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Reactions of vanadium, molybdenum and rhenium tris(pyrazolyl)borate-stabilised oxometal complexes with $B(C_6F_5)_3$: crystal structures of $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(S_2CNMe_2)]$ and $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(OCH_2CH_2O)]$ (dmpz = 3,5-dimethylpyrazolyl)

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The tris(pyrazolyl)borate oxometal complexes $[MoO\{HB(dmpz)_3\}L_2]$ (dmpz = 3,5-dimethylpyrazolyl, $L_2 = OCH_2CH_2O$ or S_2CNMe_2), $[VO\{HB(dmpz)_3\}(acac)]$ and $[ReO\{HB(pz)_3\}L_2]$ [pz = pyrazolyl; $L_2 = (OEt)_2$, OCH_2CH_2O or C_2O_4] reacted with the strong Lewis acid $B(C_6F_5)_3$ at their M=O functionality to yield stable Lewis acid–metal complex adducts. The structures of the complexes $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(S_2CNMe_2)]$ and $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(OCH_2CH_2O)]$ have been determined by X-ray crystallography.

Many hetero- and homo-geneous catalytic processes rely upon transition-metal complexes containing strong π-donor (*e.g.* oxo, imido) and/or moderate π-donor ligands (*e.g.* alkoxide).[1,2] The role played by these ligands is critical in stabilising and fine tuning the reactivity of the metal centre.[3] Certain of these catalytic reactions require the addition of a Lewis-acid co-catalyst. It is believed that the Lewis acid binds to the metal complex and assists in the push-pull of electron density from the metal centre during the catalytic process.[4] However several nucleophilic sites in such metal complexes may be available to the Lewis acid; the M=O unit, electron lone pairs of the ancillary ligands such as alkoxide, halide, *etc.* The nature of the interactions between the metal complex and the Lewis acid is often ill defined although a few examples of interaction between the Lewis acid and an oxometal functionality have been reported.[5,6]

Recently we have described the synthesis of stable complexes containing the $M{=}O{-}B(C_6F_5)_3$ moiety and a brief exploration of the strength of the interaction between the M=O bond and strong Lewis acids.[7,8] We now turn our attention to hydridotris(pyrazolyl)borate-stabilised metal complexes containing a variety of nucleophilic atom sites (oxo, alkoxide and oxalate) and have investigated their reactivity towards $B(C_6F_5)_3$.

Results and Discussion

Treatment of $[MoO\{HB(dmpz)_3\}(S_2CNMe_2)]$ (dmpz = 3,5-dimethylpyrazolyl) with 1 equivalent of $B(C_6F_5)_3$ produces an immediate change from emerald to lime green and the Lewis-acid oxometal adduct $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(S_2CNMe_2)]$ **1** is obtained. Spectroscopic and analytical data for compound **1** are given in Table 1. Crystals suitable for study by X-ray diffraction were grown from toluene and the molecular structure of compound **1** is shown in Fig. 1 with selected bond angles and bond distances in Table 2.

The compound displays no surprising structural features when compared to previously reported oxometal $B(C_6F_5)_3$ adducts.[7,8] The B–O bond length of 1.531(2) Å is typical of a single bond and the Mo=O bond distance of 1.767(1) Å is elongated by approximately 0.1 Å on co-ordination to the Lewis acid, for $[MoO\{HB(dmpz)_3\}(S_2CNR_2)]$; R = Et, Mo–O 1.699(3) Å;[9] R = Pr^i, Mo–O 1.676(4) Å.[10] The Mo–O–B bond angle [166.1(1)°] deviates slightly from linearity. This is a common feature of all structurally characterised compounds containing the $M{=}O{-}B(C_6F_5)_3$ group.

