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Molybdenum-mediated cocyclisation reactions involving prop-2-ynyl, alkyne and carbon monoxide ligands*

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Reaction of the σ,η^2(3e)-prop-2-ynyl/η^2(4e)-alkyne complex $[Mo\{\sigma,\eta^2(3e)\text{-}CH_2C_2Me\}\{\eta^2(4e)\text{-}MeC_2Me\}(\eta\text{-}C_5H_5)]$ with hexafluorobut-2-yne led to a novel cyclisation reaction affording an X-ray crystallographically identified complex containing an $(\eta\text{-}C_5H_5)Mo$ fragment η^3,η^4 bonded to a bicyclo[4.3.0]nonyl ring system formed by the cocyclisation of two molecules of $CF_3C_2CF_3$, a but-2-yne molecule and a prop-2-ynyl fragment. A mechanism of formation is proposed involving, in the final step, the placement of a hydrogen substituent on the opposite face of the bicyclo-ring system to which the molybdenum is attached, *via* the ionisation of an acidic Mo–H bond. The reactions of $[Mo\{\sigma,\eta^2(3e)\text{-}CH_2C_2R\}\{\eta^2(4e)\text{-}MeC_2R\}(\eta\text{-}C_5H_5)]$ (R = Me or Ph) with carbon monoxide led to novel cocyclisation reactions and the formation of the X-ray crystallographically identified complexes $[Mo\{\eta^2,\eta^3\text{-}\overline{C(R)C(O)C(Me)C(R)C}CH_2\}(CO)(\eta\text{-}C_5H_5)]$. Protonation ($HBF_4{\cdot}Et_2O$) of the methyl-substituted system was shown by X-ray crystallography to involve protonation of the keto-group, rather than the η^3-allylic CH_2 group, to give the cationic complex $[Mo\{\eta^3,\eta^3\text{-}\overline{C(Me)C(OH)C(Me)C(Me)C}CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$.

We have recently[2,3] shown that addition of the base $Li[N(SiMe_3)_2]$ to the halogenobis(alkyne) complexes $[MoBr(\eta^2\text{-}MeC_2R)_2(\eta\text{-}C_5H_5)]$ (R = Me or Ph) results in a dehydrohalogenation reaction and the formation of the σ,η^2(3e)-prop-2-ynyl/η^2(4e)-alkyne complexes $[Mo\{\sigma,\eta^2(3e)\text{-}CH_2C_2R\}\{\eta^2(4e)\text{-}MeC_2R\}(\eta\text{-}C_5H_5)]$ (R = Me **1** or Ph **2**). These species are interesting because they contain a prop-2-ynyl $[\sigma,\eta^2(3e)\text{-}C_3H_3]$ fragment, a type of ligand which has recently attracted attention.[4–13] Reactivity studies with such species have so far focused on the reaction of nucleophiles with the cationic complexes, where it was found that reaction occurs at the central carbon atom of the prop-2-ynyl ligand. The neutral complexes **1** and **2** offer a different opportunity for reactivity studies because of the potential for the η^2-alkyne (4e ⟶ 2e) and the σ,η^2-prop-2-ynyl (3e ⟶ 1e) ligands to switch their bonding modes, thus providing a co-ordination site for reactive molecules. In this paper we describe studies of the reactivity of **1** and **2** towards hexafluorobut-2-yne and carbon monoxide.

Results and Discussion

Treatment (−78 to +25 °C) of a solution of complex **1** in toluene with an excess of hexafluorobut-2-yne resulted in the rapid formation of a white polymeric precipitate, and work-up of the toluene-soluble products by simple recrystallisation afforded an orange crystalline complex **3** (40% yield). An elemental analysis and a mass spectrum suggested that **3** had the molecular formula $[Mo(\eta\text{-}C_5H_5)\{C_9H_2Me_3(CF_3)_4\}]$, this conclusion being supported by examination of the ^1H, $^{13}C\text{-}\{^1H\}$ and ^{19}F NMR spectra. Particularly interesting was the appearance of resonances corresponding to three methyl groups, a CH group, three trifluoromethyl environments, and a $CH(CF_3)$ group, suggesting that an unusual coupling reaction had occurred between the methyl-substituted prop-2-ynyl fragment, the co-ordinated but-2-yne and two molecules of hexafluorobut-2-yne. Although in earlier work insertion, coupling and cyclisation reactions with one, two and three molecules of hexafluorobut-2-yne have been observed[13–17] at a variety of metal centres, it was evident that a new type of reaction was involved in the formation of **3**. The structural identity of **3** was established by a single-crystal X-ray diffraction study. The resulting structure is shown in Fig. 1, selected bond lengths and angles being listed in Table 1.

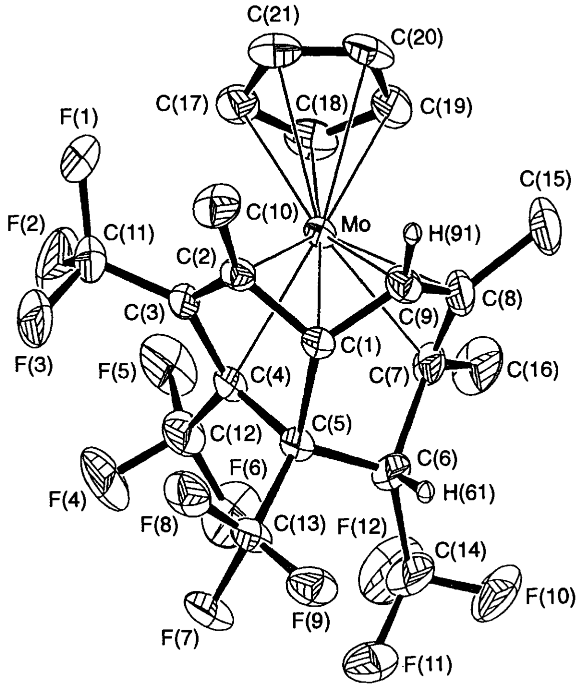

Fig. 1 Molecular structure of compound **3**

The molecule **3** contains an $(\eta^5\text{-}C_5H_5)Mo$ fragment co-ordinated to an η^3,η^4-bonded bicyclo[4.3.0]nonyl ring system, which exhibited a torsion angle for C(2)–C(1)–C(5)–C(6) of 154.0° and for C(9)–C(1)–C(5)–C(4) of −114.39° with an angle between the planes of C(1)–C(2)–C(3)–C(4) and C(1)–C(9)–C(8)–C(7) of 52.42°. The bonding between the molybdenum

