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Alkyne, cyclobutadiene and cyclopentadienone complexes of molybdenum and tungsten

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Abstract

Reactions of $[MoX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = Br, I) with $CF_3C{\equiv}CCF_3$ in a sealed tube give the tetrakis(trifluoromethyl)cyclopentadienone derivatives $[MoX(CO)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (**3b, c**) whereas if the liberated carbon monoxide is removed at intervals the bis-alkyne complexes $[MoX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2b, c**) are obtained preferentially. With X = I the former reaction also gives $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**4a**) containing an η^4-tetrakis(trifluoromethyl)cyclobutadiene ring. Under similar conditions the tungsten complexes $[WX(CO)_3(\eta^5\text{-}C_5H_5)]$ and $CF_3C{\equiv}CCF_3$ give only the bis-alkyne derivative $[WX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (X = Br, I) with no evidence for alkyne cyclisation products. $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ reacts with carbon monoxide to give $[MoCl(CO)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (**3a**), showing that the the bis alkyne complexes are intermediates in the formation of the tetrakis(trifluoromethyl)cyclopentadienone derivatives. Complexes $[MoX(CO)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ and $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ react with t-butyl isocyanide to give carbonyl substitution products $[MoX(CN^tBu)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (X = Br, I) (**3d, e**) and $[MoI(CN^tBu)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**4b**), respectively. Isomerism in complexes **3** has been studied by ^{19}F NMR spectroscopy and ascribed to the existence of η^2- and η^4-bonded $C_4(CF_3)_4CO$ ring systems, each of which can adopt two preferred orientations *prone* and *supine*. Dynamic ^{19}F NMR studies of **4a, b** revealed a high barrier to cyclobutadiene rotation about the metal–ring axis.

Introduction

Reactions between alkynes and metal carbonyls frequently lead to complexes containing cyclobutadiene ligands formed by metal-promoted cyclodimerisation of the alkyne [1]. Alternatively cyclodimerisation may proceed with CO incorporation into the ring to give cyclopentadienone or, less frequently, quinone derivatives [2]. The preferred reaction pathway depends both on the metal complex and the substituents on the alkyne as demonstrated by reactions of $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (**1a**) with MeC≡CMe, PhC≡CPh and $CF_3C{\equiv}CCF_3$ which give quinone, $[MoCl(CO)\{\eta^4\text{-}C_4Me_4(CO)_2\}(\eta^5\text{-}C_5H_5)]$ [3], cyclobutadiene, $[MoCl(CO)\{\eta^4\text{-}C_4Ph_4\}(\eta^5\text{-}C_5H_5)]$ [4] and cyclopentadienone $[MoCl(CO)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (**3a**) [3] derivatives. Interestingly it was noted that with alkynes MeC≡CMe and PhC≡CPh the halogen ligand had no effect on the reaction pathway although differences in reaction rate were observed. It was decided to extend these studies to reactions with

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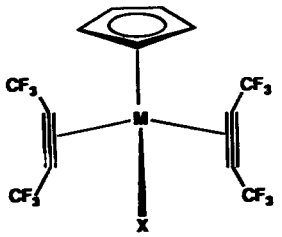
$CF_3C{\equiv}CCF_3$ where previously we observed that $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ gives different products depending on conditions [3,4]. In a sealed tube reaction the product is the aforementioned cyclopentadienone [3] derivative **3a** whereas if the liberated carbon monoxide is removed at intervals a bis alkyne complex $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2a**) is obtained preferentially [4]. This points to a cyclisation mechanism proceeding via **2a** to give the cyclopentadienone **3a**. Evidence for this possibility was sought in the present studies some of which have been reported previously in a preliminary communication [5].