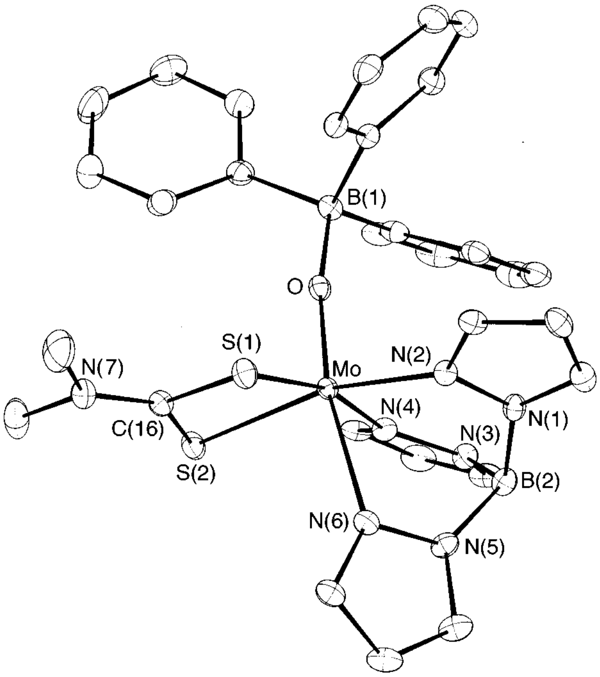

Fig. 1 Molecular structure of compound **1**. Methyl groups on the $HB(dmpz)_3$ ligand and hydrogen and fluorine atoms omitted for clarity

The analogous reactions of $[MoO\{HB(dmpz)_3\}(OCH_2CH_2O)]$[11] or $[VO\{HB(dmpz)_3\}(acac)]$[12] with 1 equivalent of $B(C_6F_5)_3$ also lead to the formation of 1 : 1 adduct species in good yields. Spectroscopic and analytical data for $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(OCH_2CH_2O)]$ **2** and $[V\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(acac)]$ **3** are given in Table 1. Crystals of compound **2** suitable for study by X-ray diffraction were grown from dichloromethane–pentane and the molecular structure is shown in Fig. 2 with selected bond angles and bond distances in Table 3.

The structure displays no surprising features although it is worthwhile noting the Mo–O bond length of 1.767(3) Å. The structure of $[MoO\{HB(dmpz)_3\}(OCH_2CH_2O)]$ has not been determined by X-ray diffraction but a statistical study of oxometal multiple bond lengths has demonstrated that the M=O

