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FULL PAPER

Reactions of organometallic oxometal complexes with $B(C_6F_5)_3$: synthesis, structure, bonding and reactivity of $[Mo(\eta^5\text{-}C_5H_4Me)_2\text{-}\{OB(C_6F_5)_3\}]$

Jane R. Galsworthy,[a] Jennifer C. Green,[a] Malcolm L. H. Green[a] and Matthias Müller[b]

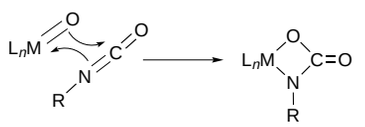
[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford, UK OX1 3PD*

Organometallic oxo complexes $[M(C_5H_4R)_2O]$ reacted with the strong Lewis acid $B(C_6F_5)_3$ at their oxo functionality to yield $[M(C_5H_4R)_2\{OB(C_6F_5)_3\}]$ (M = Mo, R = Me **1**; M = W, R = H **2**). The structure of **1** has been determined by X-ray crystallography. Density functional theory (DFT) calculations on $[Mo(C_5H_5)_2O]$ and $[Mo(C_5H_5)_2(OBF_3)]$ have been used to model the changes in geometry to the $[Mo(C_5H_5)_2O]$ fragment on co-ordination by $B(C_6F_5)_3$ and indicate that this process is charge rather than orbitally controlled. Compound **1** reacted with PhNCO to yield $[\overline{Mo(C_5H_4Me)_2\{OC(O)N}Ph\}\{B(C_6F_5)_3\}]$; spectroscopic evidence and DFT calculations suggest that the Lewis acid is bound to the molybdenum oxygen atom.

Bis(cyclopentadienyl)oxo complexes of molybdenum and tungsten contain oxo ligands which display enhanced nucleophilic character. Thus the metal–oxygen bonds undergo [2 + 2] cycloaddition reactions with both organic and organometallic substrates to yield stable metallocycles (Scheme 1).[1–4] These reactions are thought to proceed in a stepwise fashion, initiated by attack of the oxo group on the electrophilic carbon atoms of the various substrates. Photoelectron spectroscopy and extended-Hückel molecular-orbital calculations upon these systems show that $[M(C_5H_5)_2O]$ (M = Mo or W) has two electrons occupying a high-lying orbital which is mainly localised on the cyclopentadienyl ligands and the oxygen. It is believed that these high-lying electrons are responsible for the enhanced basic and nucleophilic character of these oxometal compounds.[5] However the highest occupied molecular orbital (HOMO) is metal based leading to three possible sites for electrophilic attack: at a cyclopentadienyl ring, at the metal centre or at the oxo functionality. The former type of reactivity is exemplified by the formation of $[W(C_5H_5)\{C_5H_4BRCl_2\}H_3]$ from $[W(C_5H_5)_2H_2]$ and $BRCl_2$ (R = Pr^i or Bu^t).[6] A smaller Lewis acid, such as BF_3, has been reported to react at the metal to yield $[W(C_5H_5)_2H_2\text{-}(BF_3)]$ although subsequent investigations throw some doubt on these initial results.[7] Previous reports have shown that methylation of $[Mo(C_5H_5)_2(NR)]$ with MeI occurs at the metal centre.[8] The third type of reactivity is implicated in the formation of $[MO_x\{OB(C_6F_5)_3\}(acac)_2]$ species (x = 1, M = V or Ti; x = 2, M = Mo; acac = acetylacetonate).[9] Herein we report investigations into the reactivity of $[M(C_5H_4R)_2O]$ (M = Mo, R = Me; M = W, R = H) complexes towards the strong Lewis acid $B(C_6F_5)_3$, and the reactivities of the newly formed products.