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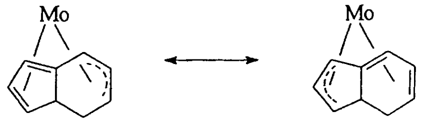
* Reactions of co-ordinated ligands. Part 62.[1]

Table 1 Selected bond lengths (Å) and angles (°) for complex **3**

Mo–C(1)	2.119(4)	Mo–C(2)	2.196(4)
Mo–C(3)	2.239(4)	Mo–C(4)	2.269(4)
Mo–C(5)	2.747(4)	Mo–C(7)	2.343(4)
Mo–C(8)	2.337(4)	Mo–C(9)	2.241(4)
C(1)–C(2)	1.447(6)	C(1)–C(3)	2.249(6)
C(1)–C(4)	2.241(5)	C(1)–C(5)	1.543(5)
C(1)–C(9)	1.451(6)	C(2)–C(3)	1.424(6)
C(2)–C(10)	1.525(6)	C(3)–C(4)	1.465(6)
C(3)–C(11)	1.502(7)	C(4)–C(5)	1.541(6)
C(4)–C(12)	1.480(6)	C(5)–C(6)	1.525(6)
C(5)–C(13)	1.542(6)	C(6)–C(7)	1.563(7)
C(6)–C(14)	1.537(7)	C(7)–C(8)	1.423(7)
C(7)–C(16)	1.535(7)	C(8)–C(9)	1.399(7)
C(8)–C(15)	1.505(7)		
C(9)–C(1)–C(2)	113.8(4)	C(3)–C(2)–C(1)	103.1(3)
C(10)–C(2)–C(1)	125.1(4)	C(10)–C(2)–C(3)	131.1(4)
C(4)–C(3)–C(2)	109.5(4)	C(11)–C(3)–C(2)	120.8(5)
C(11)–C(3)–C(4)	128.9(4)	C(5)–C(4)–C(3)	107.9(4)
C(12)–C(4)–C(1)	167.9(4)	C(12)–C(4)–C(3)	119.6(4)
C(12)–C(4)–C(5)	124.6(4)	C(4)–C(5)–C(1)	93.2(3)
C(6)–C(5)–C(1)	102.1(3)	C(6)–C(5)–C(4)	117.0(4)
C(13)–C(5)–C(1)	111.8(3)	C(13)–C(5)–C(4)	114.2(4)
C(13)–C(5)–C(6)	115.3(4)	C(7)–C(6)–C(5)	106.6(3)
C(14)–C(6)–C(5)	123.7(5)	C(14)–C(6)–C(7)	114.9(5)
C(8)–C(7)–C(6)	111.9(4)	C(16)–C(7)–C(6)	119.6(5)
C(16)–C(7)–C(8)	118.9(5)	C(9)–C(8)–C(7)	113.8(4)
C(15)–C(8)–C(7)	125.4(5)	C(15)–C(8)–C(9)	120.7(5)
C(8)–C(9)–C(1)	115.9(4)	C(9)–C(1)–C(5)	127.6(4)

and the bicyclic ligand can be described as an asymmetric η^3-allylic interaction from the C_6 ring with Mo–C(9), Mo–C(8) and Mo–C(7) distances of 2.241(4), 2.337(4) and 2.343(4) Å respectively, along with an asymmetric η^4-1,3-diene interaction between the metal and the C_5 ring with Mo–C(1), Mo–C(2), Mo–C(3) and Mo–C(4) distances of 2.119(4), 2.196(4), 2.239(4) and 2.269(4) Å respectively. However, a more accurate picture of the bonding is provided by the two canonical forms illustrated in Scheme 1. From Fig. 1, pyramidalisation also occurs on carbon C(1), and a measure of this effect is provided by the fact that this carbon atom is 0.213 Å out of the plane defined by C(2), C(9) and C(5). Interestingly, pyramidalisation has also been observed with η^4-trimethylenemethane metal complexes[18] and the reasons for this effect have been discussed by Hoffmann and co-workers.[19] The effect observed with **3** can be similarly explained.

Although the linking of alkynes at one or two metal centres has attracted considerable attention, there is no precedent for a reaction of the type involved in the formation of complex **3**. A mechanism, which can explain this compound's formation, must show how the bicyclic system is formed, and also explain how a hydrogen atom, which has its origin in the prop-2-ynyl methylene group, is transferred onto the opposite face of the bicyclic system to which the molybdenum is co-ordinated. This last feature is especially interesting because the well established reaction paths[20] for hydrogen-shift processes would all place this hydrogen, *i.e.* H(61) in Fig. 1, on the same face as the metal. A possible reaction pathway which meets these structural and stereochemical requirements is illustrated in Scheme 2. As is shown, reaction of **1** with a molecule of hexafluorobut-2-yne might reasonably be expected to result in co-ordination to the molybdenum centre with a concomitant switch (3e $\longrightarrow$ 1e) in the bonding mode of the prop-2-ynyl fragment. Migration (**A** $\longrightarrow$ **B**) of the resulting σ-allenyl group onto the co-ordinated hexafluorobut-2-yne could then provide access to the intermediate **B** carrying a co-ordinated allene and an η^2(4e)-bonded but-2-yne. Reaction of **B** with a second molecule of hexfluorobut-2-yne would be expected to promote coupling of the co-ordinated allene and but-2-yne (4e $\longrightarrow$ 2e switch) to form the metallabicyclo[3.3.0]octyl ring system present in **C**.