Table 1 Analytical and spectroscopic data for compounds **1**–**6**

Complex[a]	Spectroscopic data[b]
1 [Mo{OB(C_6F_5)$_3$}{HB(dmpz)$_3$}(S_2CNMe_2)] C, 41.6 (41.5); H, 2.7 (2.7); B, 1.9 (2.1); N, 9.4 (9.4); S, 6.1 (6.1)	IR: 3025–2927w, 2551w, 1646s, 1545s, 1519vs, 1471vs, 1417s, 1400s, 1384m, 1362m, 1283s, 1248m, 1208m, 1156m, 1095vs, 1073s, 1061s, 1036s, 983vs, 890vs, 853s, 821m, 790m, 774m, 762m, 749m, 733m, 685m, 674m, 658m, 637m, 604m, 577m ^{1}H: 5.60 (2 H, s, CH), 4.92 (1 H, s, CH), 2.65 (6 H, s, NMe_2), 2.30 (6 H, s, CH_3), 2.27 (6 H, s, CH_3), 1.94 (3 H, s, CH_3), 1.69 (3 H, s, CH_3) ^{13}C-{^{1}H}:[c] 147.9 (d, *J* 240, C_6F_5), 140.4 (d, *J* 250, C_6F_5), 137.1 (d, *J* 260, C_6F_5), 153.6 (s, *C*CH_3), 151.7 (s, *C*CH_3), 147.9 (s, *C*CH_3), 141.8 (s, *C*CH_3), 108.6 (s, CH), 107.1 (s, CH), 40.4 (s, NCH_3), 15.2 (s, C*C*H_3), 13.5 (s, C*C*H_3), 12.4 (s, C*C*H_3), 12.1 (s, C*C*H_3) ^{11}B-{^{1}H}: 2.5 (br), −9.7 (br)
2 [Mo{OB(C_6F_5)$_3$}{HB(dmpz)$_3$}(OCH_2CH_2O)] C, 42.6 (42.8); H, 2.7 (2.7); B, 2.2 (2.2); N, 8.3 (8.6)	IR: 2965–2885w, 2572w, 1645s, 1544s, 1519vs, 1471vs, 1418s, 1386m, 1367s, 1284s, 1200s, 1089vs, 1061s, 1010s, 982vs, 909s, 888vs, 854m, 791s, 774m, 760m, 751m, 689s, 674s, 644s, 557m
3 [V{OB(C_6F_5)$_3$}{HB(dmpz)$_3$}(acac)] C, 47.0 (46.8); H, 3.2 (3.0); B, 2.0 (2.3); N, 8.6 (8.6)	IR: 3025–2932w, 2549m, 1645m, 1565s, 1542s, 1516vs, 1468vs, 1419s, 1386s, 1369s, 1334m, 1287m, 1205s, 1094s, 1075m, 1061m, 1044m, 1029m, 983s, 930m, 885s, 860m, 852m, 791m, 774m, 762m, 748m, 733m, 687m, 675w, 659w, 635m, 578m ^{11}B-{^{1}H}: −3.3 (br)
4 [Re{OB(C_6F_5)$_3$}{HB(pz)$_3$}(OCH_2CH_2O)] C, 34.7 (35.2); H, 1.3 (1.4); B, 1.9 (2.2); N, 8.2 (8.5)	IR: 2933–2868w, 2527w, 1646vs, 1520vs, 1471vs, 1408s, 1392m, 1317s, 1287s, 1216s, 1190m, 1108vs, 1056vs, 975vs, 925s, 897s, 842m, 816m, 771s, 729m, 714m, 673s, 659m, 638m, 617m, 590w, 576w, 561w, 528w ^{1}H:[d] 7.36 (d, 2 H), 7.12 (d, 2 H), 6.96 (d, 1 H), 6.49 (d, 1 H), 5.51 (t, 2 H), 5.26 (t, 1 H), 5.0 (4 H, vbr, CH_2) ^{13}C-{^{1}H}:[d] 148.4 (d, *J* 235, C_6F_5), 140.7 (d, *J* 245, C_6F_5), 137.3 (d, *J* 255, C_6F_5), 149.9, 139.3, 106.2 (pyrazole *trans* to glycolate), 141.7, 134.7, 105.5 (pyrazole *trans* to oxo), 90.5 (vbr, CH_2) ^{11}B-{^{1}H}: 4.6 (br) and −5.0 (br)
5 [Re{OB(C_6F_5)$_3$}{HB(pz)$_3$}(OEt)$_2$] C, 36.7 (36.6); H, 2.0 (2.0); B, 2.1 (2.2); N, 8.3 (8.3)	IR: 3155w, 3139w, 2977–2868w, 1647m, 1519vs, 1470vs, 1407s, 1380m, 1352m, 1315s, 1284m, 1214m, 1186m, 1105vs, 1056vs, 972vs, 932s, 913s, 841m, 816m, 773s, 731m, 714m, 677m, 648m, 618m, 590m, 577m ^{1}H: 7.33 (2 H), 6.79 (1 H, CH), 6.56 (2 H, CH), 6.43 (1 H, CH), 5.58 (2 H, CH), 5.25 (1 H, CH), 4.3 (2 H, vbr, CH_2), 4.0 (2 H, vbr, CH_2), 1.46 (6 H, t, *J* 6.7, CH_3) ^{13}C-{^{1}H}: 148.5 (d, *J* 240, C_6F_5), 140.2 (d, *J* 230, C_6F_5), 137.1 (d, *J* 240, C_6F_5), 149.5, 144.7, 107.7 (pyrazole *trans* to OEt), 139.2, 138.4, 106.5 (pyrazole *trans* to oxo), 95.9 (s, OCH_2), 18.1 (s, CH_3) ^{11}B-{^{1}H}: 4.0 (br) and −4.9 (br)
6 [Re{OB(C_6F_5)$_3$}{HB(pz)$_3$}(C_2O_4)] C, 34.2 (34.3); H, 1.1 (1.0), B, 2.0 (2.2); N, 8.3 (8.3)	IR: 3162w, 3138w, 2563w, 1759vs, 1647s, 1618s, 1647m, 1520vs, 1472vs, 1432m, 1407s, 1386m, 1317s, 1289m, 1215m, 1195m, 1182m, 1110vs, 1054vs, 988vs, 917w, 857w, 838w, 820m, 790s, 770s, 751m, 737m, 711m, 689m, 674m, 644m, 631m, 610m, 579m ^{1}H: 8.14 (2 H, d), 7.95 [2 H, d(br)], 7.53 (1 H, d), 6.97 (1 H, d), 6.64 (2 H, t), 6.10 (1 H, t) ^{13}C-{^{1}H}: 165 [s(br), C_2O_4], 148.1 (d, *J* 240, C_6F_5), 140.4 (d, *J* 220, C_6F_5), 137.1 (d, *J* 225, C_6F_5), 148.8, 141.5, 110.0 (pyrazole *trans* to oxalate), 140.9, 136.7, 106.5 (pyrazole *trans* to oxo) ^{11}B-{^{1}H}: −0.1 (br) and −4.6 (br) overlapping

[a] Analytical data given as found (calculated) in %. [b] Infrared data (cm^{-1}) determined as KBr discs; NMR data in C_6D_6 at 298 K, unless otherwise stated, given as chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment]. [c] The CN carbon atom was not observed. [d] In CD_2Cl_2.