Results and Discussion

Treatment of $[Mo(C_5H_4Me)_2O]$ with 1 equivalent of $B(C_6F_5)_3$ under ambient conditions yields a Lewis-acid adduct, $[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ **1**. Full spectroscopic and analytical data for compound **1** are given in Table 1. The ^{11}B NMR spectrum exhibits a signal at δ 2.3 characteristic of a four-co-ordinate boron atom and typical of other compounds containing the $MOB(C_6F_5)_3$ moiety.[9] Two signals assignable to cyclopentadienyl ring protons are visible in the ^1H NMR spectrum of **1**, as expected for an AA′BB′ system, indicating that the cyclopentadienyl rings are free to rotate about their metal axis.



Scheme 1 [2 + 2] Addition reactions of M=O species

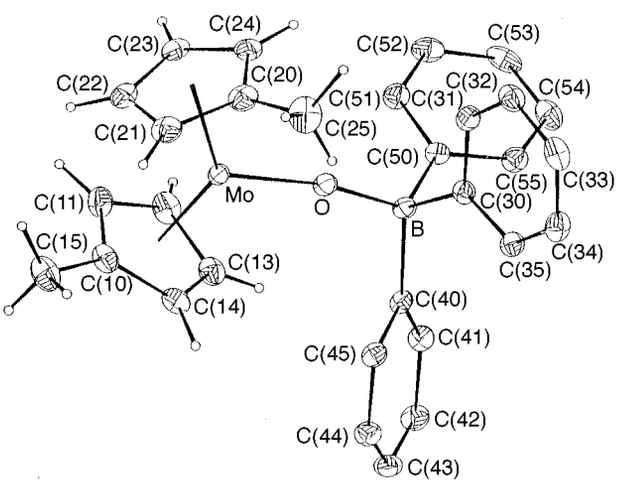


Fig. 1 View of the structure of $[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ **1**. Fluorine atoms omitted for clarity

The molecular structure of compound **1** is shown in Fig. 1 and selected bond angles and distances are given in Table 2. The molybdenum centre is co-ordinated in an η^5 fashion to two C_5H_4Me rings which are staggered with respect to each other. The interplanar angle between the C_5H_4Me rings is 47.1°. The Mo–O distance of 1.835(1) Å is significantly longer than that of the parent compound (1.72 Å)[10] reflecting a reduction in bond order on complexation of the boron Lewis acid to the oxo group. The B–O distance of 1.484(2) Å is the shortest boron–oxygen single bond yet reported for this type of compound[9] and the Mo–O–B angle is 164.9(1)°.

The closely related tungsten compound, $[W(C_5H_5)_2\{OB(C_6F_5)_3\}]$ **2**, has been prepared and fully characterised (Table 1). Its spectroscopic data suggest that its structure is analogous to that of compound **1**. A previous example of an oxotungsten complex co-ordinated to a Lewis acid, $[W(OAlBr_3)(CH_2Bu^t)_3Br]$, has been crystallographically characterised and this exhibits a W–O–Al unit which deviates from linearity by 8(1)°.[11]

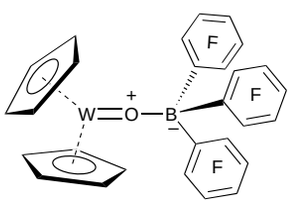
Table 1 Analytical and spectroscopic data for compounds **1**–**3**