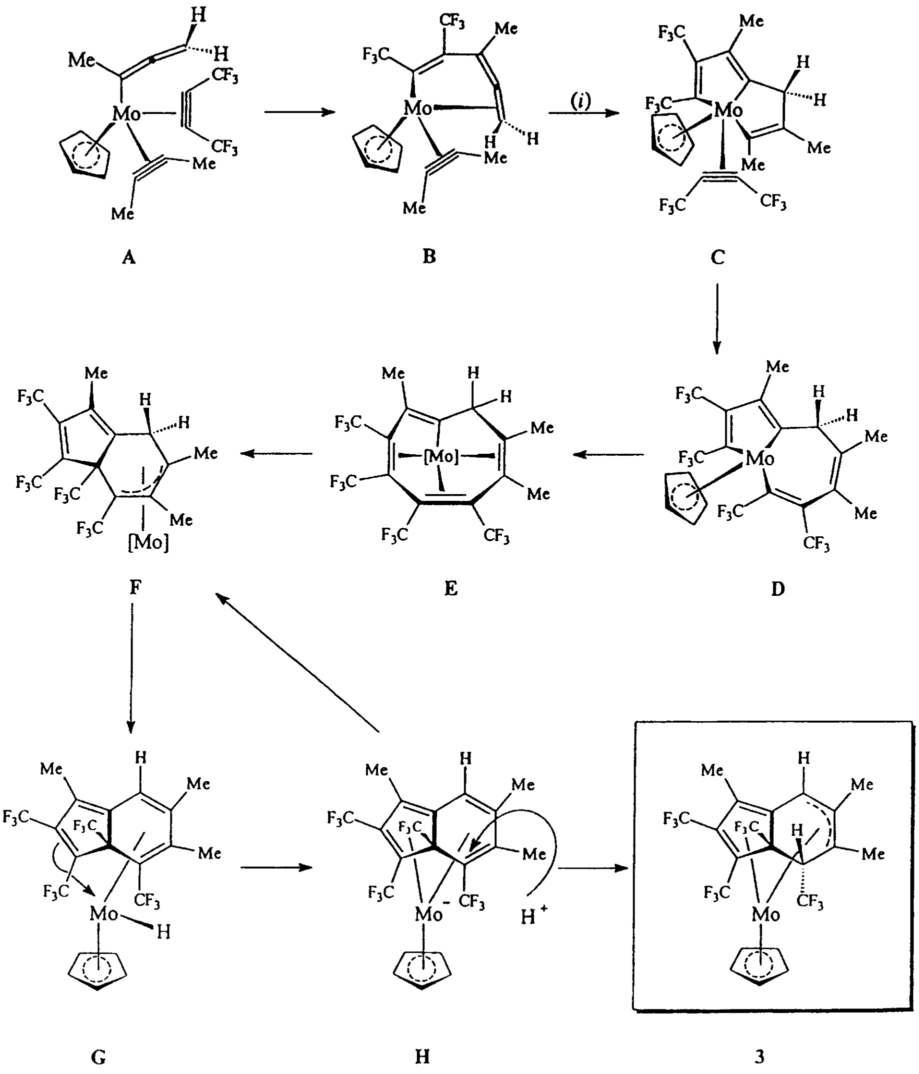
Scheme 1

Ring expansion (5 $\longrightarrow$ 7) *via* migration of the dimethyl-substituted σ-vinyl group onto the co-ordinated hexafluorobut-2-yne then affords the metallabicyclo[5.3.0]decyl intermediate **D**.

In order to transform **D** into complex **3** it is necessary to relocate a hydrogen and also form the carbon–carbon bond present at the bicyclic ring junction. This C–C bond can be formed in two steps. First, a reductive elimination reaction (**D** $\longrightarrow$ **E**) affords the cyclononatetraene complex **E**, and then a ring-closure reaction, *i.e.* migration of a molybdenum vinyl onto a co-ordinated alkene, results in the formation of the bicyclo[4.3.0] system **F**. Although all of the methyl and trifluoromethyl substituents present in **F** are in the same positions as found in the final product **3**, it is evident that a hydrogen atom also needs to be moved onto the face opposite to the metal. As mentioned earlier this poses a problem in terms of metal-assisted processes, and it is also interesting that since a suprafacial 1,7-hydrogen process is a disallowed reaction[21] such a process cannot be involved in the transformation of **E** into the final product. This mechanistic problem can, however, be solved by the step **F** $\longrightarrow$ **G** followed by ionisation of the resultant molybdenum–hydrogen bond. This last step would be expected to be assisted by the presence of the electronegative groups present in **G**. The ionic species **H** could then reprotonate on both faces and at both the CH and $C(CF_3)$ carbons. Since attack on either face at CH simply leads back to **F**, whilst attack *cis* to the metal at $C(CF_3)$ places the hydrogen vulnerable to transfer back to the metal to give **G** again, this leaves the remaining possibility, *i.e.* proton attack on $C(CF_3)$ on the opposite face to the metal, which results in irreversible formation of the isolated product **3**.

Attention was next turned to the reaction of carbon monoxide with the σ,η^2(3e)-prop-2-ynyl/η^2(4e)-alkyne complexes **1** and **2**. A stream of CO was bubbled at room temperature through a solution of **1** in tetrahydrofuran. After a short time it changed from red to yellow, and work-up by recrystallisation from CH_2Cl_2–hexane gave an excellent yield of the orange-yellow crystalline complex **4**. The IR spectrum showed two C–O stretching frequencies attributable to a terminal carbonyl (1916s cm^{-1}) and an acyl carbonyl (1595m cm^{-1}), and in agreement with these structural features elemental analysis and a mass spectrum suggested that the reaction involved incorporation of two molecules of CO. Examination of the ^1H and $^{13}C-\{^1H\}$ NMR spectra revealed resonances corresponding to the presence of three methyl environments and a CH^aH^b group with a small $J(H^aH^b)$ coupling constant of 2.2 Hz, suggesting that a novel cyclisation reaction had occurred involving CO, but-2-yne and the prop-2-ynyl fragment. Interestingly, a similar reaction between carbon monoxide and the unsymmetrically substituted complex $[Mo\{\sigma,\eta^2(3e)\text{-}CH_2C_2Ph\}\{\eta^2(4e)\text{-}MeC_2Ph\}(\eta\text{-}C_5H_5)]$ **2** led to a regioselective reaction and the formation of the analogous complex **5**, there being no evidence for the formation of isomers.