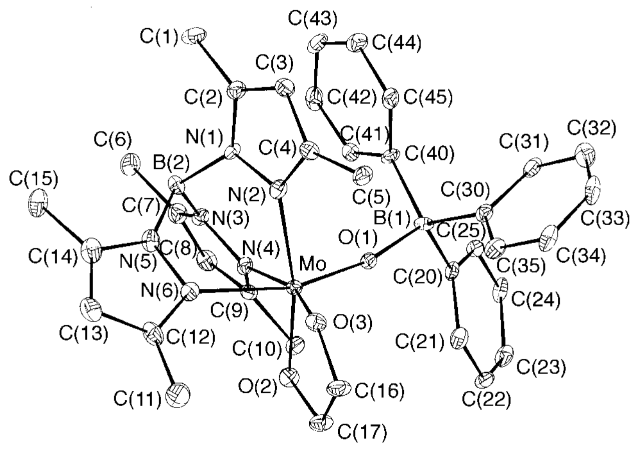

Fig. 2 Molecular structure of compound **2**. Details as in Fig. 1

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Mo–O	1.767(1)	O–Mo–B(1)	166.1(1)
Mo–N(2)	2.157(2)	S(1)–Mo–S(2)	72.73(2)
Mo–N(4)	2.169(2)	N(2)–Mo–N(4)	92.64(6)
Mo–N(6)	2.308(2)	O–Mo–N(6)	164.85(5)
Mo–S(1)	2.4181(5)	O–B(1)–C(20)	105.3(1)
Mo–S(2)	2.4020(5)	O–B(1)–C(30)	107.5(1)
O–B(1)	1.531(2)	O–B(1)–C(40)	111.2(1)

bond lengths in monooxo compounds fall in a narrow range [mean = 1.678 Å, width (twice the standard deviation) = 0.056 Å] and are not generally a sensitive function of the co-ordination number or the oxidation state of the metal.[13] Three closely related compounds, [MoO{HB(dmpz)$_3$}(*p*-OC_6H_4-Me)$_2$],[14] [MoO{HB(dmpz)$_3$}(*o*-OC_6Cl_4O)][15] and [MoO{HB-(dmpz)$_3$}(OPh)$_2$],[16] have been structurally characterised and exhibit Mo=O bond lengths which fall within this range (see Table 4). Thus we can be reasonably confident that the M=O bond distance in [MoO{HB(dmpz)$_3$}L_2] complexes is largely independent of the nature of L and predict a Mo=O bond length of around 1.68 Å for [MoO{HB(dmpz)$_3$}(OCH_2CH_2O)] which then lengthens by approximately 0.1 Å upon co-ordination to B(C_6F_5)$_3$. The B–O bond distance [1.538(7) Å] represents a normal B–O single bond and the Mo–O–B bond angle [166.4(3)°] closely resembles those found in analogous species.[7,8]

The vanadium complex [V{OB(C_6F_5)$_3$}{HB(dmpz)$_3$}(acac)] **3** could also be isolated in good yield as analytically pure orange microcrystals which were unsuitable for X-ray diffraction. The paramagnetic nature of the complex meant that little useful data could be obtained from NMR spectroscopy. However, on the basis of IR spectroscopy, elemental analyses (Table 1) and by comparison with our earlier results,[7] we propose a structure for this compound (Fig. 3) analogous to those of **1** and **2**.

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

Mo–O(1)	1.767(3)	O(1)–Mo–B(1)	166.4(3)
Mo–N(2)	2.231(4)	O(2)–Mo–O(3)	83.47(16)
Mo–N(4)	2.184(4)	N(2)–Mo–N(4)	94.27(16)
Mo–N(6)	2.260(4)	O(1)–Mo–N(6)	162.52(16)
Mo–O(2)	1.919(4)	O(1)–B(1)–C(20)	107.6(4)
Mo–O(3)	1.910(4)	O(1)–B(1)–C(30)	109.8(4)
O(1)–B(1)	1.538(7)	O(1)–B(1)–C(40)	103.2(4)

Table 4 Comparison of the Mo=O and Mo–N bond distances in $[MoO\{HB(dmpz)_3\}L_2]$ complexes