Complex[a]	Spectroscopic data[b]
1 $[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ C, 46.4 (46.0); H, 1.6 (1.8); B, 1.3 (1.4)	IR: 3070–2850w, 1643s, 1518vs, 1462vs, 1403s, 1392s, 1087vs, 1050m, 1030m, 974vs, 941m, 914s, 904m, 896m, 847m, 841m, 815m, 771m, 764m, 745m, 736m, 684m, 677m, 663m ^{1}H:[c] 5.05 (4 H, t, *J* 2.3, C_5H_4), 4.43 (4 H, m, *J* 2.3, C_5H_4), 1.11 (6 H, s, CH_3) ^{13}C:[c] 148.2 (d, *J* 240, C_6F_5), 139.7 (d, *J* 232, C_6F_5), 137.1 (d, *J* 270, C_6F_5), 116.8 (s, *C*CH_3), 106.3 (s, CH), 100.3 (s, CH), 14.4 (s, CH_3) ^{11}B:[c] 2.3 (s)
2 $[W(C_5H_5)_2\{OB(C_6F_5)_3\}]$ C, 39.8 (40.0); H, 1.1 (1.2); B, 1.2 (1.3)	IR: 2963–2866w, 1647s, 1516vs, 1462vs, 1430vs, 1403m, 1393m, 1380m, 1371m, 1283vs, 1100vs, 1089vs, 1016m, 975vs, 920vs, 880s, 844m, 820m, 791m, 772m, 764m, 747m, 735m, 728m, 687m, 675m, 663m ^{1}H: 5.74 (s, C_5H_5) ^{13}C: 147.8 (d, *J* 248, C_6F_5), 139.4 (d, *J* 277, C_6F_5), 136.9 (d, *J* 245, C_6F_5), 98.8 (s, C_5H_5) ^{11}B: 1.6 (s)
3 $[\overline{Mo(C_5H_4Me)_2\{OC(O)N}Ph\}\{B(C_6F_5)_3\}]$, beige solid C, 49.7 (49.3); H, 2.0 (2.1); B, 1.1 (1.2); N, 1.6 (1.8)	IR: 3135–2830w, 1900–1790w, 1646m, 1600w, 1533m, 1516s, 1465vs, 1447vs, 1351s, 1325m, 1237m, 1203m, 1069m, 1026m, 1014m, 920s, 904vs, 845m, 804m, 757s, 746m, 737m, 700s, 620m, 606s, 595m, 515m, 508m ^{1}H:[c] 7.20–7.09 (5 H, m, C_6H_5), 4.29 (2 H, dd, *J* 4.7, 2.3, C_5H_4), 4.18 (2 H, dd, *J* 4.9, 2.9, C_5H_4), 3.66 (2 H, dd, *J* 4.3, 2.1, C_5H_4), 3.52 (2 H, dd, *J* 4.9, 2.9, C_5H_4), 1.19 (6 H, s, CH_3) ^{13}C:[c] 169.1 (s, CO), 148.7 (d, *J* 240, C_6F_5), 139.2 (d, *J* 235, C_6F_5), 137.5 (d, *J* 240, C_6F_5), 129.1 (s, C_6H_5], 123.5 (s, C_6H_5), 123.4 (s, C_6H_5), 122.2 (s, C_6H_5), 101.8 (s, C_5H_5), 101.1 (s, C_5H_5), 93.3 (s, *C*CH_3), 90.0 (s, C_6H_5), 13.4 (s, CH_3) ^{11}B: −3.7 (s)
light brown crystals C, 49.6 (49.3); H, 2.3 (2.1); B, 1.1 (1.2); N, 1.7 (1.6)	As for beige solid

[a] Analytical data given as found (calculated) in %. [b] IR data (cm^{-1}) determined as KBr discs, NMR data in C_6D_6 at 298 K, unless otherwise stated, chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment]. [c] In $CDCl_3$.

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

Mo–C(10)	2.420(2)	Mo–C(21)	2.317(2)
Mo–C(11)	2.371(2)	Mo–C(22)	2.309(2)
Mo–C(12)	2.273(2)	Mo–C(23)	2.284(2)
Mo–C(13)	2.257(2)	Mo–C(24)	2.371(2)
Mo–C(14)	2.318(2)	O–B	1.484(2)
Mo–C(20)	2.413(2)	Mo–O	1.835(1)
Mo–O–B	164.9(1)		



2

Calculation of the optimum geometry of $[Mo(C_5H_5)_2O]$ **4** and $[Mo(C_5H_5)_2(OBF_3)]$ **5** gave bond lengths within 4% of those observed for $[Mo(C_5H_4Me)_2O]$ **6** and **1** (Table 3). The calculations reproduced the main features of the structures but not the details. In particular they reproduced the lengthening of the Mo–O distance on co-ordination by the Lewis acid, and the small deviation from linearity of the Mo–O–B unit.

