative orientations of the benzyl groups, *e.g.* as in Fig. 2, could be a factor in determination of the preferred solid-state structure. While the determination of the structure of at least one of these new complexes was our principal objective, the effect of the 4-substituent on the well established electrochemical properties of these compounds was also of interest.

## Experimental

The IR and electronic spectra were measured using Perkin-Elmer PE 1600 and PE-Lambda 2 spectrophotometers, $^1$H NMR spectra on a JEOL GX270 spectrometer, electron-impact (EI) and fast atom bombardment (FAB) mass spectra on a VG Autospec instrument (the latter using 3-nitrobenzyl alcohol as matrix) and EPR spectra at room temperature on a Bruker ESP-300E spectrometer. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene–ferrocenium couple. The solvent was $CH_2Cl_2$, purified by distillation from $CaH_2$, containing 0.1 mol dm$^{-3}$ $[NBu_4][PF_6]$ as base electrolyte. Reductions *'in situ'* in the EPR cavity were performed using a platinum-gauze working electrode in an EPR flat cell. The platinum-wire working electrode and SCE reference were positioned in a reservoir of solvent ($CH_2Cl_2$ containing 0.1 mol dm$^{-3}$ $[NBu_4][PF_6]$) attached to the top of the EPR flat cell. The potential at the working electrode was applied using an EG&G PAR model 264A polarographic analyser.

*3-Benzylpentane-2,4-dione.*—To a vigorously stirred suspension of anhydrous $K_2CO_3$ (14 g, 0.1 mol) in acetone (50 cm$^3$) containing pentane-2,4-dione (20.5 cm$^3$, 0.2 mol) was added benzyl bromide (24 cm$^3$, 0.2 mol). The mixture was stirred overnight, the solid was filtered off and washed with acetone. The filtrate was combined with the washings, the solvent evaporated *in vacuo* and the residue was fractionated under vacuum. The product was collected at 103 °C, 0.4 mmHg (*ca.* 53 Pa) (15 g, 39%).

*4-Benzyl-3,5-dimethylpyrazole.*—Hydrazine hydrate (5 g, 0.1 mol) was added dropwise and with vigorous stirring to a solution of 3-benzylpentane-2,4-dione (15 g, 0.08 mol) in ethanol (50 cm$^3$). The reaction is exothermic and the mixture refluxed, during which time a white precipitate formed. After cooling and standing overnight, the solid was filtered off and crystallised from hot acetone affording long needles of the compound (14.9 g, 80%). $^1$H NMR spectrum ($CD_2Cl_2$): δ 9.77 (1 H, s, $C_3N_2H$), 7.17 (5 H, m, $C_6H_5CH_2$), 3.73 (2 H, s, $PhCH_2$) and 2.14 [6 H, s, $(CH_3)_2(PhCH_2)C_3N_2$].

*Potassium Tris(4-benzyl-3,5-dimethylpyrazolyl)hydroborate.*—A mixture of 4-benzyl-3,5-dimethylpyrazole (12 g, 65 mmol) and $KBH_4$ (0.86 g, 16.2 mmol) was heated at 170 °C. After 900 cm$^3$ hydrogen had evolved, the temperature was raised to 230 °C and the reaction was stopped after a total of 1100 cm$^3$ hydrogen had been collected. The mixture was cooled to *ca.* 150 °C and toluene (60 cm$^3$) was added. The mixture was stirred and boiled for *ca.* 1 h, and the white solid which had formed was filtered off and dried in air (3.5 g, 36% based on $KBH_4$). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.17 (15 H, m, $C_6H_5CH_2$), 3.69 (6 H, s, $PhCH_2$), 2.19 (9 H, s) and 2.04 [9 H, s, $(CH_3)_2(PhCH_2)C_3N_2$].

*Dicarbonyl(nitrosyl)[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]molybdenum*, $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$.—A solution of $K[HB(bdmpz)_3]$ (3.0 g, 5 mmol) and $[Mo(CO)_6]$ (2.0 g, 7.6 mmol) in dry tetrahydrofuran (thf) (70 cm$^3$) was stirred and refluxed for 5 h under dinitrogen. The resulting orange suspension was cooled to room temperature, glacial acetic acid (1 cm$^3$) added and the mixture stirred for 30 min. A solution of *N*-methyl-*N*-nitrosotoluene-4-sulfonamide (1.5 g, 7 mmol) in thf (15 cm$^3$) was added with stirring over 30 min, and stirring was continued for 2 h. The white solid which had formed was filtered off, the solvent was evaporated to dryness *in vacuo* and the orange residue redissolved in chloroform. The solution was filtered to remove toluenesulfonamide, and ethanol was added to precipitate the orange compound as microcrystals. The product was recrystallised from dichloromethane–diethyl ether, filtered off and dried *in vacuo* giving orange hexagonal crystals (2.7 g, 72% based on $K[HB(bdmpz)_3]$). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.20 (15 H, m, $C_6H_5CH_2$), 3.72 (4 H, s), 3.66 (2 H, s, $PhCH_2$), 2.39 (6 H, s), 2.33 (6 H, s) and 2.29 [6 H, s, $(CH_3)_2(PhCH_2)C_3N_2$].