Compound	Elongation of *trans* Mo–N bond */Å	Mo=O/Å
1	0.145	1.767(1)
$[MoO\{HB(dmpz)_3\}(S_2CNEt_2)]$[9]	0.277	1.669(3)
$[MoO\{HB(dmpz)_3\}(S_2CNPr^i_2)]$[10]	0.285	1.676(4)
$[MoO\{HB(dmpz)_3\}\{S_2P(OEt)_2\}]$[17]	0.279	1.644(6)
2	0.053	1.767(3)
$[MoO\{HB(dmpz)_3\}(p\text{-}OC_6H_4Me)_2]$[14]	0.169	1.677(3)
$[MoO\{HB(dmpz)_3\}(o\text{-}OC_6Cl_4O)]$[15]	0.188	1.675(3)
$[MoO\{HB(dmpz)_3\}(OPh)_2]$[16]	0.147	1.680(3)

* Calculated as the difference in bond length between the N atom of the pyrazole ring *trans* and the average of the two N atoms of the rings *cis* to the terminal oxo ligand.

A comparison of the structural features of compounds **1** and **2** with those of $[MoO\{HB(dmpz)_3\}L_x]$ complexes (L = ancillary ligands) may be made. In both classes of compound a *trans* influence is observed such that the Mo–N bond *trans* to the oxo ligand is lengthened relative to the Mo–N bond *cis* to the Mo=O unit. However the *trans* influence appears to be smaller in compounds **1** and **2** (Table 4) suggesting that the Lewis acid withdraws electron density away from the metal centre, through the oxo unit, encouraging stronger bonding between the molybdenum centre and the nitrogen atom *trans* to it. No other significant differences between the remaining bond distances and angles of the tris(pyrazolyl)borate ligand in compounds **1** and **2** and their non-co-ordinated counterparts are seen.[18]

The precursor complex $[MoO\{HB(dmpz)_3\}(OCH_2CH_2O)]$ possesses two types of nucleophilic oxygen sites; a terminal oxo moiety and two alkoxyl substituents. However compound **2** preferentially reacts with the sterically demanding Lewis acid $B(C_6F_5)_3$ at its Mo=O unit. The same pattern of reactivity is observed in the formation of $[Re\{OB(C_6F_5)_3\}\{HB(pz)_3\}(OCH_2CH_2O)]$, **4**, through the reaction of $[ReO\{HB(pz)_3\}(OCH_2CH_2O)]$ (pz = pyrazolyl) with 1 equivalent of $B(C_6F_5)_3$. Full spectroscopic and analytical data for compound **4** are in Table 1. The ^1H NMR spectra of **4** and $[ReO\{HB(pz)_3\}(OCH_2CH_2O)]$ display the same pattern of signals,[19] a result which is consistent with co-ordination of the Lewis acid to the Re=O unit; in both species the signals due to the pyrazolyl ring protons are present in a 2:1 ratio consistent with one ring oriented *trans* to the terminal oxo moiety and the two remaining rings *trans* to the glycol ligand (Fig. 3). The $^{11}B\text{-}\{^1H\}$ NMR spectrum of compound **2** exhibits two overlapping signals at δ 4.6 and −5.0 and, whilst both signals are characteristic of a four-co-ordinate boron atom, the latter may be assigned to the boron atom of the $HB(pz)_3$ ligand and the former to the $Re{=}O{-}B(C_6F_5)_3$ fragment. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[ReO\{HB(pz)_3\}(OCH_2CH_2O)]$ displays a single resonance due to the methylene carbon atoms of the glycolate moiety indicating that the carbon atoms of the ethylene backbone are rapidly equilibrating. The equivalent resonance of compound **4** is broadened suggesting that co-ordination of a bulky $B(C_6F_5)_3$ moiety to the Re=O unit impedes this fluxional process.

The closely related compound $[Re\{OB(C_6F_5)_3\}\{HB(pz)_3\}(OEt)_2]$ **5**, may be prepared in an analogous fashion. Characterising data are detailed in Table 1 and are comparable to those for compound **4** suggesting that the salient features of the two species are similar (Fig. 3). Most significantly in the ^1H NMR spectrum of **5** the signals due to the $HB(pz)_3$ are consistent with an approximately octahedral *fac* ReN_3L_2L' geometry indicating that the Lewis acid has reacted with the Re=O unit and not one of the alkoxide ligands.

