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FULL PAPER

Synthesis, structure, spectroscopic and electrochemical study of the paramagnetic compound [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$]†

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The reaction of [NEt_4][7-*nido*-$TeB_{10}H_{11}$] **1** with [Mo(CO)$_3$(η^7-C_7H_7)][BF_4] **2** in dichloromethane yields the novel paramagnetic, B-fluorinated, "mixed-sandwich" compound [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** in 19% yield. An X-ray diffraction study of **3** establishes the *closo* twelve-vertex $MoTeB_{10}$-cage structure with two B–F units at adjacent positions. The structure of **3** was solved in space group $Pna2_1$ with unit cell dimensions of $a = 16.7598(18)$, $b = 12.5500(11)$, $c = 7.2607(18)$ Å, and $Z = 4$. The final R factor was 0.0291 for 1471 observed reflections. Principal interatomic distances are Mo–Te 2.7083(8), B–F 1.396(9) and 1.410(9) Å. In the $MoTeB_{10}$ cage interatomic distances are in the ranges; Mo–B 2.363(8) to 2.481(9), Te–B 2.293(9) to 2.373(9) and B–B 1.720(13) to 1.943(12) Å. EPR spectra confirm the paramagnetic nature of **3** with the unpaired electron located in a mainly molybdenum-based molecular orbital. The cyclic voltammetric response of **3** exhibits a reversible one-electron reduction at $E^{0'} = -0.39$ V in dichloromethane solvent.

Paramagnetic metallacarbaborane clusters with *commo* structures of the general type [3,3′-*commo*-M-(1,2-*closo*-$C_2B_9H_{11}$)$_2$]$^{n-}$, have been known for thirty years with metals such as chromium,[2] iron,[3] nickel,[4] copper,[3] palladium, and gold.[5] Similarly, paramagnetic "mixed sandwich" compounds with a combination of carbaborane and η^n-C_nH_n hydrocarbon ligands have been known since the late 1960's but are somewhat rarer than the *commo* species. Examples include neutral complexes such as [3-(η^5-C_5H_5)-3,1,2-*closo*-$MC_2B_9H_{11}$] for M = Cr,[2] or Fe,[3] [1,2-Et_2-3-(η^5-C_5Me_5)-3,1,2-*closo*-$FeC_2B_4H_4$],[6] [1,2-Et_2-3-(η^8-C_8H_8)-3,1,2-*closo*-$VC_2B_4H_4$],[7] and radical cations [1,2-Et_2-3-(η^6-C_6Me_6)-3,1,2-*closo*-$FeC_2B_4H_4$]$^+$,[8] and, more recently, [1-(η^5-C_5H_5)-2-Me-1,2,3,4-*closo*-$FeC_3B_7H_9$]$^+$.[9] Because of their unpaired electron status these compounds are of intrinsic interest to cluster chemists concerned with the relationships between cluster structures and electron counts.

Although the Group 16 heteroborane ligands {$XB_{10}H_{10}$} (X = S, Se, Te) are considered to be electronically equivalent to {$C_2B_9H_{11}$}, there are apparently no well-characterised paramagnetic mixed sandwich clusters with {$XB_{10}H_{10}$} and η^n-C_nH_n hydrocarbon ligands. However, an example of a paramagnetic *closo commo* compound has been reported.[10] It was noted that the attempted purification in air of the diamagnetic green Fe(II) complex, [Me_4N]$_2$[2,2′-*commo*-Fe-(1-*closo*-$TeB_{10}H_{10}$)$_2$], afforded a yellow-green product whose ^{11}B NMR spectrum had a large chemical shift range,[10] similar to those of known iron(III) paramagnetic compounds.[3]

In this paper, we report the first example of a paramagnetic transition element complex with hydrocarbon and telluraborane ligands. The compound, [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], **3**, is formed in a reaction which apparently involves the exchange of the hydrides of two adjacent B–H units by fluorides and contains molybdenum in an oxidation state of I with 17 valence electrons. According to Wade's rules, compound **3** is one electron short of the number required for a twelve-atom *closo* cluster. The characterisation of **3** by X-ray techniques, EPR spectroscopy and electrochemical studies is reported.