*Dicarbonyl(nitrosyl)[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]tungsten*, $[W(CO)_2(NO)\{HB(bdmpz)_3\}]$.—A solution of $K[HB(bdmpz)_3]$ (3.0 g, 5 mmol) and $[W(CO)_6]$ (2.6 g, 7.4 mmol) in acetonitrile (70 cm$^3$) was stirred and refluxed under nitrogen for 4 h. The orange reaction mixture was cooled to room temperature, glacial acetic acid (1 cm$^3$) added, and the mixture stirred for 30 min. A solution of *N*-methyl-*N*-nitrosotoluene-4-sulfonamide (1.5 g, 7 mmol) in thf (15 cm$^3$) was added at room temperature over 30 min, and stirring maintained at 60 °C for 2 h. The solvent was then evaporated *in vacuo* and the orange residue redissolved in chloroform, the solution being filtered through Kieselguhr. Ethanol was then added to precipitate an orange solid which was recrystallised from dichloromethane–diethyl ether affording the desired complex. This was filtered off, dried *in vacuo*, giving orange hexagonal crystals (2.8 g, 66% based on $K[HB(bdmpz)_3]$). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.17 (15 H, m, $C_6H_5CH_2$), 3.73 (4 H, s), 3.65 (2 H, s, $PhCH_2$), 2.43 (6 H, s), 2.34 (6 H, s), 2.31 (3 H, s) and 2.29 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2]$.

*Dichloro(nitrosyl)[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]molybdenum*, $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$.—A mixture of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ (1.1 g, 1.5 mmol), iodine (0.5 g, 2 mmol) and benzyl chloride (5 cm$^3$, 43.5 mmol) was refluxed in dry toluene (50 cm$^3$) under dinitrogen for 4 h. It was then cooled, toluene evaporated *in vacuo* and hexane (50 cm$^3$) added to precipitate a dark brown powder. This was filtered off, redissolved in dichloromethane and precipitated by hexane. The product was filtered off, dried at 150 °C under vacuum affording a brown powder (1.0 g, 87%). The compound may be recrystallised from acetone. $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.18 (15 H, m, $C_6H_5CH_2$), 3.73 (4 H, s), 3.68 (2 H, s, $PhCH_2$), 2.36 (6 H, s), 2.35 (3 H, s), 2.34 (6 H, s) and 2.26 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2]$.

*Diiodo(nitrosyl)[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]molybdenum*, $[Mo(NO)\{HB(bdmpz)_3\}I_2]$.—A mixture of iodine (0.4 g, 1.6 mmol) and $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ (1.0 g, 1.3 mmol) was refluxed in toluene (50 cm$^3$) overnight under dinitrogen. The mixture was cooled and evaporated to dryness *in vacuo* affording a black solid which was washed with hexane, filtered off and further washed with pentane. The product, which was dried at 150 °C under vacuum, was obtained as a black powder (10. g, 81%). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.14 (15 H, m, $C_6H_5CH_2$), 3.84 (2 H, s), 3.64 (2 H, s, $PhCH_2$), 2.63 (6 H, s), 2.55 (6 H, s), 2.22 (3 H, s) and 2.15 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2]$.

*Chloro(methoxo)nitrosyl[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]molybdenum*, $[Mo(NO)\{HB(bdmpz)_3\}Cl(OMe)]$.—A refluxing solution of $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$ (0.2 g, 0.26 mmol) in dichloromethane (20 cm$^3$) containing methanol (40 cm$^3$) became blue over 30 min, and on cooling afforded blue crystals. These were filtered off, and a further crop was obtained by partial evaporation of the filtrate. The compound collected in this way was analytically pure (quantitative yield). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.18 (15 H, m, $C_6H_5CH_2$), 5.57 (3 H, s, $OCH_3$), 3.72 (4 H, s), 3.67 (2 H, s, $PhCH_2$), 2.43 (3 H, s), 2.35 (3 H, s), 2.34 (6 H, s), 2.33 (3 H, s) and 2.15 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2]$.