In order to establish the nature and regioselectivity of these reactions single-crystal X-ray diffraction studies were carried out on suitable crystals of both complexes **4** and **5**. This established the structures shown in Figs. 2 and 3, selected bond lengths and angles being listed in Tables 2 and 3 respectively. In the structures of both **4** and **5** an η^5-$C_5H_5Mo(CO)$ fragment is bonded to a novel five-membered ring ligand, which carries an exocyclic methylene group. It is evident that this organic ligand is formed by the cocyclisation of the prop-2-ynyl and alkyne



Scheme 2 [Mo] = (η-C_5H_5)Mo. (*i*) $+F_3CC_2CF_3$

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

Mo(1)–C(1)	1.950(8)	Mo(1)–C(2)	2.296(7)	Mo(2)–C(2′)	2.314(8)	Mo–C(1′)	1.951(8)
Mo(1)–C(3)	2.318(7)	Mo(1)–C(4)	2.331(8)	Mo(2)–C(4′)	2.332(8)	Mo(2)–C(3′)	2.320(7)
Mo(1)–C(5)	2.316(7)	Mo(1)–C(6)	2.318(7)	Mo(2)–C(6′)	2.317(7)	Mo(2)–C(5′)	2.310(8)
Mo(1)–C(7)	2.637(7)	Mo(1)–C(8)	2.332(7)	Mo(2)–C(8′)	2.342(7)	Mo(2)–C(7′)	2.637(7)
Mo(1)–C(9)	2.150(7)	Mo(1)–C(10)	2.251(7)	Mo(2)–C(10′)	2.251(6)	Mo(2)–C(9′)	2.150(6)
Mo(1)–C(11)	2.390(7)	Mo(1)–C(13)	2.335(7)	Mo(2)–C(13′)	2.302(7)	Mo(2)–C(11′)	2.395(6)
O(1)–C(1)	1.168(10)	O(2)–C(7)	1.268(9)	O(2′)–C(7′)	1.269(8)	O(1′)–C(1′)	1.169(9)
C(2)–C(3)	1.420(11)	C(2)–C(6)	1.417(11)	C(2′)–C(6′)	1.417(11)	C(2′)–C(3′)	1.431(10)
C(3)–C(4)	1.403(11)	C(4)–C(5)	1.403(11)	C(3′)–C(5′)	2.287(11)	C(3′)–C(4′)	1.419(11)
C(5)–C(6)	1.451(11)	C(7)–C(8)	1.466(10)	C(4′)–C(6′)	2.290(10)	C(4′)–C(5′)	1.395(10)
C(7)–C(11)	1.434(9)	C(8)–C(9)	1.454(10)	C(7′)–C(8′)	1.463(9)	C(5′)–C(6′)	1.430(10)
C(8)–C(12)	1.501(10)	C(9)–C(10)	1.444(9)	C(8′)–C(9′)	1.451(9)	C(7′)–C(11′)	1.431(10)
C(9)–C(13)	1.435(11)	C(10)–C(11)	1.406(10)	C(9′)–C(10′)	1.453(9)	C(8′)–C(12′)	1.499(10)
C(10)–C(14)	1.515(10)			C(10′)–C(11′)	1.423(9)	C(9′)–C(13′)	1.424(10)
				C(11′)–C(15′)	1.515(10)	C(10′)–C(14′)	1.503(10)
						C(13′)–H(13b)	1.074(25)
C(8)–C(7)–O(2)	126.4(6)	C(11)–C(7)–O(2)	128.1(6)	C(11′)–C(7′)–O(2′)	128.5(6)	C(8′)–C(7′)–O(2′)	126.0(6)
C(11)–C(7)–C(8)	105.3(6)	C(9)–C98)–C(7)	107.7(6)	C(9′)–C(8′)–C(7′)	108.5(6)	C(11′)–C(7′)–C(8′)	105.5(6)
C(12)–C(8)–C(7)	124.2(6)	C(12)–C(8)–C(9)	125.7(6)	C(12′)–C(8′)–C(9′)	125.5(6)	C(12′)–C(8′)–C(7′)	124.0(6)
C(10)–C(9)–C(8)	106.8(6)	C(13)–C(9)–C(8)	117.4(6)	C(13′)–C(9′)–C(8′)	118.8(6)	C(10′)–C(9′)–C(8′)	106.6(5)
C(13)–C(9)–C(10)	121.1(6)	C(11)–C(10)–C(9)	108.1(6)	C(11′)–C(10′)–C(9′)	107.6(6)	C(13)–C(9′)–C(10′)	119.2(6)
C(14)–C(10)–C(9)	125.5(6)	C(14)–C(10)–C(11)	126.3(6)	C(14′)–C(10′)–C(11′)	126.6(6)	C(14′)–C(10′)–C(9′)	125.6(6)
C(10)–C(11)–C(7)	109.8(6)	C(15)–C(11)–C(7)	122.2(6)	C(15′)–C(11′)–C(7′)	121.9(6)	C(10′)–C(11′)–C(7′)	109.8(6)
C(15)–C(11)–C(10)	125.7(6)					C(15′)–C(11′)–C(10′)	126.2(6)

ligands with a molecule of carbon monoxide. In the reaction with the unsymmetrically substituted complex **2**, the single product **5** which is formed has the phenyl substituents in the 3 and 5 positions.

Table 3 Selected bond lengths (Å) and angles (°) for complex **5**

C(7)–Mo	2.664(9)	C(8)–Mo	2.368(8)
C(9)–Mo	2.162(8)	C(10)–Mo	2.247(8)
C(11)–Mo	2.407(8)	C(12)–Mo	2.284(8)
C(1)–O(1)	1.142(8)	C(7)–O(2)	1.243(8)
C(8)–C(7)	1.471(9)	C(11)–C(7)	1.453(9)
C(9)–C(8)	1.458(9)	C(14)–C(8)	1.492(9)
C(10)–C(9)	1.448(9)	C(12)–C(9)	1.412(9)
C(11)–C(10)	1.435(9)	C(20)–C(10)	1.495(9)
C(13)–C(11)	1.498(9)		
C(8)–C(7)–O(2)	128.5(7)	C(11)–C(7)–O(2)	126.0(7)
C(11)–C(7)–C(8)	105.5(6)	C(9)–C(8)–C(7)	108.6(6)
C(14)–C(8)–C(7)	124.6(6)	C(14)–C(8)–C(9)	124.6(6)
C(10)–C(9)–C(8)	106.6(6)	C(12)–C(9)–C(8)	118.2(6)
C(12)–C(9)–C(10)	119.0(6)	C(11)–C(10)–C(9)	108.7(6)
C(10)–C(11)–C(7)	108.5(6)	C(13)–C(11)–C(7)	119.9(7)
C(13)–C(11)–C(10)	128.2(7)		