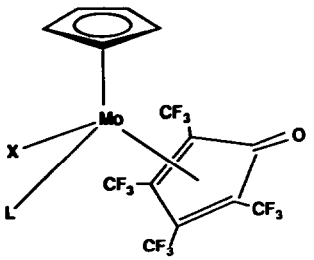
Results and discussion

Reactions of $[MoX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = Br, **1b**; I, **1c**), (ca. 500 mg), with $CF_3C{\equiv}CCF_3$ in sealed tubes (ca. 80 cm^3) at ca. 100 °C give bis-alkyne derivatives **2b**, **c** if small quantities of the tricarbonyl complex is employed [4], or alternatively with larger quantities, if the liberated carbon monoxide is removed at ca. 3 h intervals [4]. However, as with the chloro complex $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ the reaction is sensitive to the presence of carbon monoxide and if CO is not removed a cyclopentadienone complex **3b** is also obtained with X = Br. With X = I a mixture of two products was obtained, one assigned a cyclopentadienone structure **3c** the other a cyclobutadiene structure **4a**. All three complexes are orange crystalline materials, stable in air for reasonable periods of time although decomposition is more rapid in solution. The complexes are soluble in polar organic solvents CH_2Cl_2, Et_2O, etc. but the cyclopentadienone derivatives are less soluble than **4a** which allowed effective separation of **3c** and **4a** by selective extraction and fractional crystallisation.

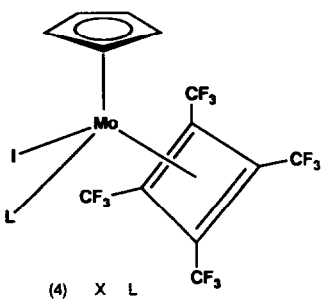
The spectroscopic properties of **3b** and **3c** are similar to those of the previously reported chloro complex **3a** with strong bands in the IR spectrum near 1700 cm^{-1} which are assigned to the ketonic ν(C=O) mode of the cyclopentadienone ligand. Similar observations have been made with a variety of complexes containing the $\eta^4\text{-}C_4(CF_3)_4CO$ ligand [6]. Two ν(CO) modes are also observed near 2100 cm^{-1} due to coordinated CO. Only one co-ordinated ν(CO) band is expected, but as the NMR data show, more than one isomeric form is present which explains the two ν(CO) modes observed. In each case, as with **3a**, the bromo and iodo derivatives show four cyclopentadienyl singlets in the ^1H NMR spectrum, two of significantly lower intensity than the others. However, the relative intensities varied with time and solvent indicating changes in equilibrium between four isomers. The ^{19}F NMR spectra are complex since in the proposed structure each CF_3 is in a unique environment. In the case of **3c** only peaks due to the two main isomers (ratio 3 : 1) were discerned. Each isomer gives rise to two quartets J = ca. 12 Hz due to CF_3 groups on the 1, and 4 positions of the cyclopentadienone ring. The internal CF_3 groups on C_2 and C_3 are septets (quartet of quartets) which appear at higher frequencies. Two of these are virtually coincident at 20 °C but at lower temperatures, e.g. −40 °C, separate into distinct septets. The ^{19}F NMR spectrum of the bromo complex **3b** is somewhat similar except that traces of a third isomers are visible in addition to which those of one of the major isomers are somewhat broadened. At higher temperatures (> 20 °C) the four peaks broaden further but at 70 °C in $(CD_3)_2CO$ show no signs of undergoing coalescence. The origins of the broadening are not clear but may be due to some form of slow exchange since the spectrum below 0 °C sharpens significantly.



(2)	M	X
a	Mo	Cl
b	Mo	Br
c	Mo	I
d	W	Cl
e	W	Br
f	W	I



(3)	X	L
a	Cl	CO
b	Br	CO
c	I	CO
d	Br	$CNBu^t$
e	I	$CNBu^t$



(4)	X	L
a	I	CO
b	I	$CNBu^t$

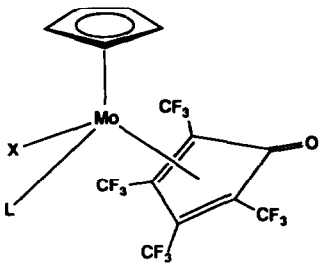
In an effort to identify the source of broadening other similar derivatives were sought. It was found that reactions of **3b** and **3c** with tertiary-butyl isocyanide proceed readily at room temperature in diethylether to give orange substitution products $[MoX(CN^tBu)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (X = Br, **3d**; X = I, **3d**). The IR spectra of these complexes are virtually identical to those of their precursors except that the carbonyl stretching modes near 2100 cm^{-1} have been replaced by $\nu(C{\equiv}N)$ modes at ca. 2200 cm^{-1}. In both cases the ^1H NMR spectra again show evidence for four isomeric forms in solution with four $\eta^5\text{-}C_5H_5$ singlets in the range δ 5.6–6. The ^{19}F NMR spectra do not exhibit the peak broadening found with **3b** and show, in each case, three sets of well resolved signals, two septets and two quartets J ca. 12 Hz for the two main isomers A and B and a septet and two quartets for a minor isomer C. The other septet is presumably obscured by major isomer signals whilst the other minor isomer peaks are too weak to be observed or are also obscured by other peaks.