*Chloro(*p*-cresolato)nitrosyl[tris(4-benzyl-3,5-dimethylpyrazolyl)borato]molybdenum*, $[Mo(NO)\{HB(bdmpz)_3\}Cl(OC_6H_4Me\text{-}p)]$.—A mixture of $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$ (0.2 g, 0.26 mmol), *p*-cresol (0.032 g, 0.3 mmol) and triethylamine (0.5 cm$^3$) was refluxed in toluene (50 cm$^3$) under dinitrogen for 1 h during which time the solution became magenta. On cooling, the solvent was partially evaporated *in vacuo*. Pentane was added to precipitate $[NHEt_3]Cl$ which was filtered off, and the filtrate was reduced to dryness *in vacuo*. The brown residue was dissolved in the minimum volume of dichloromethane and chromatographed over silica gel, using pure dichloromethane to elute unreacted $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$ and then dichloromethane–hexane (5:1 v/v) to elute the major brown fraction. On evaporation of the solvent mixture to dryness *in vacuo* and recrystallisation of the residue from dichloromethane–hexane the compound was formed as brown microcrystals which were filtered off and dried at 100 °C under vacuum (0.17 g, 77%). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.17 (19 H, m, $C_6H_5CH_2$, $OC_6H_4Me$), 3.75 (2 H, s), 3.68 (2 H, s), 3.67 (2 H, s, $PhCH_2$), 2.50 (3 H, s), 2.37 (6 H, s), 2.36 (6 H, s), 2.07 (3 H, s) and 1.98 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2, OC_6H_4CH_3]$.

*Bis(*p*-cresolato)nitrosyl[tris(4-benzyl-*3,5-dimethylpyrazolyl)-*borato]molybdenum*, $[Mo(NO)\{HB(bdmpz)_3\}(OC_6H_4Me\,p)_2]$.—This compound was prepared using procedures identical to those above, using $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$ (0.25 g, 0.26 mmol), *p*-cresol (0.13 g, 1.2 mmol) and triethylamine (1.0 cm$^3$), and was obtained as brown microcrystals (0.16 g, 69%). $^1$H NMR spectrum ($CD_2Cl_2$): δ 7.06 (23 H, m, $C_6H_5CH_2$, $OC_6H_4Me$), 3.69 (4 H, s), 3.64 (2 H, s, $PhCH_2$), 2.36 (6 H, s), 2.35 (3 H, s), 2.32 (6 H, s), 2.16 (6 H, s) and 1.93 (3 H, s) $[(CH_3)_2(PhCH_2)C_3N_2, OC_6H_4CH_3]$.

*Crystal and Molecular Structure of* $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$.—*Crystal data*. $C_{38}H_{40}BMoN_7O_3$, $M$ = 749.5, orange hexagonal prism of dimensions 0.50 × 0.50 × 0.55 mm, trigonal, space group $P\bar{3}$, $a$ = 15.157(4), $c$ = 9.076(4) Å, $U$ = 1806(1) Å$^3$, $Z$ = 2, $D_c$ = 1.38 g cm$^{-3}$, $F(000)$ = 774, graphite-monochromated Mo-Kα radiation, $\bar{\lambda}$ = 0.710 73 Å, μ(Mo-Kα) = 4.9 cm$^{-1}$.

The crystal was mounted in a sealed glass capillary under dinitrogen. All measurements were performed using a Siemens R3m/V four-circle diffractometer at room temperature. Of the 6696 data collected (Wyckoff ω scans, $5 \leqslant 2\theta \leqslant 50°$), 1683 unique data had $F \geqslant 4.0\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz and polarisation effects. An empirical absorption correction was applied using a method based upon azimuthal scan data.[3]

The structure was solved by direct methods, and refinement was by full-matrix least squares (on $F^2$). All non-hydrogen atoms were refined with anisotropic thermal parameters. The position of the BH hydrogen atom was refined. All remaining hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. The complex has crystallographically imposed symmetry with the Mo and B atoms lying on a three-fold axis of symmetry. The pyrazolylborate ligand has three-fold symmetry and appears well ordered but the nitrosyl and two carbonyl ligands are necessarily completely disordered and were modelled by a single CO ligand in the refinement. Final $R$ = 0.041 ($R'$ = 0.041) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005F^2]$ and goodness of fit $S$ 1.18. The final electron-density difference synthesis showed no peaks > 0.29 or < −0.81 e Å$^{-3}$. All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[3] Scattering factors with corrections for anomalous dispersion were taken from ref. 4. Atom coordinates are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

*Synthetic and Spectroscopic Studies*.—The ion $[HB(bdmpz)_3]^-$ was obtained by benzylation of C$^3$ in pentane-2,4-dione, followed by conversion of the diketone into the appropriate pyrazole by reaction with hydrazine and heating the pyrazole with $KBH_4$. The yield of the salt was fair. The dicarbonyl nitrosyls $[M(CO)_2(NO)\{HB(bdmpz)_3\}]$ (M = Mo or W) were prepared *via* conversion of $[M(CO)_6]$ into the carbonylate ions $[M(CO)_3\{HB(bdmpz)_3\}]^-$, which were not isolated, followed by acidification and treatment with $MeC_6H_4SO_2N(NO)Me$, a well established route.[5] These compounds were obtained as air-stable orange crystals (analytical data, Table 1).