Results and discussion

The compound [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], **3**, was prepared from the reaction between [NEt_4][7-*nido*-$TeB_{10}H_{11}$] **1** and [Mo(CO)$_3$(η^7-C_7H_7)][BF_4] **2** in equimolar ratio in dichloromethane solution heated at reflux for 21 h. Subsequent purification by preparative TLC and crystallisation from dichloromethane–toluene solution afforded [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** in 19% yield. Absorptions due to carbonyl ligands, which were clearly present in **2**, were notably absent from the infrared spectrum of **3**.[11]

Dark red crystals of [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** suitable for single crystal X-ray analysis were grown by the slow evaporation of a dichloromethane–toluene solution of **3**. Crystal data and relevant structure solution data are given in the experimental section. The X-ray analysis revealed that complex **3** has a twelve-vertex *closo* structure with the molybdenum atom occupying a site adjacent to the tellurium atom, Fig. 1.

Compound [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** is the first fluorinated telluraborane derivative to be synthesised and the first to be structurally characterised. The *exo*-cage fluorides are attached to the two boron atoms furthest away

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† Metallaheteroborane Chemistry Part 15.[1]

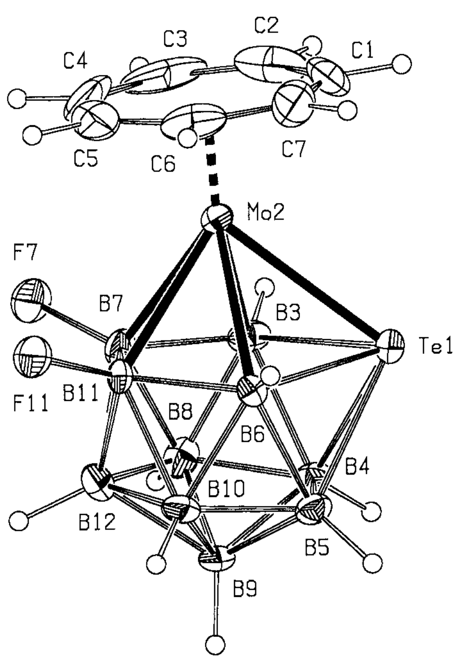

Fig. 1 View of compound **3**, [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], showing the numbering scheme. Anisotropic displacement elipsoids are drawn at the 30% probability level.

from the tellurium atom in the TeB_4 face which is bound to the molybdenum atom, Fig. 1. The B–F distances in **3**, 1.396(9) and 1.410(9) Å, greatly exceed the B–F distances in BF_3 which has a mean B–F distance of 1.289 Å,[12] and are slightly longer than the mean value of 1.389 Å for the corresponding bonds in the $H_3N{\cdot}BF_3$ complex.[13] In the case of the fluorinated carbaborane 8,9,10,12-F_4-1,2-*closo*-$C_2B_{10}H_8$, which contained the four fluorine atoms at the positions furthest away from the cage carbon atoms, the B–F bond distances were between 1.358(12) and 1.367(2) Å.[14]

The Mo–Te bond distance in [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** is 2.7083(8) Å. The mean distance between molybdenum and boron atoms, B(3) and B(6), which are also bonded to Te is 2.478(9) Å, whereas, the mean value for the interactions of molybdenum with B(7) and B(11) which are not attached to Te is shorter at 2.366(9) Å. The molybdenum atom is approximately equidistant from all seven C_7H_7-carbon atoms, with an average Mo–C distance of 2.248(13) Å and with a range from 2.223(11)–2.264(10) Å. The Te–B distances Te–B(3) and Te–B(6) are longer, mean 2.369(9) Å, than Te–B(4) and Te–B(5), mean 2.296(9) Å. The large variations in B–B distances from B(5)–B(6) 1.943(12) to B(5)–B(10) 1.720(13) Å are typical of heteroborane cage structures.

In both [Mo(CO)$_3$(η^7-C_7H_7)][BF_4], **2**,[15] and [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], **3**, the C_7 ring appears as a fully delocalised planar system. However, there was one carbon–carbon bond in **2** which was notably long, *i.e.* C(1)–C(7) which was 1.425(17) Å compared with the mean value for all carbon–carbon bonds of 1.400(17) Å. In the solid state the C(1)–C(7) bond in **2** was located directly above the $[BF_4]^-$ counterion which, however, was not well-defined in the crystal of **2** and had a large range of B–F distances, 1.213(20) to 1.305(16) Å, and F–B–F angles, 96(2) to 118(1)°.[15] In the structure of **3** the mean value for all carbon–carbon bonds is 1.38(3) Å.