The variable temperature ^{19}F spectra of **3d** and **3e** are virtually identical. The only temperature dependent feature is that as the temperature is reduced one of the the two isomer B quartets broadens and disappears into the baseline below $-70\,^\circ C$. The isomer B septets meanwhile have become degenerate giving rise to a single resonance. No significance is attached to the latter effect but a possible explanation for the quartet broadening may be slowing of CF_3 rotation due to steric affects, a

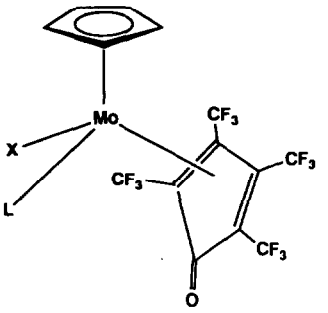
phenomenon we have observed in a variety of perfluoro methyl derivatives obtained from oligomerisation of co-ordinated $CF_3C{\equiv}CCF_3$ ligands [7]. A possible source of isomerism in complexes of this type is the orientation of the cyclopentadienone ligand with respect to the rest of the molecule. This follows from the well known ability of dienes to adopt *prone* and *supine* conformations in complexes such as $[MXY(diene)(\eta^5\text{-}C_5H_5)]^+$ [8]. X-ray structures of cyclopentadienone complexes of this type have not been determined to my knowledge although in earlier studies the structural characterisation of the related iminocyclopentadiene derivative $[Mo(CF_3)(CN^tBu)\{\eta^4\text{-}C_4(CF_3)_4CN^tBu\}(\eta^5\text{-}C_5H_5)]$ was carried out [9]. In the solid state the latter adopts a *prone* conformation but in solution two isomeric forms are observed, ratio 3 : 1 at ambient temperature and 6 : 1 at $-60\,^\circ C$. An interesting feature of the structure is the exact orientation of the diene which lies with its plane of symmetry virtually coincident with the Mo–CF_3 bond axis. In contrast recent structural studies of [W(CO)(η^4-1,3-cyclohexadiene)($\eta^{5:1}$-2-cyclopentadiendiyl-ethyl)] [10] and [W(CO)(η^4-1,3-butadiene)($\eta^{5:1}$-2-cyclopentadiendiylethyl) [11] revealed that the dienes adopt the alternative orientation with the diene parallel to the W–CO axis. In contrast the diene ligand in [Mo(Me)(CO)(η^4-1,3-butadiene)(η^5-C_5Me_5)] adopts a conformation where the C_2 axis of the diene lies between the Mo–CO and Mo–CH_3 axes [12]. This preference is usually found in more symmetrical derivatives such as $[MoCl_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$, $[NbCl_2(\eta^4\text{-}C_4H_2Me_4)(\eta^5\text{-}C_5Me_5)]$ and [Mo(dppe)(η^4-C_6H_8)(η^5-C_5Me_5)]PF_6 and is the lowest energy conformation in such species according to EHMO studies [13].