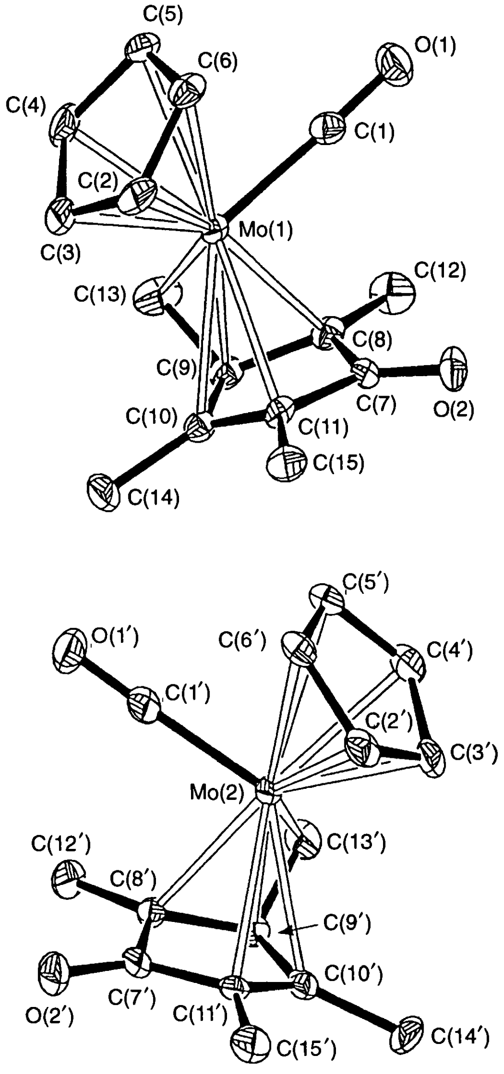


Fig. 2 Molecular structure of compound **4**

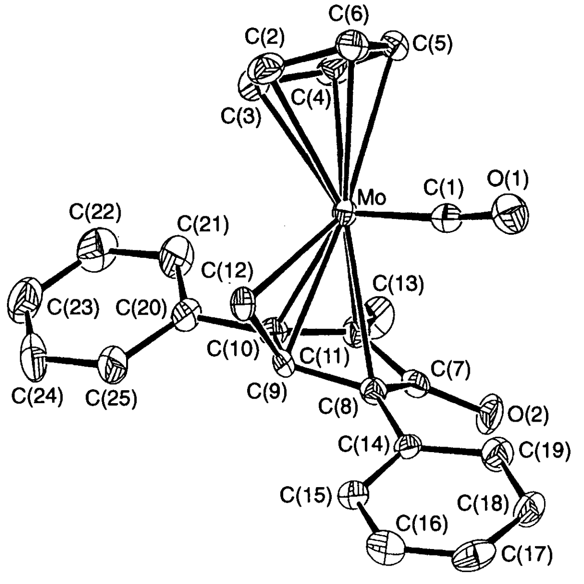
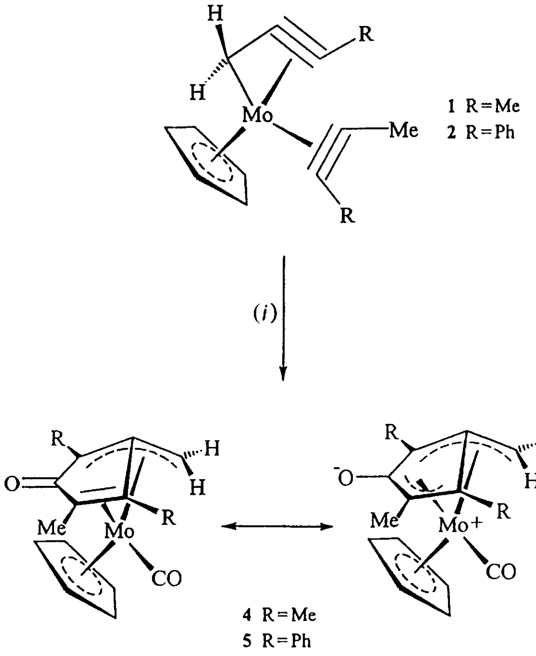


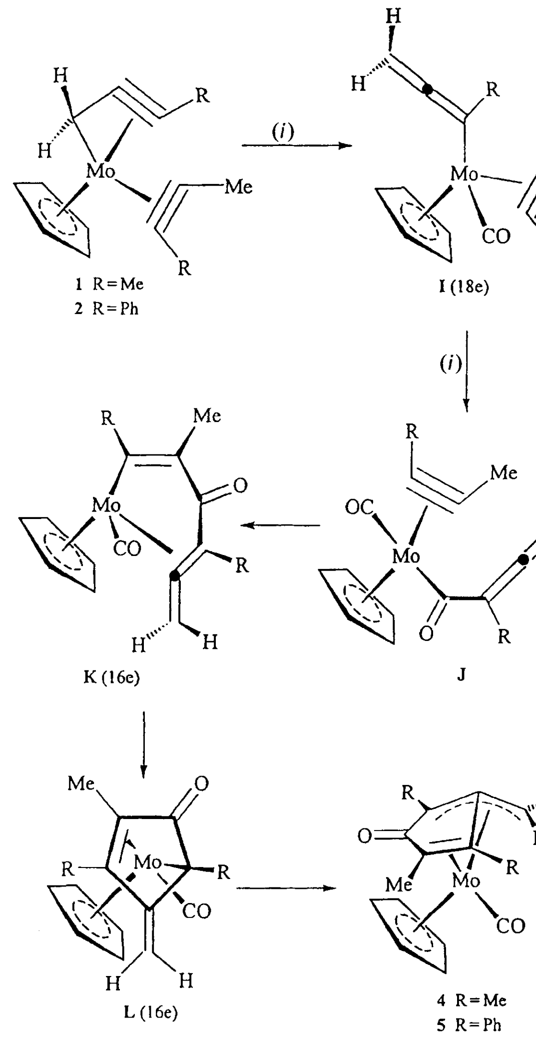
Fig. 3 Molecular structure of compound **5**