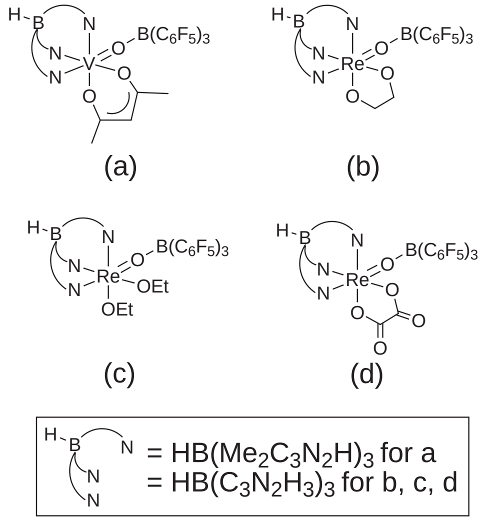

Fig. 3 Proposed structures of compounds **3** (a), **4** (b), **5** (c) and **6** (d)

The complex $[ReO\{HB(pz)_3\}(C_2O_4)]$ offers three types of nucleophilic oxygen atoms; two derived from the oxalate ligand, M–O–C and C=O groups, and a third formed by a terminal Re=O site.[19] Addition of 1 equivalent of $B(C_6F_5)_3$ produces a Lewis acid–metal complex adduct, $[Re\{OB(C_6F_5)_3\}\{HB(pz)_3\}(C_2O_4)]$ **6**. As observed for compounds **4** and **5**, ^1H NMR spectroscopy clearly indicates that the pattern of signals due to the $HB(pz)_3$ ligand in **6** is consistent with an approximately octahedral *fac* ReN_3L_2L' geometry indicating that the Lewis acid has reacted with the Re=O unit (Table 1). The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **6** exhibited a broad resonance due to the oxalate carbon atoms at δ 165 which is very similar to the signal assigned to the oxalate ligand in the starting complex (δ 161.8). In addition IR spectroscopy revealed absorptions assigned to the $C_2O_4{}^{2-}$ unit at 1759 and 1618 cm^{-1} which are very similar to those observed for the starting metal complex at 1753, 1732 and 1676 cm^{-1}.[19] These findings indicate that little perturbation of the oxalate ligand has occurred and suggest that the Lewis acid has preferentially attacked the Re=O unit (Fig. 3).

Crystals of compounds **4**, **5** and **6** suitable for study by X-ray diffraction could not be grown to confirm the proposed structures but spectroscopic data indicate that the Lewis acid exhibits a clear preference for the electron density presented by the Re=O moiety over the oxygen lone pairs offered by the alkoxide or oxalate ligands.

Herein and elsewhere we have demonstrated that the Lewis acid $B(C_6F_5)_3$ readily forms adducts with many terminal oxo-metal functionalities. However, in our hands, the complexes $[ReO\{HB(pz)_3\}Cl_2]$[19] and $[MoO\{HB(dmpz)_3\}Cl_2]$[11] failed to react with $B(C_6F_5)_3$. This suggests that electron density is more delocalised in $[MOCl_xL_y]$ systems, due to the presence of extended π systems and the strong electron withdrawing effect of the chloride ligands reducing the nucleophilicity of the M=O unit.

In conclusion, we have demonstrated that hydridotris(pyrazolyl)borate-stabilised metal complexes containing a variety of nucleophilic oxygen atom sites (oxo, alkoxide and oxalate) readily react with $B(C_6F_5)_3$. Stable complexes containing the $M{=}O{-}B(C_6F_5)_3$ moiety are formed and two of these, $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(S_2CNMe_2)]$ **1** and $[Mo\{OB(C_6F_5)_3\}\{HB(dmpz)_3\}(OCH_2CH_2O)]$ **2** have been structurally characterised. No evidence for electrophilic attack at alkoxide or oxalate ligands was observed.

Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. The compounds [ReO{HB(pz)$_3$}Cl$_2$],[19] [ReO{HB(pz)$_3$}(OEt)$_2$],[20] [ReO{HB(pz)$_3$}(OCH$_2$CH$_2$O)],[19] [ReO{HB(pz)$_3$}(C$_2$O$_4$)],[19] [MoO{HB(dmpz)$_3$}Cl$_2$],[11] [MoO{HB(dmpz)$_3$}(OCH$_2$CH$_2$O)],[11] [MoO{HB(dmpz)$_3$}(S$_2$CNMe$_2$)],[9] [VO{HB(dmpz)$_3$}(acac)][12] and B(C$_6$F$_5$)$_3$[21] were prepared as previously described.

Fourier-transform ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 and 96 MHz respectively, ^{13}C NMR spectra on a Bruker AM 300 spectrometer at 75.5 MHz or Varian Unity plus 500 spectrometer at 125 MHz: ^{1}H and ^{13}C shifts are reported with respect to δ 0 for SiMe$_4$, ^{11}B with respect to δ 0 for BF$_3$·OEt$_2$; all downfield shifts are positive. Infrared spectra were recorded on either a Mattson 'Polaris' Fourier-transform, Perkin-Elmer FT 1710 spectrophotometer or a Perkin-Elmer 457 grating spectrometer. Microanalyses were obtained from the microanalytical laboratory of this department.