The paramagnetic nature of [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** was investigated in the solid state with EPR spectroscopy. The room temperature spectrum of **3** can be suitably interpreted in terms of a $S = \frac{1}{2}$ electron spin Hamiltonian with a nearly isotropic shape. The second derivative signal exhibits a slightly unsymmetrical form, which arises from two slightly different anisotropic *g* values. Computer simulation permitted the evaluation of the relevant anisotropic parameters:[16]

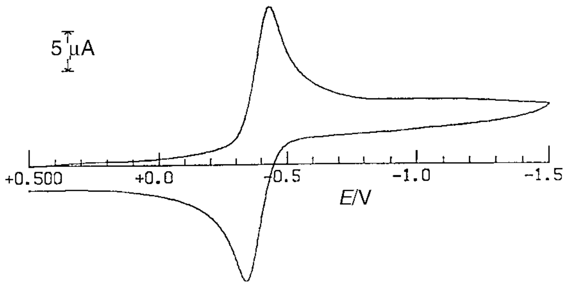

Fig. 2 Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution containing [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3** ($1.1{\times}10^{-3}$ mol dm^{-3}) and [NBu_4]PF_6 (0.2 mol dm^{-3}). Scan rate 0.2 V s^{-1}.

$$g_\perp = 1.997 \pm 0.003;\ g_\parallel = 1.988 \pm 0.003$$

$$\langle g\rangle = \tfrac{1}{3}(g_\parallel + 2g_\perp) = 1.994 \pm 0.003;\ \Delta H = 32 \pm 3\ \mathrm{G}$$

The linewidth is consistent with the "in-metal" character of the unpaired electron. The outer spectral features indicate an unusual broad absorption without detectable resolution of the hyperfine structure of the two magnetically active Mo nuclei [^{95}Mo, ^{97}Mo; $I = 5/2$], suggesting that the overall linewidth largely overlaps the satellite signals. An approximate evaluation of the upper limit of any such expected hyperfine interaction is $\Delta H_{exp} = 32\ \mathrm{G} \geq 5\ a_i[^{95/97}\mathrm{Mo}]$, where a_i represents the hyperfine coupling constant in the perpendicular and parallel regions. At liquid nitrogen temperature (100 K) the solid state spectrum of **3** remains quite similar. These data suggest the effective delocalisation of the unpaired electron over the whole cluster but with the SOMO strongly molybdenum-based.

The dichloromethane solution EPR spectra of **3** recorded at 100 and 300 K are quite similar, even with the expected line broadening at the liquid nitrogen temperature. The corresponding parameters were:

$$g_{\mathrm{averaged}} = 1.995 \pm 0.003;\ \Delta H_{\mathrm{averaged}} = 30 \pm 3\ \mathrm{G\ at}\ T = 100\ \mathrm{K\ and}$$
$$g_{\mathrm{averaged}} = 1.997 \pm 0.003;\ \Delta H_{\mathrm{iso}} = 28 \pm 3\ \mathrm{G\ at}\ T = 300\ \mathrm{K}$$

The isotropic pattern displayed in solution confirms the metallic SOMO symmetry of the unpaired electron. A similar observation *i.e.* that the unpaired electron in the iron(III) mixed sandwich species [1,2-Et_2-3-(η^5-C_5Me_5)-3,1,2-*closo*-$FeC_2B_4H_4$] was localised in a metal-centred molecular orbital has been made elsewhere.[6]

In the solution EPR spectrum at 300 K, $^{95/97}$Mo satellite peaks appear with computed hyperfine splitting of 20 ± 3 G. The narrowing of the signal with increasing temperature reflects the fact that the increase of the effective molecular dynamics induces an increase in the rate of the electron relaxation process.