Treatment of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ with a mixture of iodine and benzyl chloride afforded good yields of the brown dichloride $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$, the reaction probably proceeding *via* the corresponding diiodide, itself obtained by direct iodination of the dicarbonyl. The conversion of molybdenum tris(pyrazolyl)borate iodides into chlorides *via* chlorination by reactive chloroalkanes, *e.g.* $CH_2Cl_2$, $CHCl_3$, $CCl_4$, $PhCH_2Cl$, has been observed previously,[6] and is a reliable route to $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$.

As in the tris(3,5-dimethylpyrazolyl)borato system, reaction of $[Mo(NO)\{HB(bdmpz)_3\}Cl_2]$ with methanol afforded the monomethoxide, $[Mo(NO)\{HB(bdmpz)_3\}Cl(OMe)]$,[7] while treatment with *p*-cresol in appropriate stoichiometries in the presence of triethylamine afforded the brown cresolates, $[Mo(NO)\{HB(bdmpz)_3\}Cl(OC_6H_4Me\text{-}p)]$ and $[Mo(NO)\{HB(bdmpz)_3\}(OC_6H_4Me\text{-}p)_2]$.[8] These complexes were obtained as air-stable microcrystalline solids the EI mass spectra of which exhibited parent ions consistent with their formulation (Table 1).

The IR spectra of the new compounds were entirely typical of this class of compounds, exhibiting $\nu_{BH}$ at *ca*. 2500 cm$^{-1}$. For $[M(CO)_2(NO)\{HB(bdmpz)_3\}]$ (M = Mo or W) the carbonyl stretching frequencies appeared at 1998 and 1898 (M = Mo) and 2014 and 1921 cm$^{-1}$ (M = W), respectively, again typical for this class of compound, $\nu_{CO}$ being comparable to those found for $[M(CO)_2(NO)\{HB(dmpz)_3\}]$. All compounds exhibited NO stretching frequencies (Table 1) similar to those in closely related tripodal borate derivatives, the value of $\nu_{NO}$ decreasing in the order Cl > I, Cl > $OC_6H_4Me$-*p* > OMe and (Cl, $OC_6H_4Me$-*p*) > $(OC_6H_4Me\text{-}p)_2$, commensurate with the electronegativity of the halide, alkoxide and aryloxide groups, as has been detected before.[9]

The $^1$H NMR spectra of the compounds are in agreement with our formulations (Experimental section). The protons of the methoxy group in $[Mo(NO)\{HB(bdmpz)_3\}Cl(OMe)]$ resonate at relatively low field, δ 5.57, a feature of alkoxide compounds already discussed for the related systems.[10] This effect is caused by the powerful electronegativity of the coordinatively unsaturated $Mo(NO)\{HB(bdmpz)_3\}^{2+}$ group.

The complexes $[M(NO)\{HB(bdmpz)_3\}X_2]$ (M = Mo or W, X = CO; M = Mo, X = Cl or $OC_6H_4Me$-*p*) contain a pseudo-plane of symmetry defined by H–B•••M–NO. This requires that the benzyl $CH_2$ groups should and do appear as two signals, of relative intensities 2:1. For $[Mo(NO)\{HB(bdmpz)_3\}Cl(OC_6H_4Me\text{-}p)]$ these resonances occur as three signals of relative intensity 1:1:1, but for $[Mo(NO)\{HB(bdmpz)_3\}Cl(OMe)]$ the signals form a 2:1 pattern, perhaps due to accidental degeneracy.

**Table 1** Analytical, mass spectral and selected IR spectroscopic data obtained for 4-benzyl-3,5-dimethylpyrazole, K[HB(bdmpz)$_3$] and [M(NO){HB(bdmpz)$_3$}X(Y)]

| Compound | | | Analysis$^a$ (%) | | | | |
|---|---|---|---|---|---|---|---|
| M | X | Y | C | H | N | $m/z^{a,b}$ | IR$^c$/cm$^{-1}$ |
| Mo | CO | CO | 60.3 (60.9) | 5.6 (5.4) | 12.8 (13.1) | 751 (749.5) | 1655$^d$ |
| W | CO | CO | 53.9 (54.5) | 5.4 (4.8) | 11.3 (11.7) | 837 (837.4) | 1639$^e$ |
| Mo | Cl | Cl | 56.6 (56.6) | 5.3 (5.3) | 12.8 (12.8) | 765 (763.6) | 1716 |
| Mo | I | I | 46.2 (45.6) | 4.4 (4.3) | 10.2 (10.3) | 949 (947.3) | 1709 |
| Mo | Cl | OMe | 58.5 (58.5) | 5.7 (5.7) | 12.9 (12.9) | 761 (759.6) | 1676 |
| Mo | Cl | $OC_6H_4Me$ | 62.0 (61.8) | 5.8 (5.7) | 11.7 (11.7) | 837 (835.7) | 1681 |
| Mo | $OC_6H_4Me$ | $OC_6H_4Me$ | 66.2 (66.2) | 6.3 (6.0) | 10.8 (10.8) | 909 (907.8) | 1654 |
| Hbdmpz | | | 56.6 (56.6) | 5.3 (5.3) | 12.8 (12.8) | 186 (186.3) | 3454$^f$ |
| K[HB(bdmpz)$_3$] | | | 70.9 (71.3) | 7.2 (6.6) | 13.7 (13.9) | (606.7) | — |