The one-electron wavefunctions for complex **4** are very similar to those found by extended-Hückel[5] and *ab initio* calculations.[12] Comparison of such wavefunctions for **4** and **5** shows the following changes. On binding of BF_3 seven of the top eight occupied orbitals of **4** are little changed in spatial distribution, but have energies lower by 1.1–1.3 eV (106–125 kJ mol^{-1}). The eighth, the Mo–O σ-bonding orbital, $1a_1$, loses most of its molybdenum character, and is stabilised by 3.0 eV (289 kJ mol^{-1}), transforming into an O–B–F bonding orbital. These energy shifts are represented diagrammatically in Fig. 2. Some of the key molecular orbitals (MOs) of **5** are shown in Fig. 3. The labelling is consistent with that given by Bridgeman *et al.*[5] Thus the frontier orbitals and the π interaction in the Mo–O bond is little affected by BF_3 co-ordination. The weakening and lengthening of the Mo–O bond on co-ordination can be traced to the depletion of the σ-bonding character.

Table 3 Comparison of calculated bond lengths (Å) and angles (°) for $[Mo(C_5H_5)_2O]$ **4** and $[Mo(C_5H_5)_2(OBF_3)]$ **5** with experimental bond lengths and angles for $[Mo(C_5H_4Me)_2O]$ **6** and $[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ **1**

	4	**6**	**5**	**1**
Mo–O	1.78	1.72	1.84	1.84
Mo–C	2.39–2.56	2.32–2.42	2.37–2.49	2.26–2.42
C–C*	1.42–1.45	1.41–1.43	1.43–1.44	1.41–1.43
O–B			1.54	1.48
Ring–ring	36.6	46.3	39.2	47.1
Mo–O–B			174.2	164.9

* Bond distances within the C_5H_4R (R = H or Me) rings only.

The conventional view of the interaction of a Lewis acid with a Lewis base is that the HOMO of the base interacts with the lowest unoccupied molecular orbital (LUMO) of the acid forming a donor–acceptor electron-pair bond. Within this context, the interaction we have found here is unconventional in that the acid interacts directly with the eighth occupied orbital of the molecule and not either of the two high-lying electron pairs. In this sense the binding of the Lewis acid is not orbitally controlled.

Examination of the molecular potential of complex **4** shows the negative potential to be concentrated on the O pointing away from the Mo (Fig. 4). This appears to be the source of attraction for the Lewis acid rather than the high-lying $2b_2$ orbital which is largely unperturbed by the co-ordination.

The reactions between $[Mo(C_5H_5)_2O]$ and organic compounds containing unsaturated heteronuclear functionalities have been reported.[1–4] That with phenyl isocyanate proceeds *via* [2 + 2] addition to yield $[\overline{Mo(C_5H_5)_2\{OC(O)N}Ph\}]$.[1]

The reaction of compound **1** with 5 equivalents of PhNCO is complete after 3 h. A ^{1}H NMR spectrum of the crude reaction mixture indicated the presence of two new products in a 2:1 ratio. The major product can be precipitated as a beige solid, by diffusion of pentane into a toluene solution, or crystallised as laminar light brown crystals from cold toluene (−20 °C). The

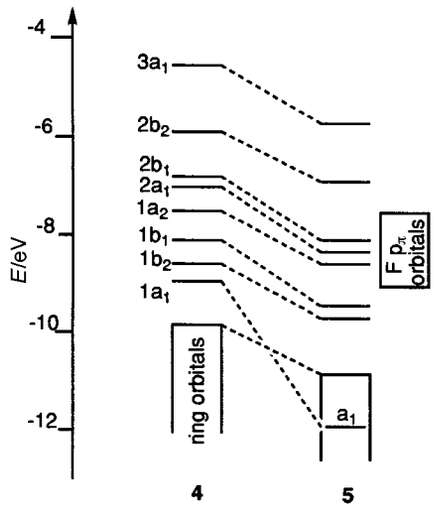


Fig. 2 Correlation of the top occupied orbitals of complexes **4** and **5**. For **5** the energy region of the fluorine p_π orbitals overlaps with that of the cyclopentadienyl π orbitals