Preparations

[Mo{OB(C$_6$F$_5$)$_3$}{HB(dmpz)$_3$}(S$_2$CNMe$_2$)] 1. Emerald green [MoO{HB(dmpz)$_3$}(S$_2$CNMe$_2$)] (548 mg, 1.04 mmol) was suspended in toluene (20 cm^3) and a toluene solution of B(C$_6$F$_5$)$_3$ (530 mg, 1.04 mmol) added. After stirring for 1 h a yellow-green solution had formed. The solvent was removed *in vacuo* and the residue washed with pentane before being extracted with toluene. Concentration of the toluene filtrate and cooling to −20 °C resulted in the formation of yellow-green block shaped crystals of compound **1**. Yield: 955 mg, 88%.

[Mo{OB(C$_6$F$_5$)$_3$}{HB(dmpz)$_3$}(OCH$_2$CH$_2$O)] 2. Blue [MoO{HB(dmpz)$_3$}(OCH$_2$CH$_2$O)] (469 mg, 1.0 mmol) was suspended in toluene (20 cm^3) and a toluene solution of B(C$_6$F$_5$)$_3$ (512 mg, 1.0 mmol) added. After stirring for 1 h a bright green solution had formed. The solvent was removed *in vacuo* and the residue washed with pentane before being extracted with toluene. Bright green block shaped crystals were obtained by layering a dichloromethane solution of compound **2** with pentane. Yield: 795 mg, 81%.

[V{OB(C$_6$F$_5$)$_3$}{HB(dmpz)$_3$}(acac)] 3. Pale blue [VO{HB(dmpz)$_3$}(acac)] (405 g, 0.906 mmol) was dissolved in toluene (20 cm^3) to give a mid-blue solution. A toluene solution of B(C$_6$F$_5$)$_3$ (445 mg, 0.869 mmol) was added slowly resulting in the formation of an orange solution. After stirring for 1.5 h the solvent was removed *in vacuo* and the residue washed with pentane (3 × 10 cm^3). Compound **3** was then extracted with toluene. Concentration of the toluene solution and cooling to −20 °C resulted in the formation of orange microcrystals. Yield: 636 mg, 73%.

[Re{OB(C$_6$F$_5$)$_3$}{HB(pz)$_3$}(OCH$_2$CH$_2$O)] 4. Blue-violet [ReO{HB(pz)$_3$}(OCH$_2$CH$_2$O)] (210 mg, 0.441 mmol) was suspended in hexane (20 cm^3) and a hexane solution (20 cm^3) of B(C$_6$F$_5$)$_3$ (226 mg, 0.441 mmol) added. The reaction was stirred for 5 h resulting in the formation of a turquoise precipitate. The very pale violet filtrate was removed, the solid washed with hexane (2 × 15 cm^3) and then dried *in vacuo*. Yield: 405 mg, 93%.

[Re{OB(C$_6$F$_5$)$_3$}{HB(pz)$_3$}(OEt)$_2$] 5. Blue [ReO{HB(pz)$_3$}(OEt)$_2$] (505 mg, 1 mmol) was partially dissolved in toluene (20 cm^3) to give a deep blue solution and a toluene solution (20 cm^3) of B(C$_6$F$_5$)$_3$ (512 mg, 1 mmol) slowly added. An immediate change to dark green occurred and the reaction mixture was stirred for 1.5 h by which time it had become dark brown. After removal of solvent *in vacuo* the residual brown oil was washed with hexane and a blue filtrate removed. On standing dark brown crystals of analytically pure compound **5** formed from these blue washings. The residual brown oil was extracted with toluene and then layered with hexane which led to the precipitation of **5** in the form of a brown oil. Combined yield 724 g, 71%.

[Re{OB(C$_6$F$_5$)$_3$}{HB(pz)$_3$}(C$_2$O$_4$)] 6. Violet [ReO{HB(pz)$_3$}(C$_2$O$_4$)] (231 mg, 0.459 mmol) was suspended in toluene (20 cm^3) and B(C$_6$F$_5$)$_3$ (235 mg, 0.459 mmol) dissolved in toluene (20 cm^3) was added slowly. The blue-violet suspension was stirred for 2 h and then CH$_2$Cl$_2$ (15 cm^3) added. The reaction was stirred for 16 h and then the solvent removed *in vacuo*. The solid was washed with toluene and a mid-blue filtrate removed. The residual solid was extracted with CH$_2$Cl$_2$ to yield compound **6** as a lilac solid. It can be crystallised from CH$_2$Cl$_2$–pentane at −20 °C as blue needle-like crystals. Yield: 284 mg, 61%.