$^a$ Found (calculated). $^b$ Value for parent ion from EI mass spectrum. $^c$ NO stretching frequencies unless otherwise stated, in $CH_2Cl_2$. $^d$ $\nu_{CO}$ 1998, 1898 cm$^{-1}$. $^e$ $\nu_{CO}$ 2014, 1921 cm$^{-1}$. $^f$ $\nu_{NH}$.

**Table 2** Electrochemical properties of [M(NO){HB(3,5-Me$_2$-4-Z-C$_3$N$_2$)$_3$}X(Y)] in dichloromethane

| M | Z | X | Y | $E_f^a$ | $E^b$ | $\Delta E^c$ |
|---|---|---|---|---|---|---|
| Mo | $PhCH_2$ | CO | CO | +0.46 | +0.91 | 170 |
| W | $PhCH_2$ | CO | CO | +0.41 | +0.89 | 160 |
| Mo | $PhCH_2$ | Cl | Cl | −0.45 | 0.00 | 170 |
| Mo | H | Cl | Cl | −0.45 | 0.00 | 120 |
| Mo | $PhCH_2$ | I | I | −0.38$^d$ | +0.12 | 100 |
| Mo | $PhCH_2$ | Cl | OMe | −1.25 | −0.78 | 200$^e$ |
| Mo | $PhCH_2$ | Cl | $OC_6H_4Me$-*p* | +1.02<br>−0.97 | +1.47 | $E_p^a$ only$^f$<br>190 |
| Mo | $PhCH_2$ | $OC_6H_4Me$-*p* | $OC_6H_4Me$-*p* | +0.74<br>$^g$ | +1.19 | $E_p^a$ only$^f$ |

$^a$ In V, *vs.* [Fe(C$_5$H$_5$)$_2$]–[Fe(C$_5$H$_5$)$_2$]$^+$ couple, at scan rate of 0.2 V s$^{-1}$. $^b$ In V *vs.* saturated calomel electrode. $^c$ $\Delta E = E_p^c - E_p^a$, in mV; for the [Fe(C$_5$H$_5$)$_2$]–[Fe(C$_5$H$_5$)$_2$]$^+$ couple, $\Delta E$ = 120 mV under the conditions of these experiments. $^d$ Small anodic peaks probably due to the couple $I^- \rightleftharpoons \frac{1}{2}I_2 + e^-$, significantly enhanced by addition of [NBu$^n_4$]I. $^e$ Cathodic and anodic peaks broad. $^f$ Only the anodic peak detected; irreversible process. $^g$ No reduction process observed down to −2.0 V.

*Electrochemical Studies.*—The electrochemical properties of the new complexes were investigated by cyclic voltammetry in dichloromethane using a platinum-bead electrode, the data being referenced to the ferrocene–ferrocenium couple. All complexes exhibited some electrode behaviour (Table 2), the dicarbonyls undergoing a quasi-reversible oxidative electron transfer, presumably generating [M(CO)$_2$(NO){HB(bdmpz)$_3$}]$^+$ as has been detected in the cyclic voltammetric behaviour of [Mo(CO)$_2$(NO){HB(dmpz)$_3$}] in acetonitrile.[11]