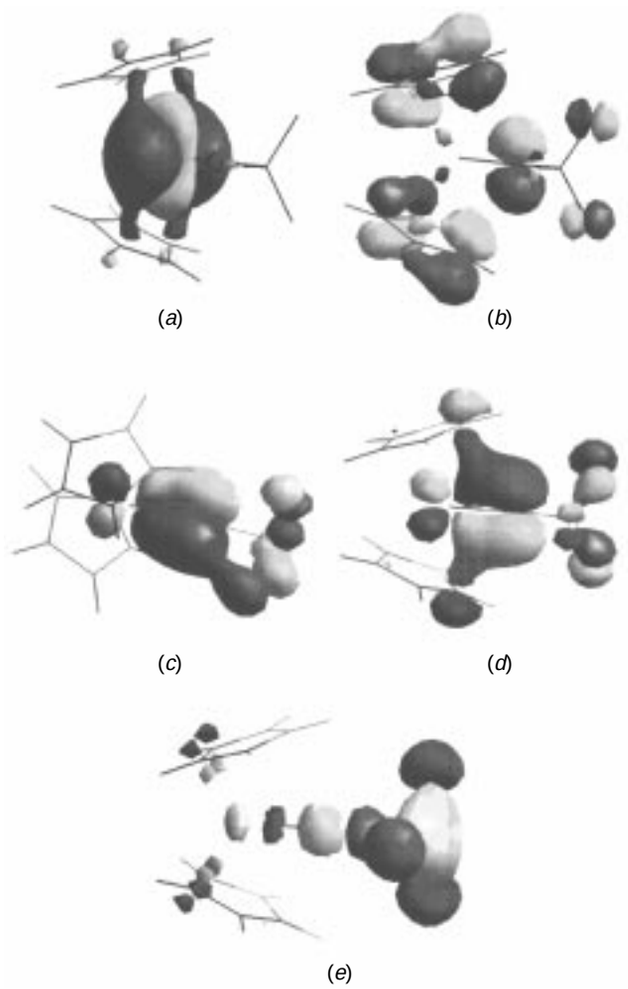


Fig. 3 Selected one-electron wavefunctions for $[Mo(C_5H_5)_2(OBF_3)]$: (*a*) $3a_1$ HOMO, (*b*) $2b_2$, (*c*) $1b_1$, (*d*) $1b_2$ and (*e*) $1a_1$. Orbital numbering corresponds to that of the analogous obrbital in $[Mo(C_5H_5)_2O]$[5]

spectroscopic and analytical data for the compound in both forms (Table 1) are consistent with the molecular formula $[\overline{Mo(C_5H_4Me)_2\{OC(O)N}Ph\}\{B(C_6F_5)_3\}]$ **3**. Compound **3** displays four multiplet signals in the cyclopentadienyl region of its ^1H NMR spectrum compared to two resonances exhibited by the precursor complex **1**. This is consistent with [2 + 2] addition of the isocyanate across the Mo=O bond to generate a four-membered $\overline{MoOC(O)N}Ph$ metallocycle perpendicular

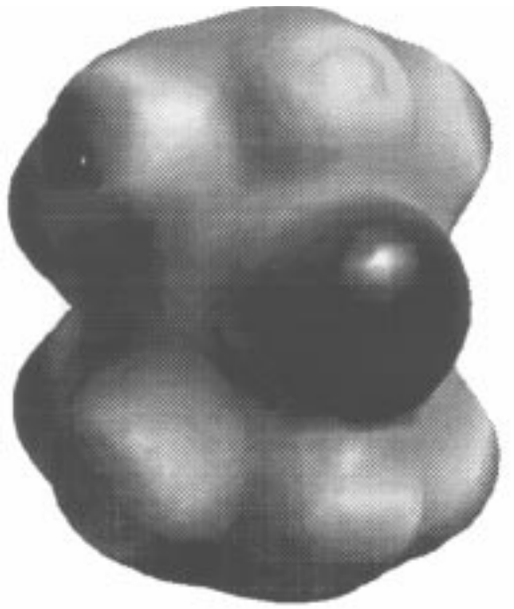
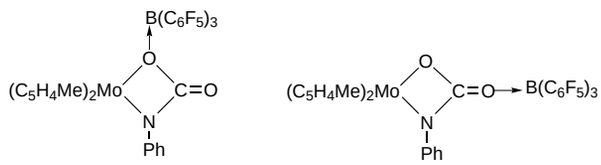