A simple explanation for the isomerism in complexes **3** is that it results from the presence of two basic forms **3i**-*prone and* **3i**-*supine*. In principle each of these can exist in two forms, one with the $\eta^5\text{-}C_4(CF_3)_4CO$ ligand lying approximately parallel to the halide ligand X and the other with the orientation parallel to the carbonyl or isonitrile ligand L. The fact that changes in isomer population are observed in solution but fast exchange on the NMR time scale is not implies that a high rotational barrier exists even between rotamers which differ presumably by only ca. 90°. The simplest mechanism for exchange between the four isomers would involve rotation of the dienone about the metal ligand axis. Interestingly *prone–supine* isomerism in a wide variety of early transition metal diene complexes has been observed and in some cases exchange between the two forms occurs via a ring flip mechanism involving an intermediate η^2-bonded diene. However, this mechanism is not available to cyclic dienes as in **3** where only rotation is possible. The latter mechanism is however, well known for late transition metal derivatives but recently has also been established unequivocally for certain early metal complexes [14].

The main problem with the above observations is that in other diene complexes studied to date only two isomers have been observed, one *prone* and one *anti* form. It is conceivable that this is also the case here ie the two main isomers are of this type. An alternative explanation for the presence of two additional isomers follows from the fact that that iminocyclopentadiene complexes $[MX(CN^tBu)\{C_4(CF_3)_4\text{-}CN^tBu\}(\eta^5\text{-}C_5H_5)]$ can adopt a novel bonding mode where X = SR. X-ray diffraction studies of $[W(S^iPr)(CN^tBu)\{C_4(CF_3)_4CN^tBu\}(\eta^5\text{-}C_5H_5)]$ have shown that the iminocyclopentadiene ligand bonds to the metal via the exocyclic η^2-C–N moiety [15]. The possibility that the two minor isomers of **3** may exhibit the equivalent structures **3ii**-*prone* and **3ii**-*supine*, must therefore be considered. Interestingly the iminocyclopentadiene ligand adopts a preferred orientation with the C–N bond



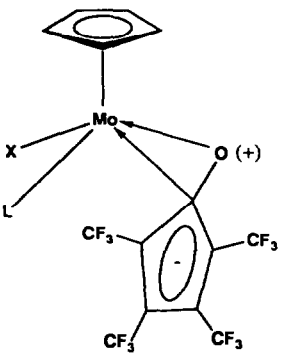
(3i) *supine*



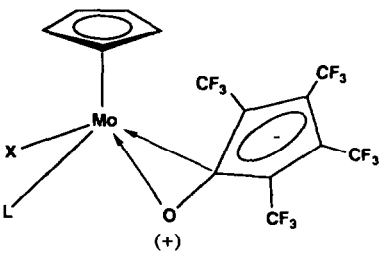
(3i) *prone*

lying approximately parallel to the metal-sulphur bond. The equivalent situation in complexes **3** would result in the metal co-ordinated C–O bond lying parallel to the metal–halogen bond.

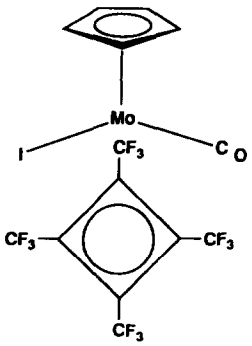
In support of this proposal it should be noted that the presence of CF_3 groups in the cyclopentadienone ligand should enhance the polarisation inherent in the η^2-structure; this is illustrated by the fact that phosphines form ylides with tetrakisfluoromethyl cyclopentadienone as a result of attack at oxygen [16]. Unfortunately attempts to obtain spectroscopic evidence for structures **3ii-*prone*** and **3ii-*supine*** using $^{13}C\{^{19}F\}$ NMR were unsuccessful since poor quality spectra with low signal/noise ratios were obtained. This is not surprising since the complexes are not particularly soluble in addition to which the structurally sensitive quaternary carbons would have low intrinsic sensitivity. The problems are also compounded by the fact that the minor isomers are only present in very small concentrations; as indicated earlier in one case neither of the minor isomers could be observed even by ^{19}F NMR spectroscopy. Unfortunately the IR spectra do not provide supporting evidence for the structures but again this this is explicable, taking into account the low intensity of ν(C=C) bands which might distinguish between the possible structures, combined with the small amounts of the isomeric forms present in solution.