Despite the potentially interesting redox properties of paramagnetic metallaheteroborane complexes, relatively few electrochemical studies of these derivatives have been described (see for example refs. 6–10 and 17–19). Fig. 2 shows the cyclic voltammetric response exhibited by [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], **3**, in dichloromethane solution. It displays a cathodic peak which is accompanied by a directly associated reoxidation peak in the reverse scan. An irreversible multielectron oxidation process (not shown in Fig. 2) is also present at $E_p = +1.2$ V and affords products of unknown composition. Controlled potential coulometry in correspondence to the cathodic process ($E_w = -0.9$ V) consumes one-electron/molecule. As a result, the original pink solution turns emerald-green, and it displays a cyclic voltammetric profile quite complementary to that shown in Fig. 2, thus proving the chemical reversibility of the [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$]$^{0/-}$ redox change ($E^{0\prime} = -0.39$ V). The subsequent one-electron re-oxidation ($E_w = -0.4$ V) restores the original pink colour. In view of the EPR results, the reversible reduction process is assigned to the Mo(I)/Mo(0) redox couple. Unfortunately, there are no comparable data on other mixed sandwich compounds with Group 16 heteroborane ligands in the literature.

Analysis of the cyclic voltammetric responses of **3** with scan rate, *v*, varying from 0.02 to 5.12 V s^{-1} shows that, (i) in agreement with the macroelectrolysis experiment, the backward-to-forward peak current ratios (i_{pa}/i_{pc}) are constantly equal to 1, (ii) the peak-to-peak separation (ΔE_p) progressively increases from 68 mV at 0.02 V s^{-1} to 274 mV at 5.12, V s^{-1}, and (iii) the current function $i_{pc}v^{-1/2}$ remains constant. In view of the fact that under the same experimental conditions the one-electron oxidation of ferrocene ($E^{0'} = +0.44$ V) displays essentially the same features, we assume that the departure at relatively high scan rates of ΔE_p from the constant value of 60 mV theoretically expected for an electrochemically reversible one-electron transfer is due to uncompensated solution resistances.[20,21] Hence the substantial electrochemical reversibility of the [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8]^{0/-}$ reduction step suggests that the Mo(0) monoanion probably maintains the original gross molecular structure,[21] *i.e.* no significant geometrical reorganization takes place upon one-electron addition to **3** to produce an anion with the correct electron count for a twelve-vertex *closo* cluster.

The fluorination of the $TeB_{10}H_{10}$-cage in the reaction which generates **3** is novel and of interest from several points of view including the role of the tetrafluoroborate ion as a fluorinating agent and the part played by the molybdenum atom during the reaction. In general, fluorine derivatives of borane-based species are much less common than other halogen derivatives. Typical reagents for the synthesis of B–X bonds (X = Cl, Br or I) from B–H bonds are the halogens, X_2, usually reacted under Friedel–Crafts conditions, or *N*-halosuccinimides (see ref. 22 for examples of halogenation of metallacarbaboranes with *N*-halosuccinimides). Recently fluorinated derivatives of the *closo*-anions $[B_{10}H_{10}]^{2-}$, $[CB_{11}H_{12}]^-$, $[CB_9H_{10}]^-$, and $[XB_{11}H_{11}]^-$ (X = As, Sb, Bi) have been synthesised in high yield and with high isomeric purity using liquid anhydrous HF or 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) as electrophilic fluorinating agents.[23] In an alternative approach, the formation of the B-fluorinated $[7,9\text{-}R_2\text{-}7,9\text{-}C_2B_9H_9F]^-$ anions (R = Ph, 4-FC_6H_4) from the reaction between tetrabutylammonium fluoride hydrate and 1,7-diaryl-1,7-dicarbaboranes has been reported.[24] The initial products were substituted at the 10-position but isomerised to the 3-isomer on heating in refluxing THF solution.