The complexes [Mo(NO){HB(bdmpz)$_3$}X(Y)] (X = Y = Cl or I; X = Cl, Y = OMe or $OC_6H_4Me$-*p*) undergo a reversible or quasi-reversible one-electron reduction, generating [Mo(NO){HB(bdmpz)$_3$}X(Y)]$^-$. The potentials for this electron-transfer process follow expected trends, being determined by the nature of X and Y. Thus, [Mo(NO){HB(bdmpz)$_3$}I$_2$] is reduced at a potential *ca.* 70 mV more anodic than its chloro-analogue, exhibiting dissociation of I$^-$, as has been noted previously. Comparison of the $E_{\frac{1}{2}}$ value for the reduction of [Mo(NO){HB(bdmpz)$_3$}Cl$_2$] with that of [Mo(NO){HB(dmpz)$_3$}Cl$_2$] shows that they are identical, within experimental error, and we conclude that the presence of the 4-benzyl substituent has virtually no effect on the redox behaviour of this system. Reduction of [Mo(NO){HB(bdmpz)$_3$}Cl($OC_6H_4Me$-*p*)] is more anodic than that of the corresponding methoxide, reflecting the σ-donor/π-acceptor behaviour of the oxide ligands. The complexes [Mo(NO){HB(bdmpz)$_3$}Cl($OC_6H_4Me$-*p*)] and [Mo(NO){HB(bdmpz)$_3$}($OC_6H_4Me$-*p*)$_2$] are the only ones which exhibit oxidation behaviour. This is irreversible (only the anodic oxidation peak was detected) and may be due to the generation of an unstable monocation, [Mo(NO){HB(bdmpz)$_3$}X(Y)]$^+$. We were unable to detect a reduction process in the cyclic voltammogram of [Mo(NO){HB(bdmpz)$_3$}($OC_6H_4Me$-*p*)$_2$], presumably because it is very cathodic and falls within the decomposition processes of the medium.

*Crystal and Molecular Structure of* [Mo(CO)$_2$(NO){HB(bdmpz)$_3$}].—The molecular structure of the complex is shown in Fig. 3 and internuclear distances and angles are listed in Table 4. The complex has crystallographically imposed three-fold symmetry with the Mo and B atoms lying on the three-fold axis. The pyrazolylborate ligand can readily attain three-fold symmetry and therefore appears well ordered. In contrast, the nitrosyl and the two carbonyl ligands are necessarily disordered about the three-fold axis of symmetry and were modelled by a single CO ligand in the refinement. The bond lengths and angles within the molybdenum co-ordination sphere are typical for complexes of this class and the disordered carbonyl and nitrosyl ligands are almost perfectly staggered with respect to the pyrazolylborate ligand.

As noted in the Introduction, interest centres on the preferred orientations of the benzyl substituents attached at the 4 positions of the pyrazolyl rings. The presence of the crystallographic three-fold axis of symmetry dictates a symmetric structure (Fig. 4). The *ipso*-carbon of the phenyl ring is staggered about the CH$_2$–C (pyrazolyl) bond with respect to the plane of the pyrazolyl ring [torsion angle C(*ipso*)–CH$_2$–C(pyrazolyl)–C(14) 44.7°] thereby minimising unfavourable steric repulsion between the phenyl group and the 3-methyl substituent of the pyrazolyl ring. The phenyl ring is also twisted about the C(*ipso*)–CH$_2$ bond so as further to minimise steric repulsions between the phenyl hydrogen atoms and the 3-methyl group. The resulting structure resembles a shallow inverted bowl with the BH unit at its centre and the phenyl rings defining the edge (Fig. 5). The angle subtended at the central boron by the outermost hydrogen atoms of the 'bowl' is *ca.* 128°.

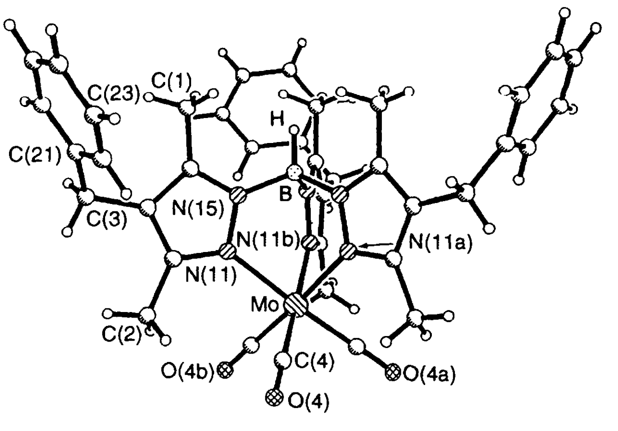

**Fig. 3** The molecular structure of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ showing the atom labelling and the relative dispositions of the phenyl rings of the benzyl groups

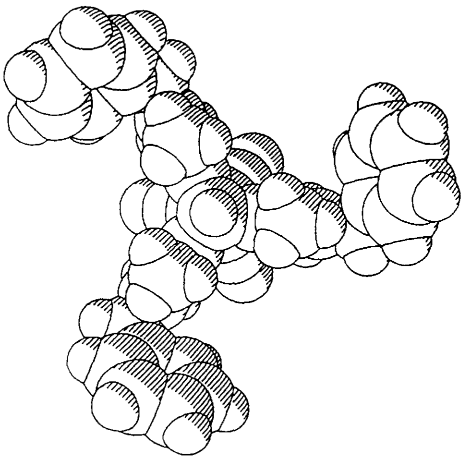

**Fig. 4** Space-filling representation of the molecular structure of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ as seen down the HB ··· Mo three-fold axis