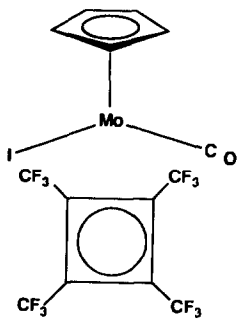
(3ii) *supine*



(3ii) *prone*



(4i)



(4ii)

Spectroscopic data for the cyclobutadiene complex **4a** are in accord with the proposed structure with the IR spectrum exhibiting a single ν(CO) mode at 2069 cm^{-1} and three ν(C–F) modes around 1200 cm^{-1}. The simplicity of the ν(C–F) region clearly implicates a high local symmetry for the CF_3 groups. The ^{19}F NMR spectrum is temperature dependent showing four septets (quartets of quartets with equal coupling constants, ca. 3.5 Hz) at $-60\,^{\circ}C$. At higher temperatures the four peaks broaden simultaneously and coalesce to a singlet above ca. $25\,^{\circ}C$. These data clearly indicate that at low temperatures the η^4-$C_4(CF_3)_4$ ring adopts a fixed orientation with respect to the rest of the molecule. Although two forms are possible, staggered-**4i** and eclipsed-**4ii**, we assume the former is preferred since this is observed in the solid state with [MoI(CO)(η^4-C_4Ph_4)(η^5-C_5H_5)] [17], [Mo(S_2-$CNMe_2$){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] [17] and related cyclobutadiene complexes [18] structurally characterised by X-ray diffraction studies. At higher temperatures the ring undergoes rotation leading to simultaneous exchange of all four CF_3 groups.

Rotation of η^4-cyclobutadiene ligands (as with η^5-C_5R_5, η^6-C_6R_6 etc. rings) has generally been found to be a low energy process. Increased barriers are generally found when bulky groups are present on the ring or alternatively on other ligands present in the complex. The latter is responsible for the recent report of the first observation of restricted rotation in an unsubstituted cyclopentadienyl ring, in this case in [M(H_2C=C(H)R)(PPh_3)$_2$(η^5-C_5H_5)]BF_4 (M = Ru, Os; R = Ph; M = Ru, R = H) [19]. High barriers to cyclobutadiene rotation have also been found in η^4-$C_4(CF_3)_4$ complexes [Mo(L–L){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] (L–L = S_2CNMe_2, S_2CNEt_2 or $S_2C_5H_4N$) derived from **4a** [20]. As discussed previously it is not clear if the high barriers in these complexes have steric or electronic origins and the present work does little to clarify this issue. However we note that tetraphenylcyclobutadiene complexes [MoX(CO)(η^4-C_4Ph_4)(η^5-C_5H_5)] (X = Cl, Br, I) [21] also show evidence for restricted rotation indicating that the phenomenon is not dependent on the presence of CF_3 groups on the cyclobutadiene ring.