Fig. 4 Molecular potential superimposed on a representation of the electron density of $[Mo(C_5H_5)_2O]$; the very dark area on the oxygen represents the most negative potential while the cyclopentadienyl hydrogens show a positive potential



to the plane defined by the molybdenum atom and the centres of the cyclopentadienyl rings. Such a geometrical arrangement has been crystallographically confirmed for $[\overline{Mo(C_5H_5)_2\{OC(O)N}Ph\}]$.[1] A ^{11}B NMR spectrum of compound **3** reveals a resonance at δ −3.7 indicative of a four-co-ordinate boron centre. There are two sites on the four-membered metallocycle which could potentially bind a Lewis acid: the oxygen atom within the metallocycle (**3a**), which is the atom to which $B(C_6F_5)_3$ is originally bound, or the *exo* C-bonded oxygen atom derived from the isocyanate ligand (**3b**). There is always the possibility that $B(C_6F_5)_3$ could become detached during the course of the reaction. Infrared spectroscopy does not allow us to distinguish between these two possibilities as strong stretches assigned to the $B(C_6F_5)_3$ unit obscure the region of carbon–oxygen bond stretches. However the ^{13}C NMR spectroscopic resonances for the ring carbon atoms in four-membered metallocycles display characteristic signals at δ 170.2, $[\overline{Mo(C_5H_5)_2\{OC(O)N}Ph\}]$,[4] 174.3 $[\overline{W(C_5H_5)_2\{OC(O)N}Ph\}]$,[4] and 169.1, compound **3**. The similarity of the chemical shift of these three carbon atoms suggests that the metallocycle carbon atom in **3** is not substantially different from those in the other two species. Thus we propose that the $B(C_6F_5)_3$ moiety is co-ordinated to the molybdenum-bound oxygen atom (**3a**).

Density functional theory (DFT) calculations were used to compare the two different bonding sites. Geometries were optimised with BF_3 bound to the carbonyl oxygen of $[\overline{Mo(C_5H_5)_2\{OC(O)N}H\}]$ and to the ether oxygen of $[\overline{Mo(C_5H_5)_2\{OC(O)N}H\}]$. The latter was found to be more stable by 21.5 kJ mol^{-1}. Space-filling models were used to test the steric interaction of the $B(C_6F_5)_3$ in both sites. The O–B bond lengths and angles were taken from the optimised structures for the BF_3 complexes and the geometry of $B(C_6F_5)_3$ was

taken from that found for **1**. There was no evidence for steric hindrance when $B(C_6F_5)_3$ was bound to the carbonyl oxygen. When $B(C_6F_5)_3$ was bound to the ether oxygen the group could be accommodated by interleaving one of the fluorophenyl rings between the two cyclopentadienyl rings, however the structure appeared more crowded. Thus co-ordination to the ether oxygen is predicted to be slightly more favourable on energetic grounds but may be sterically less favourable.

Attempts to synthesize a 2,6-bis(isopropyl)phenyl isocyanate analogue of compound **3** by the reaction of $[Mo(C_5H_4Me)_2O]$ with 2,6-$Pr^i_2C_6H_3NCO$ were not successful. Although NMR spectroscopic studies of the crude reaction mixture indicated that high-yield synthesis of the desired product had occurred, subsequent reactions and decomposition precluded isolation of a well defined product.

It is interesting that the readiness of $[M(C_5H_5)_2O]$ complexes (M = Mo or W) to undergo [2 + 2] cycloaddition reactions with isocyanates has been ascribed to the enhanced nucleophilic character of the oxide ligand.[4] The reactions are thought to proceed in a stepwise fashion, initiated by oxygen attack on the electrophilic carbon of the substrate. From our studies it is clear that formation of a four-membered metallacarbamate is not impeded by co-ordination of $B(C_6F_5)_3$ to the metal oxide ligand. Indeed, the presence of very similar frontier orbitals for the two species would suggest that such orbitally controlled reactions should be similar.