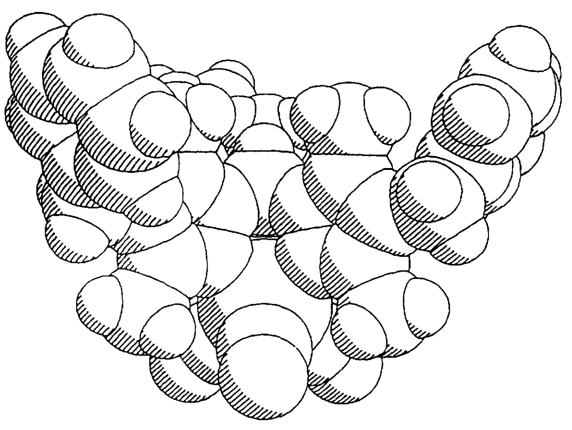

**Fig. 5** Space-filling representation emphasising the bowl-like structure of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$

The principal intramolecular constraints on the orientation of the benzyl substituents arise from the symmetrically disposed 3- and 5-methyl substituents of the pyrazolyl rings. Rotation of the benzyl groups about the $CH_2$–C (pyrazolyl) bond might therefore generate energetically favourable but less-symmetric oblate structures (Fig. 2) and it is possible that bowls encompassing the $Mo(CO)_2(NO)$ group are also accessible.

**Table 3** Atomic positional parameters (fractional coordinates × $10^4$) for $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$, with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 6 667 | 3 333 | 1 622(1) |
| B | 6 667 | 3 333 | 5 232(8) |
| C(4) | 6 785(3) | 4 412(3) | 393(4) |
| O(4) | 6 856(3) | 5 065(3) | −371(3) |
| N(11) | 7 862(2) | 4 387(2) | 3 183(3) |
| N(15) | 7 674(2) | 4 232(2) | 4 675(3) |
| C(12) | 8 786(3) | 5 222(3) | 3 039(4) |
| C(13) | 9 202(3) | 5 604(3) | 4 428(4) |
| C(14) | 8 484(3) | 4 959(3) | 5 425(4) |
| C(1) | 8 529(3) | 4 976(3) | 7 068(4) |
| C(2) | 9 251(3) | 5 623(3) | 1 564(4) |
| C(3) | 10 222(3) | 6 529(3) | 4 778(5) |
| C(21) | 10 181(3) | 7 201(3) | 5 962(4) |
| C(22) | 9 528(3) | 7 591(3) | 5 818(5) |
| C(23) | 9 460(4) | 8 193(4) | 6 905(6) |
| C(24) | 10 060(4) | 8 411(4) | 8 148(7) |
| C(25) | 10 710(4) | 8 039(4) | 8 295(6) |
| C(26) | 10 775(3) | 7 439(3) | 7 206(5) |

**Table 4** Bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Mo–C(4) | 1.912(4) | Mo–N(11) | 2.225(3) |
| B–N(15) | 1.537(3) | C(4)–O(4) | 1.168(6) |
| N(11)–N(15) | 1.379(4) | N(11)–C(12) | 1.344(4) |
| N(15)–C(14) | 1.354(4) | C(12)–C(13) | 1.399(5) |
| C(12)–C(2) | 1.493(5) | C(13)–C(14) | 1.377(4) |
| C(13)–C(3) | 1.513(4) | C(14)–C(1) | 1.492(5) |
| C(3)–C(21) | 1.503(6) | C(21)–C(22) | 1.389(7) |
| C(21)–C(26) | 1.375(6) | C(22)–C(23) | 1.377(8) |
| C(23)–C(24) | 1.375(8) | C(24)–C(25) | 1.365(10) |
| C(25)–C(26) | 1.380(8) | | |
| C(4)–Mo–N(11) | 93.6(1) | C(4)–Mo–C(4a) | 89.4(1) |
| C(4)–Mo–N(11a) | 93.1(2) | C(4)–Mo–N(11b) | 176.1(1) |
| N(11)–Mo–N(11a) | 83.8(1) | N(15)–B–N(15a) | 109.7(3) |
| Mo–C(4)–O(4) | 179.3(4) | Mo–N(11)–N(15) | 118.6(2) |
| Mo–N(11)–C(12) | 134.8(2) | N(15)–N(11)–C(12) | 106.6(2) |
| B–N(15)–N(11) | 120.2(3) | B–N(15)–C(14) | 130.6(3) |
| N(11)–N(15)–C(14) | 109.2(2) | N(11)–C(12)–C(13) | 110.1(3) |
| N(11)–C(12)–C(2) | 121.9(3) | C(13)–C(12)–C(2) | 128.0(3) |
| C(12)–C(13)–C(14) | 105.4(3) | C(12)–C(13)–C(3) | 127.8(3) |
| C(14)–C(13)–C(3) | 126.8(3) | N(15)–C(14)–C(13) | 108.7(3) |
| N(15)–C(14)–C(1) | 122.2(3) | C(13)–C(14)–C(1) | 129.2(3) |
| C(13)–C(3)–C(21) | 114.1(3) | C(3)–C(21)–C(22) | 120.0(4) |
| C(3)–C(21)–C(26) | 121.4(5) | C(22)–C(21)–C(26) | 118.6(4) |
| C(21)–C(22)–C(23) | 120.7(4) | C(22)–C(23)–C(24) | 119.8(6) |
| C(23)–C(24)–C(25) | 119.9(6) | C(24)–C(25)–C(26) | 120.5(5) |
| C(21)–C(26)–C(25) | 120.5(5) | | |