With reference to the formation of compound **3**, there is a substantial amount of evidence showing that fluoride containing ions interact with transition element centres and their associated ligands in both the solid state and in solution. In the solid state infrared spectrum of the 16-electron molybdenum complex, $[Mo(CO)_3(\eta^5\text{-}C_5H_5)][BF_4]$, the tetrafluoroborate ion was observed to be weakly coordinated to the molybdenum.[25] In solution the coordinated fluorine and the "free" terminal fluorine atoms of the $[BF_4]^-$ ligand were clearly distinguishable from their ^{19}F NMR signals.[26] An X-ray crystallographic study of [3-(η^2,η^2-1,5-C_8H_{12})-4-SMe_2-3,1,2-*closo*-$PdC_2B_9H_{10}$]-$[BF_4]$ showed a molecular conformation in the solid state which was substantially affected by ligand H · · · F interion contacts involving both the cyclooctadiene and dimethyl sulfide ligands.[27] A study of the electrochemical oxidation of the 17-electron complex $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_6Ph_6)]$ in dichloromethane with $[^nBu_4N][PF_6]$ as supporting electrolyte concluded that a 16-electron product $[(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_6Ph_6)]^+$ was in equilibrium with an ion-pair adduct formulated as $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Ph_6)Mo \cdots FPF_5]$ which was thermodynamically favoured.[28] Interestingly, neither $[BF_4]^-$ nor $[ClO_4]^-$ showed the same degree of interaction with the 16-electron $[(\eta^5\text{-}C_5H_5)\text{-}Mo(\eta^6\text{-}C_6Ph_6)]^+$ species. Generally, with polyene–$M(CO)_n$ complexes such as **2**, it has been shown that nucleophilic substitution by, *e.g.* OR^- or I^-, can occur at the polyene ring, or at the metal, or at a carbonyl carbon atom and these reactions may involve several steps and more than one site.[29] The investigation of the kinetics of the reaction between $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]\text{-}[BF_4]$ and excess iodide ion in acetone led to the suggestion that the reaction proceeded *via* rapid initial formation of an intermediate with a Mo–I bond followed by iodide transfer to the C_7H_7 ligand and subsequent formation of the final product, $[Mo(CO)_2I(\eta^7\text{-}C_7H_7)]$.[29] In the case of the reaction between $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$, **2**, and $[Et_4N]$[7-*nido*-$TeB_{10}H_{11}$] it is reasonable to speculate that the initial loss of a CO ligand creates an unsaturated cationic molybdenum centre which interacts directly with the nucleophilic $[BF_4]^-$ ion as a $\{Mo \cdots FBF_3\}$ moiety, leading to a weakening of the coordinated B–F bonds. Hence, the $[BF_4]^-$ ion would be brought into the intimate reaction sphere prior to reaction with the [7-*nido*-$TeB_{10}H_{11}]^-$ anion. It is possible that the reaction proceeds with loss of the two remaining CO ligands and formation of the $\{MoTeB_{10}\}$-cage with transfer of fluorine from the molybdenum to the telluraborane cage rather than the polyene ligand. In this context, the preference for substitution at B–H rather than C–H may be determined by the weaker B–H compared to C–H bonds (mean thermochemical bond energies 380 and 414 kJ mol^{-1} respectively) in the reactants and the superior bond strength of B–F compared to C–F bonds in the product (mean thermochemical bond energies 644 and 489 kJ mol^{-1} respectively).[30]

Experimental

General

All preparative experiments and crystallisations were carried out in an inert atmosphere. Both $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$[31] and the tetraethylammonium salt of the [7-*nido*-$TeB_{10}H_{11}]^-$ anion[10] were prepared by literature methods. The infrared spectrum of **3** was recorded from a KBr disc on a Perkin-Elmer Paragon FT spectrometer.

EPR Spectroscopy

The EPR spectra were recorded on a Bruker 200 DD-SRC instrument operating at 9.78 GHz (X-band) and equipped with a variable-temperature ER 411 VT unit. The external magnetic field H_0 was calibrated with a microwave bridge ERO41 MR Bruker wavemeter. The samples were placed in quartz flat cells positioned in the resonance cavity. In order to estimate accurate *g* values, 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used as a suitable field marker [$g_{iso} = 2.0036$].