Scheme 3 (*i*) +CO

The bonding between the organic C_6 ligand and the molybdenum centre can be understood in terms of the two canonical forms depicted in Scheme 3, one involving η^2,η^3 and the other η^3,η^3 bonding. Pyramidalisation occurs on C(13) of complex **4** and C(12) of **5**. A measure of this interesting effect (see ref. 19) is that in the case of **4**, atom C(13) lies 0.92 Å above the plane defined by C(8)–C(9)–C(10)–C(11), whereas, with complex **5** the atom C(12) lies 0.84 Å above the plane C(8)–C(9)–C(10)–C(11). These carbons form part of an asymmetric η^3-allylic system with Mo–C(8) 2.332(7), Mo–C(9) 2.150(7) and Mo–C(13) 2.335(7) Å (complex **4**) and Mo–C(8) 2.368(8), Mo–C(9) 2.162(8) and Mo–C(12) 2.284(8) (**5**) where the central carbon, which is more closely bonded to the molybdenum, forms the apex of the pyramid. The two canonical forms differ with respect to the bonding of the ring carbons C(7), C(10) and C(11). Interestingly, there appears to be a substituent effect on the relative contributions of the two forms. Thus, the ring C–O distances observed for **4** [1.268(9) Å] and **5** [1.243(8) Å] indicate a greater contribution from the zwitterionic η^3,η^3-bonded form in **4**, than in **5**, and this is also reflected in the ring C–C bond lengths C(7)–C(11) [1.434(9) in **4** and 1.453(9) Å in **5**].

The formation of complexes **4** and **5** involves an unprecedented reaction, and therefore a discussion of a possible reaction pathway is justified. It is suggested that the first step (see Scheme 4) involves co-ordination of a molecule of carbon monoxide facilitated by a switch in the bonding mode of the prop-2-ynyl ligand from σ,η^2(3e) to σ(1e), the resulting intermediate **I** being a member of the family of complexes $[MoR(CO)\{\eta^2(4e)\text{-alkyne}\}(\eta\text{-}C_5H_5)]$.[22] In agreement with the known reactivity of such species it is reasonable therefore to

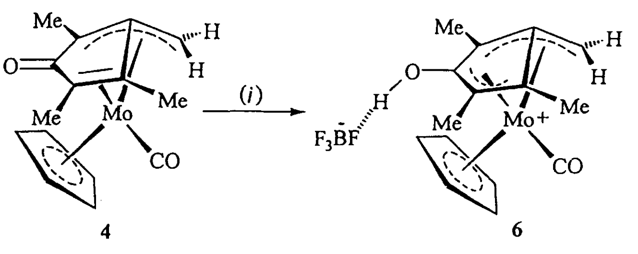


Scheme 4 (*i*) +CO

postulate migration of the σ(1e)-bonded allenyl fragment onto the CO ligand with concomitant co-ordination of a second molecule of carbon monoxide thus leading to the formation of species **J**. Migration of the acylallenyl fragment onto the co-ordinated alkyne might then reasonably be expected to give the intermediate **K**, which could undergo a cyclisation reaction to form the penultimate intermediate **L**. Co-ordination of the exocyclic double bond facilitated by pyramidalisation then affords the isolated products. In this sequence of steps it is the migration reaction **J** ⟶ **K** which determines the regioselectivity of the reaction with an unsymmetrically substituted alkyne.

Finally, the protonation of complex **4** was examined, there being two obvious sites for attack, the keto-oxygen and the exocyclic methylene carbon. Addition (−78 °C) of $HBF_4{\cdot}OEt_2$ to a solution of **4** in dichloromethane resulted in the formation in high yield of the crystalline cationic pale yellow complex **6**. Examination of the IR spectrum demonstrated a shift (1916s ⟶ 1980s cm^{-1}) in the terminal carbonyl C–O stretch and also the disappearance of the organo keto C–O stretching frequency. This suggested that protonation had occurred on the keto group (Scheme 5), and this was supported by the elemental analysis and by the ^1H and ^{13}C-{^1H} NMR spectra, the ^1H spectra showing a new singlet resonance at δ 7.24 attributable to an OH group. Confirmation of these structural assignments was provided by a single-crystal X-ray diffraction study, the resulting structure being shown in Fig. 4; selected bond lengths and angles are listed in Table 4.

Thus, protonation occurs on the keto-oxygen this being reflected in the C–O distance of 1.345(6) Å, and by the changes in the bond parameters associated with C(7), C(11) and C(10). In agreement with the η^3,η^3-bonded structure depicted in Scheme 5, there is a shortening of the C(7)–C(11) distance from 1.434(9) observed in the parent **4** to 1.400(7) Å, and a decrease [2.637(7) in **4**, 2.414(5) Å in **6**] in the Mo–C(7) distance. Interestingly, there is no major change in the C(9)–C(13) bond length on protonation [1.435(11) in **4**, 1.423(7) Å in **6**], which would have been expected if there was a contribution from the canonical form $[Mo(CO)(\eta^5\text{-}1,3\text{-}HOC_5H_3CH_2{}^+)(\eta\text{-}C_5H_5)]$, and in agreement pyramidalisation at C(9) is maintained [C(13) lies 0.90 Å above the plane C(8)–C(9)–C(10)–C(11)] on protonation.