Reaction of [ReO{HB(pz)$_3$}Cl$_2$] with B(C$_6$F$_5$)$_3$

Turquoise [ReO{HB(pz)$_3$}Cl$_2$] (251 mg, 0.5 mmol) was suspended in toluene (20 cm^3) and a toluene solution (20 cm^3) of B(C$_6$F$_5$)$_3$ (256 mg, 0.5 mmol) gradually added. The mixture was stirred at room temperature and after 16 h no apparent reaction had occurred. Addition of CH$_2$Cl$_2$ (15 cm^3) followed by stirring for 24 h produced no reaction and the starting reagents were recovered unchanged.

Reaction of [MoO{HB(dmpz)$_3$}Cl$_2$] with B(C$_6$F$_5$)$_3$

Emerald green [MoO{HB(dmpz)$_3$}Cl$_2$] (240 mg, 0.5 mmol) was suspended in toluene (20 cm^3) and a toluene solution (20 cm^3) of B(C$_6$F$_5$)$_3$ (256 mg, 0.5 mmol) gradually added. The mixture was stirred at room temperature and after 16 h no apparent reaction had occurred. Addition of CH$_2$Cl$_2$ (15 cm^3) followed by stirring for 24 h produced no reaction and the starting reagents were recovered unchanged.

Crystallography

A crystal of compound **1** was grown from toluene solution at 253 K whilst crystals of **2** were grown from CH$_2$Cl$_2$ solution layered with pentane at 293 K. For the structure determinations a crystal was immersed in highly viscous perfluoropolyether to exclude oxygen and prevent solvent loss. It was then mounted on a glass fibre and plunged in a cold (150 K) nitrogen stream.

Crystal data. Compound **1**, C$_{36}$H$_{28}$B$_2$F$_{15}$MoN$_7$OS$_2$, M = 1041.32, monoclinic, space group $P2_1/c$, a = 11.518(1), b = 14.248(1), c = 25.231(1) Å, β = 101.349(1)°, U = 4059.7 Å^3, Z = 4, D_c = 1.70 g cm^{-3}, μ = 5.20 cm^{-1}, lime green crystals, crystal dimensions 0.3 × 0.3 × 0.3 mm.

Compound **2**, C$_{35}$H$_{26}$B$_2$F$_{15}$MoN$_6$O$_3$, M = 981.16, monoclinic, space group $C2/c$, a = 24.737(7), b = 22.835(6), c = 15.395(3) Å, β = 123.54(2)°, U = 7502.5 Å^3, Z = 4, D_c = 1.74 g cm^{-3}, μ = 4.60 cm^{-3}, green crystals, crystal dimensions 0.36 × 0.41 × 0.60 mm.

Data collection and processing. The data were collected at 150 K on an Enraf-Nonius DIP2000 image plate diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). An Oxford Cryosystems CRYOSTREAM cooling system was used. The images were processed with the DENZO and SCALEPACK programs.[22] Corrections for Lorentz-polarisation effects were performed but not for absorption.

Structure solution and refinement. Crystal structures were solved by direct methods and refined by full-matrix leastsquares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically and refined isotropically except where described otherwise below. All crystallographic calculations were carried out using the CRYSTALS program package.[23] Neutral atom scattering factors were taken from ref. 24.

For compound **1** 7349 unique reflections were collected and 5473 observed $[I > 10\sigma(I)]$ and refined on F with 690 parameters. A correction for secondary extinction was applied and refinement completed with a Chebychev weighting scheme[25] with parameters 1.71, 0.441 and 1.30. Final residuals were $R = 0.0215$ and $R' = 0.0220$ and minimum and maximum residual electron densities of -0.41 and 0.31 e Å^{-3}.

For compound **2** 7605 unique reflections were collected and 7391 observed $[I > 3\sigma(I)]$ and refined on F with 563 parameters. Refinement was completed with a weighting scheme $w^{-1} = 0.0010\ F + 12.1(\sigma^2 F + 12.0)$. Final residuals were $R = 0.0811$ and $R' = 0.0855$ and minimum and maximum residual electron densities -1.59 and 0.98 e Å^{-3}. The residuals are somewhat high but all atoms were well behaved in the refinement and there was no indication of disorder or any other species in the asymmetric unit.

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