This suggests that the observed solid-state structure may be partially dictated by the efficient packing achieved by a three-fold symmetric molecule in space group *P*$\bar{3}$.

If the solid-state structure were maintained in solution all three benzyl groups would be chemically inequivalent. As noted earlier the NMR data for the complex are consistent with a molecule achieving pseudo-mirror symmetry on the NMR time-scale. This requires that in solution the benzyl groups rotate about the $CH_2$–C (pyrazolyl) bond and provides support for the suggestion that the symmetric structure observed in the solid state is dictated by both inter- and intra-molecular constraints.

## Conclusion

The effect of substitution of benzyl groups for hydrogen at the 4 position in tris(3,5-dimethylpyrazolyl)borate could lead to a tripodal ligand having an oblate, normal or inverted bowl-like shape. The molecular structure of $[Mo(CO)_2(NO)\{HB(bdmpz)_3\}]$ shows that the ligand, in this compound in the solid state, adopts a shallow inverted bowl-like arrangement of the 4-benzyl groups, the BH group being inside and the $Mo(CO)_2(NO)$ group outside this bowl. The benzyl groups adopt a star-shaped configuration with respect to the H–B • • • Mo three-fold axis, generating a twist strongly reminiscent of an inverted three-legged 'Isle of Man' symbol. There are no significant intermolecular interactions within the crystals. The chemistry of $[M(CO)_2(NO)\{HB(bdmpz)_3\}]$ is very similar to that of $[M(CO)_2(NO)\{HB(dmpz)_3\}]$ (M = Mo or W), the complexes readily undergoing halogenation to give $[M(NO)\{HB(bdmpz)_3\}X_2]$, and substitution of the halide by alkoxide and aryloxide. The electronic effect of substitution of $H^4$ by the benzyl group is minimal, as evidenced by the close correspondence of $\nu_{NO}$ and $E_f$ (reduction potential) obtained from $[M(NO)\{HB(dmpz)_3\}X(Y)]$ and $[M(NO)\{HB(bdmpz)_3\}X(Y)]$.

## Acknowledgements

We are grateful to the SERC (A. W.) and the Erasmus programme (E. P.) for support of this work, and to the Politechnika Krakowska for leave of absence (to A. W.).

## References

1 M. Cano, J. V. Heras, A. Monge, E. Gutierrez, C. J. Jones, S. L. W. McWhinnie and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1992, 2435.

2 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943.

3 G. M. Sheldrick, SHELXTL programs for use with a Nicolet X-Ray System, Cambridge, 1976; updated Göttingen, 1981.

4 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

5 S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675; A. S. Drane and J. A. McCleverty, *Polyhedron*, 1983, **2**, 53; C. J. Jones, J. A. McCleverty, S. J. Reynolds and C. F. Smith, *Inorg. Synth.*, 1985, **23**, 4.

6 A. Wlodarczyk, S. S. Kurek, M. A. J. Moss, M. S. Tolley, A. S. Batsanov, J. A. K. Howard and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1993, 2027; B. Coe, C. J. Jones, J. A. McCleverty, F. McQuillan and S. L. W. McWhinnie, unpublished work.

7 J. A. McCleverty and A. Wlodarczyk, *Polyhedron*, 1988, **7**, 449.

8 N. Al Obaidi, M. Chaudhury, D. Clague, C. J. Jones, J. C. Pearson, J. A. McCleverty and S. S. Salam, *J. Chem. Soc., Dalton Trans.*, 1987, 1933.

9 J. A. McCleverty, *Chem. Rev.*, 1983, **12**, 331.

10 J. A. McCleverty, D. Seddon, N. A. Bailey and N. W. Walker, *J. Chem. Soc., Dalton Trans.*, 1976, 898.

11 T. N. Briggs, C. J. Jones, J. A. McCleverty, B. D. Neaves, N. El Murr and H. M. Colquhoun, *J. Chem. Soc., Dalton Trans.*, 1985, 1249.

*Received* 21*st March* 1994; *Paper* 4/01676I