Scheme 5 (*i*) $HBF_4{\cdot}OEt_2$

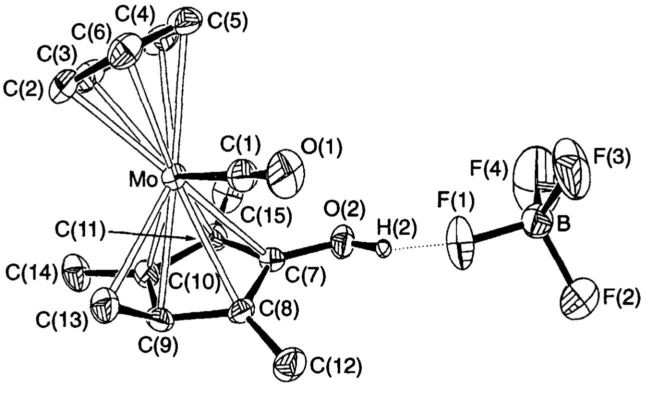


Fig. 4 Molecular structure of the cationic complex **6**

Table 4 Selected bond lengths (Å) and angles (°) for complex **6**

Mo–C(7)	2.414(5)	Mo–C(8)	2.300(4)
Mo–C(9)	2.176(4)	Mo–C(10)	2.271(5)
Mo–C(11)	2.389(4)	Mo–C(13)	2.328(6)
C(7)–C(8)	1.433(7)	C(7)–C(11)	1.400(7)
C(8)–C(9)	1.450(7)	C(8)–C(12)	1.496(7)
C(9)–C(10)	1.461(7)	C(9)–C(13)	1.423(7)
C(10)–C(11)	1.427(7)	C(10)–C(14)	1.508(8)
C(11)–C(15)	1.502(7)	B–F(1)	1.404(7)
B–F(2)	1.350(8)	B–F(2)	1.331(7)
B–F(4)	1.310(8)	F(1) ··· H(2)	1.699(21)
C(8)–C(7)–O(2)	128.7(4)	C(10)–C(7)–O(2)	156.6(4)
C(11)–C(7)–O(2)	121.1(4)	C(11)–C(7)–C(8)	109.8(4)
C(9)–C(8)–C(7)	107.0(4)	C(12)–C(8)–C(7)	125.3(5)
C(12)–C(8)–C(9)	126.8(5)	C(10)–C(9)–C(8)	106.8(4)
C(13)–C(9)–C(8)	118.0(5)	C(13)–C(9)–C(10)	117.9(5)
C(11)–C(10)–C(9)	107.8(4)	C(14)–C(10)–C(7)	161.5(4)
C(14)–C(10)–C(9)	125.3(5)	C(14)–C(10)–C(11)	126.7(5)
C(10)–C(11)–C(7)	108.4(4)	C(15)–C(11)–C(7)	124.8(4)

Experimental

The ^1H, ^{13}C-{^1H} and ^{19}F NMR spectra were recorded on JEOL GX270 and EX400 spectrometers. Data are given for room-temperature measurements unless otherwise stated. Chemical shifts are referenced relative to tetramethylsilane and external CCl_3F. Infrared spectra were recorded on a Nicolet 580 P FT-IR spectrometer. All reactions were carried out in Schlenk tubes under atmospheres of dry oxygen-free nitrogen, using freshly distilled and degassed solvents. Column

Table 5 Structure analyses for compounds **3**–**6**[a]

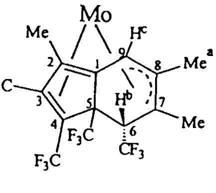
	3	**4**	**5**	**6**
Formula	$C_{21}H_{16}F_{12}Mo$	$C_{15}H_{16}MoO_2$	$C_{25}H_{20}MoO_2$	$C_{15}H_{17}BF_4MoO_2$
M	592.3	324.2	448.4	412
Space group	$P2_1/n$	$P2_1/n$	*Pcab*	$P2_1/c$
a/Å	8.847(2)	7.826(1)	13.239(1)	8.376(1)
b/Å	13.574(3)	15.098(3)	15.908(2)	8.454(1)
c/Å	17.336(4)	21.635(4)	18.038(2)	22.898(4)
β/°	93.94(2)	95.14(2)		99.96(2)
U/Å^3	2076.9	2546.0	3798.9	1597.0
Z	4	8	8	4
D_c/g cm^{-3}	1.89	1.69	1.57	1.71
F(000)	1168	1312	1824	824
μ(Mo-Kα)/cm^{-1}	7.5	10.2	7.1	8.7
Crystal dimensions/mm	0.2 × 0.2 × 0.2	0.15 × 0.15 × 0.17	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2
No. parameters refined	315	176[b]	261	245
Maximum shift/e.s.d.	0.15	0.22	0.016	0.15
Total data	3661	4480	3360	2909
Unique data, $I \geqslant 3\sigma(I)$	2432	2686	1760[c]	1903
R,*R*′	0.0309, 0.0354	0.0351, 0.0351	0.0402, 0.0416	0.0309, 0.0354
Weighting expression, *w*	$1.5675/[\sigma^2(F) + 0.0015(F)^2]$	Unit weights	$2.0668/[\sigma^2(F) + 0.001\,396(F)^2]$	$1/[\sigma^2(F) + 0.006\,097(F)^2]$
Maximum, minimum residual densities in difference map/e Å^{-3}	+0.25, −0.31	+0.55, −0.32	+0.33, −0.29	+0.29, −0.33

[a] Details in common: $T = 293$ K; λ(Mo-Kα) 0.709 30 Å; ω–2θ scans; monoclinic; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = (\Sigma|w(|F_o| - |F_c|)^2|/\Sigma|F_o|^2)^{\frac{1}{2}}$. [b] Blocked-matrix refinement, one block per molecule in asymmetric unit. [c] Number with $I > 2\sigma(I)$.

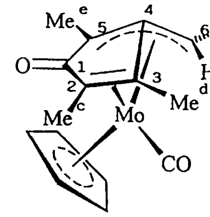
chromatography was performed using BDH alumina, Brockman activity II. The complexes [Mo{σ,η^2(3e)-CH_2C_2R}{η^2-(4e)-MeC_2R}(η-C_5H_5)] (R = Me **1** or Ph **2**) were prepared by published procedures.[2,3]

Reactions of [Mo{σ,η^2(3e)-CH_2C_2Me}{η^2(4e)-MeC_2Me}-(η-C_5H_5)] 1

With hexafluorobut-2-yne. An excess of hexfluorobut-2-yne (0.10 mmol) was condensed (−196 °C) into a Young's tube fitted with a Westof stopcock containing complex **1** (0.14g, 0.05 mmol) dissolved in toluene (10 cm^3). On warming to room temperature a white precipitate formed and an orange colour developed. The reaction mixture was filtered through Celite, the solvent was removed *in vacuo*, and the residue recrystallised from toluene–hexane to give orange *crystals* of **3** (0.07 g, 40%) (Found: C, 42.8; H, 2.8. $C_{21}H_{16}F_{12}Mo$ requires C, 42.6; H, 2.7%). NMR: ^{1}H (C_6D_6), δ 4.69 (s, 1 H, H^c), 4.46 (s, 5 H, C_5H_5), 2.68 [q, 1 H, H^b, *J*(HF) 12.46], 2.00 [q, 3 H, Me, *J*(HF) 1.47], 1.73 [q, 3 H, Me, *J*(HF) 2.38] and 1.40 (s, 3 H, Me^a); ^{13}C-{^{1}H} (CD_2Cl_2), δ 128.7 [q, CF_3, *J*(CF) 270], 125.5 [q, CF_3, *J*(CF) 280], 124.9 [q, CF_3, *J*(CF) 270], 122.3 [q, CF_3, *J*(CF) 270], 94.02 (C_5H_5), 81.0 (C^9), 56.35 [q, C^6, *J*(CF) 30.0], 19.43 (Me), 18.43 (Me) and 13.60 (Me); ^{19}F (C_6D_6), δ −49.14 to −49.25 (m, 3 F, CF_3), −53.81 [q, 3 F, CF_3^{a}, *J*(HF) 12.4 Hz], −57.01 to −57.23 (m, 3 F, CF_3) and −72.55 to −72.68 (m, 3 F, CF_3).