One general route to imidometal complexes involves the reaction of isocyanates with oxometal complexes.[13] It has been suggested that reaction proceeds through an intermediate metallocycle. However all previously reported cyclometallocarbamates have presented a remarkably stable core and attempts to extrude CO_2 by prolonged heating have produced no effect.[1] Similar results were obtained for compound **3** which may be recovered intact after several hours reflux in toluene. In contrast the reaction of $[\{Mo(C_5H_5)O(\mu\text{-}O)\}_2]$ with phenyl isocyanate, under more forcing conditions, results in the formation of an imido species, $[\{Mo(C_5H_5)(NPh)(\mu\text{-}NPh)\}_2]$, although no intermediate metallocycle was observed.[14]

Experimental

Fourier-transform ^1H 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 at 75.5 MHz or Varian Unity plus 500 at 125 MHz and ^{19}F NMR spectra on a Varian Unity plus 500 spectrometer at 470 MHz; ^1H and ^{13}C shifts are reported with respect to δ 0 for $SiMe_4$, ^{11}B with respect to δ 0 for $BF_3{\cdot}OEt_2$ and ^{19}F with respect to δ 0 for $CFCl_3$, all downfield shifts being positive. Infrared spectra were recorded on either Mattson 'Polaris' Fourier-transform, Perkin-Elmer FT 1710 spectrophotometer, or Perkin-Elmer 457 grating spectrometers. Microanalyses were obtained from the microanalytical laboratory of this department.

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 $[Mo(C_5H_4Me)_2O]$,[15] $[W(C_5H_5)_2O]$[16] and $B(C_6F_5)_3$[17] were prepared as previously described; PhNCO and 2,6-$Pr^i_2C_6H_3NCO$ were used as received (Aldrich).

Preparations

$[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ 1. The deep green compound $[Mo(C_5H_4Me)_2O]$ (0.540 g, 2 mmol) was partially dissolved in toluene (20 cm^3) and a toluene solution (20 cm^3) of $B(C_6F_5)_3$ (1.024 g, 2 mmol) added. The mixture was stirred for 2 h during which time a dark green-brown solution formed. After removal of solvent *in vacuo* the residue was washed with pentane and the desired product then extracted with toluene. This solution was concentrated and cooled to −20 °C resulting in the formation of large block-shaped green-brown crystals of **1**. Yield 1.24 g, 79%.

$[W(C_5H_5)_2\{OB(C_6F_5)_3\}]$ 2. The purple compound $[W(C_5H_5)_2O]$ (0.329 g, 1 mmol) was partially dissolved in toluene (20 cm^3) and a toluene solution (20 cm^3) of $B(C_6F_5)_3$ (0.512 g, 1 mmol) added. The mixture was stirred for 4 h during which time a brown solution formed. After removal of solvent *in vacuo* the residue was washed with pentane and the desired product then extracted with toluene. This solution was concentrated and cooled to −20 °C resulting in the formation of dark brown crystals of **2**. Yield: 0.65 g, 77%.

$[\overline{Mo(C_5H_4Me)_2\{OC(O)N}Ph\}\{B(C_6F_5)_3\}]$ 3. Compound **1** (0.391 g, 0.5 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and PhNCO (0.55 cm^3, 5 mmol) added. The mixture was stirred for 3 h during which time a red-brown solution formed. After removal of solvent *in vacuo* the residue was washed with pentane and the desired product then extracted with toluene. Concentration of the toluene solution and cooling to −20 °C resulted in the formation of laminar brown crystals. Diffusion of pentane into a toluene solution of compound **1** yields a beige precipitate. Combined yield: 0.37 g, 82%.