Electrochemistry

The cyclic voltammetric measurements were performed with a BAS 100A electrochemical analyzer. A three electrode cell was designed to allow the tip of the saturated calomel reference electrode (SCE) to approach closely, *via* a Luggin capillary, the platinum disk working electrode ($r = 0.6$ mm), which in turn was surrounded by a platinum spiral counter electrode. Controlled potential coulometry was carried out by using an AMEL-Mod. 552 potentiostat, connected to an AMEL-Mod. 558 integrator. A three-compartment cell was designed with a central unit bearing a platinum gauze working macroelectrode. The lateral compartments contained the reference (SCE) and the counter (mercury pool) electrodes, respectively. The compartments containing the working and the auxiliary electrodes were separated by a sintered glass disk. Deoxygenation of the solutions was by bubbling ultrapure nitrogen for at least 10 min. All the potential values are referred to SCE. Dichloromethane, anhydrous, 99+% (packaged under nitrogen), tetrabutylammonium hexafluorophosphate (dried and stored in a vacuum oven at 40 °C prior to use) and ferrocene were obtained commercially (Aldrich).

Synthesis of [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] 3

To a suspension of [$Mo(CO)_3(\eta^7\text{-}C_7H_7)$][$BF_4$] **2** (0.06 g, 0.17 mmol) in 5 ml CH_2Cl_2 was added a suspension of [Et_4N][7-*nido*-$TeB_{10}H_{11}$] **1** (0.064 g, 0.17 mmol) in 10 ml CH_2Cl_2. The reaction mixture was refluxed for 21 h. After filtering an insoluble black solid from the mixture, the solution was concentrated under reduced pressure and subjected to preparative TLC (100% CH_2Cl_2). Two products were isolated. Compound **3** was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–toluene affording dark red plate crystals of [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$], **3** (0.015 g, 18.8%). IR (KBr), ν_{max}/cm^{-1}: 3063(vw) (CH), 2574(s) (BH), 2537(vs, sh) (BH), 2523(s) (BH), 2508(s) (BH), 1426(w), 1122(m), 1097(vs) (BF), 1061(s), 981(m), 960(m), 911(vw), 838(m), 820(w), 796(s). The highest mass ion in the parent molecular ion envelope was at *m*/*z* 477 corresponding to $^{12}C_7{}^1H_{15}{}^{11}B_{10}{}^{19}F_2{}^{100}Mo^{130}Te$. The second product, isolated in 40% yield, was shown to be [$Mo(CO)_3$-(η^6-C_7H_8)] by IR spectroscopy {IR (KBr), CO, ν_{max}/cm^{-1}: 1969(vs), 1904(vs), 1854(vs)}. Attempts to increase the yield of **3** by carrying out the reaction for shorter times resulted in lower yields of **3**. Longer reaction times produced greater amounts of the black solid decomposition product and [$Mo(CO)_3$-(η^6-C_7H_8)].

Crystal structure analysis for compound 3

Crystal data. $C_7H_{15}B_{10}F_2MoTe$, $M = 468.84$, orthorhombic, $Pna2_1$, $Z = 4$, $a = 16.7598(18)$, $b = 12.5500(11)$, $c = 7.2607(18)$ Å, $U = 1527.2(4)$ Å^3, $D_c = 2.039$ g cm^{-3}, $F(000) = 876$, λ(Mo-K$_\alpha$) = 0.71073 Å, $\mu = 2.729$ mm^{-1}, $T = 294$ K, $R = 0.0291$ for 1471 data with $I > 2\sigma(I)$, $R_w(F^2) = 0.0685$ for all 1799 measured data.

Structure determination. Crystals were grown by the slow evaporation of a dichloromethane–toluene solution of [2-(η^7-C_7H_7)-7,11-F_2-2,1-*closo*-$MoTeB_{10}H_8$] **3**. Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares treatment of the setting angles of 25 reflections. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatised (Mo-K$_\alpha$) radiation. Intensities of three reflections measured every 2 h showed no significant decay. Data were corrected for Lorentz, polarisation and absorption effects (ψ-scans). The coordinates of the heavy atoms were determined from analysis of the three-dimensional Patterson functions and those of the remaining non-hydrogen atoms were found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations with the SHELXL-97[32] and the NRCVAX suite of programs, initially, with isotropic and later with anisotropic thermal parameters for all non-hydrogen atoms.[33] All H atoms were visible in difference maps and were allowed for as riding atoms.

CCDC reference number 151294.

See http://www.rsc.org/suppdata/dt/b0/b008692o/ for crystallographic data in CIF or other electronic format.

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