With carbon monoxide. A stream of carbon monoxide was bubbled at room temperature through a solution of complex **1** (0.14 g, 0.05 mmol) in tetrahydrofuran (20 cm^3). After 20 min the solution had changed from red to yellow, and removal of the volatile material *in vacuo* afforded a solid, which on recrystallisation (0 °C) from dichloromethane–hexane gave orange-yellow *crystals* of **4** (0.11 g, 82%) (Found: C, 55.6; H, 5.0. $C_{15}H_{16}MoO_2$ requires C, 55.7; H, 5.1%). IR (hexane): ν(CO) 1916s and 1595 cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 4.96 (s, 5 H, C_5H_5), 3.27 [d, 1 H, H^a, *J*(H^{a}H^b) 2.2], 2.94 [d, 1 H, H^b, *J*(H^{a}H^b) 2.2], 1.88 (s, 3 H, Me^c), 1.74 (s, 3 H, Me^d) and 1.64 (s,3 H, Me^e); ^{13}C-{^{1}H}, δ 241.2 (CO), 170.4 (C^1=O), 107.7 (C^3), 100.4 (C^2), 99.9 (C^4), 96.6 (C^5), 89.2 (C_5H_5), 49.96 (C^6) [^{1}H-coupled ^{13}C spectrum, dd, *J*(CH^a) 156.4, *J*(CH^b) 163.0 Hz], 12.99 (Me^e), 10.5 (Me^d) and 9.15 (Me^c). Mass spectrum: *m*/*z* 326 (M^+) and 298 (M^+ − CO).



Reaction of carbon monoxide with [Mo{σ,η^2(3e)-CH_2C_2Ph}-{η^2(4e)-MeC_2Ph}(η-C_5H_5)] 2

A similar reaction between complex **2** (0.22 g, 0.56 mmol) dissolved in tetrahydrofuran (20 cm^3) and carbon monoxide gave a yellow solid, which on crystallisation (0 °C) from dichloromethane–hexane gave yellow *crystals* of **5** (0.10 g, 40%) (Found: C, 66.9; H, 4.5. $C_{25}H_{20}MoO_2$ requires C, 67.0; H, 4.5%). IR (hexane): ν(CO) 1925s and 1603m cm^{-1}. NMR (CD_2Cl_2): ^{1}H, δ 8.0–7.3 (m, 10 H, Ph), 4.88 (s, 5 H, C_5H_5), 3.91 [d, 1 H, H^a, *J*(H^{a}H^b) 1.83], 3.34 [d, 1 H, H^b, *J*(H^{a}H^b) 2.0 Hz] and 2.29 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 244.0 (CO), 133.5 (C^1=O), 112.5, 111.9 (C^2, C^5), 90.81 (C_5H_5), 92.33, 90.29 (C^3,C^4), 56.51 (C^6) and 11.95 (Me).

Reaction of complex 4 with HBF_4·OEt_2

Tetrafluoroboric acid–diethyl ether (1 : 1) (0.075 g, 65 μl, 0.46 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of complex **4** (0.15 g, 0.46 mmol) in CH_2Cl_2 (10 cm^3). On warming to room temperature the reaction mixture was filtered through Celite, the volume reduced *in vacuo* to ≈3 cm^3 and Et_2O (20 cm^3) added. The resultant precipitate was collected and recrystallised (0 °C) from dichloromethane–diethyl ether to give pale yellow *crystals* of **6** (0.17 g, 89%)

(Found: C, 44.1; H, 4.3. $C_{15}H_{17}BF_4MoO_2$ requires C, 43.7; H, 4.2%). IR (CH_2Cl_2): ν(CO) 1980s cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 7.24 (s, 1 H, OH), 5.28 (s, 5 H, C_5H_5), 3.62 [d, 1 H, H^a, $J(H^aH^b)$ 2.57], 3.32 [d, 1 H, H^b, $J(H^aH^b)$ 2.57], 2.25 (s, 3 H, Me), 2.02 (s, 3 H, Me) and 1.71 (s, 3 H, Me); ^{13}C-{^1H} (CD_3NO_2), δ 233.4 (CO), 141.8 (C^1OH), 108.2 (C^3), 106.3 (C), 103.9(C), 100.3(C), 93.5 (C_5H_5), 52.8 (C^6), 12.2 (Me), 10.3 (Me) and 10.2 (Me).

Crystallography

Many of the details of the structural analyses are listed in Table 5. All X-ray diffraction measurements were made at ambient temperature using a CAD 4 automatic four-circle diffractometer. Cell dimensions were universally determined from the setting-angle values of 25 reflections. All structures were solved using heavy-atom techniques and refined using the SHELX suite of programs.[23] Hydrogen atoms were included at calculated positions except in the following instances, where the hydrogens were located in the penultimate Fourier-difference map and refined at fixed distances from the relevant parent atoms. In particular, H(61) and H(91) [attached to C(6) and C(9) respectively] in complex **3**, H(121) and H(122) [bonded to C(12)] in **5**, and H(131), H(132), H(13a) and H(13b) [attached pairwise to C(13) and C(13′)] in **4**, were refined at a fixed C–H distance of 1.08 Å. All hydrogens, other than those in the cyclopentadienyl ring of **6**, were positionally refined at a fixed C–H distance of 0.96 Å. All refinements were based on *F*. Low absorption coefficients for all complexes, in addition to optimum crystal size, precluded the need for application of an absorption correction to the crystallographic data.

Complex **6** exhibits an interesting hydrogen-bonding feature between F(1) in the tetrafluoroborate moiety and the alcoholic proton [H(2)] in the cation. The accompanying intermolecular F ··· H distance is 1.70(2) Å, while the F(1)–H(2)–O(2) angle is almost linear at a value of 175(7)°. As a consequence of this hydrogen bond there is a slight lengthening of the B–F(1) bond distance relative to the other B–F bonds in the anion.

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/149.

Acknowledgements

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