Reaction of 2,6-$Pr^i_2C_6H_3NCO$ with $[Mo(C_5H_4Me)_2\{OB(C_6F_5)_3\}]$ 1

Compound **1** (0.391 g, 0.5 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and 2,6-$Pr^i_2C_6H_3NCO$ (1.05 cm^3, 5 mmol) added. The mixture was stirred for 3 h during which time a red-brown solution formed. After removal of solvent *in vacuo* the residue was washed with pentane and then extracted with toluene. The NMR spectroscopic studies suggested that a single product had formed but no compound could be isolated cleanly from the reaction.

Thermolysis of compound 3

Compound **3** (60 mg, 0.067 mmol) was dissolved in toluene (10 cm^3) and the brown solution heated to reflux for 3 h. The NMR spectroscopic data indicated that no reaction had occurred.

Crystallography

A crystal of compound **1** was grown from toluene solution at 253 K and immersed in highly viscous perfluoropolyether to exclude oxygen. It was then mounted on a glass fibre and plunged in a cold (150 K) nitrogen stream.

Crystal data. $C_{30}H_{14}BF_{15}MoO$ **1**, $M = 782.16$, triclinic, space group $P\bar{1}$, $a = 10.092(1)$, $b = 10.433(1)$, $c = 14.054(1)$ Å, $\alpha = 83.679(2)$, $\beta = 85.666(2)$, $\gamma = 63.564(2)°$, $U = 1316.4$ Å^3, $Z = 2$, $D_c = 1.97$ g cm^{-3}, $\mu = 6.16$ cm^{-1}, green crystals, crystal dimensions 0.3 × 0.3 × 0.3 mm.

Data collection and processing. The data were collected at 150 K on an Enraf-Nonius DIP2020 image-plate diffractomer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). An Oxford Cryosystems CRYOSTREAM cooling system was used. 15251 Reflections were measured ($1 < \theta < 26°$, $\pm h$, $\pm k$, $\pm l$), 5101 unique giving 4803 with $I > 3\sigma(I)$. The images were processed with the DENZO and SCALEPACK programs.[18] Corrections for Lorentz-polarisation effects were performed but not for absorption.

Structure solution and refinement. The crystal structure was solved by direct methods and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined in anisotropic and all hydrogen atoms in isotropic approximation. 4803 Observations for 490 refined parameters resulted in a ratio observations : refined parameters of 9.8 : 1. A correction for secondary extinction was applied and refinement completed

using a Chebyshev weighting scheme[19] with parameters 1.71, 0.441 and 1.30. Refinement on F converged at $R = 0.025$, $R' = 0.029$ and goodness of fit = 1.072. A final Fourier-difference synthesis showed minimum and maximum residual electron densities of -0.41 and 0.40 e $Å^{-3}$. All crystallographic calculations were carried out using the CRYSTALS program package.[20] Neutral atom scattering factors were taken from ref. 21.

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Computational details

All calculations were carried out using the Amsterdam Density Functional (ADF) program system, version 2.0.1.[22] The electronic configurations of the molecular systems were described by an uncontracted triple-ζ basis set of Slater-type orbitals (STOs). Atoms H, B, C, N, O and F were given an extra polarisation function, 2p on H and 3d on B, C, N, O and F. The cores of the atoms were frozen, B, C, N, O and F up to 1s and Mo up to 4p.

Energies were calculated using Vosko, Wilk and Nusair's local exchange correlation potential,[23] with non-local-exchange corrections by Becke[24] and non-local correlation corrections by Perdew.[25,26] The non-local correction terms were utilised in calculating gradients during geometry optimisations, so as to find the non-local minimum.

Geometries were optimised for $[Mo(C_5H_5)_2O]$ **4**, $[Mo(C_5H_5)_2(OBF_3)]$ **5**, $[\overline{Mo(C_5H_5)_2\{OC(O)N}H\}]$ **7**, $[\overline{Mo(C_5H_5)_2\{O(BF_3)C(O)N}H\}]$ **8**, and $[\overline{Mo(C_5H_5)_2\{OC(OBF_3)N}H\}]$ **9**. No symmetry was assumed in any of the optimisations and all geometric parameters were allowed to vary freely. The minima found were found to be stable from a variety of nearby starting geometries.

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