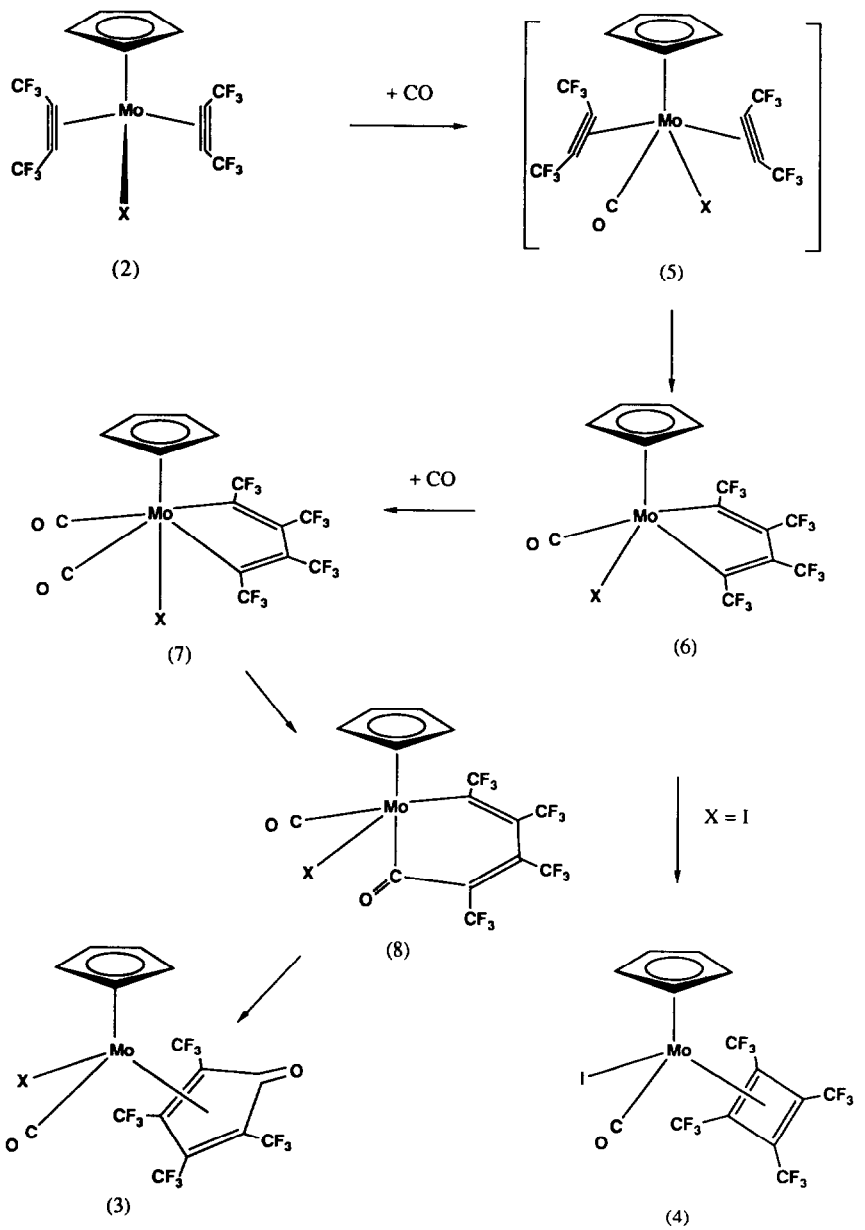
As with cyclopentadienone complexes **3b** and **3c** carbonyl substitution in **4a** by CN^{t}Bu can be effected readily ($60\,^{\circ}C$, 3 h, diethyl ether) to give the orange-red complex [MoI(CN^{t}Bu){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] (**4b**) in moderate yield (55%). The spectroscopic properties of **4b** are very similar to those of **4a** although four sharp CF_3 resonances are still observed in the ^{19}F NMR spectrum at $18\,^{\circ}C$, only $7\,^{\circ}C$ below the coalescence temperature for the latter. The equivalent spectrum for **4a** is

observed at ca. −35 °C and, since the chemical shift separation of the peaks is virtually the same for both complexes, the barrier to cyclobutadiene rotation must be significantly higher in the isocyanide derivative. This points to a contribution to the rotational barrier by steric interactions between the cyclobutadiene ring and other co-ordinated ligands. However, the presence of extensive spin–spin coupling in the ^{19}F NMR spectra prevented simple calculation of the kinetic parameters for exchange in either **4a** or **4b**.

Compounds **4a** and **4b** are noteworthy since they are among the first complexes in which a high barrier to cyclobutadiene ring rotation has been established [5]. They are also unique in being the first compounds to be isolated containing a coordinated η^4-$C_4(CF_3)_4$ ring, in particular one generated by cyclodimerisation of $CF_3C{\equiv}CCF_3$. We note that the uncomplexed $C_4(CF_3)_4$ ring has been generated at 77 K in a low temperature matrix, but as with other cyclobutadienes, is thermodynamically unstable [22]. Possible reasons why η^4-$C_4(CF_3)_4$ complexes are rarely isolated from reactions of $CF_3C{\equiv}CCF_3$ with metal complexes are the high reactivity of this alkyne towards other ligands (in particular CO) and in some cases the high stability of metallacycles $MC_4(CF_3)_4$. Moreover, in other cases, e.g. in reactions with cyclopentadienyl cobalt derivatives, cyclotrimerisation to give hexakistrifluoromethyl benzene complexes occurs in preference to cyclodimerisation observed with other alkynes [23,24].

In an attempt to induce cyclodimerisation of $CF_3C{\equiv}CCF_3$ with tungsten complexes related reactions with $[WCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (**1b**) were attempted under a variety of conditions up to 110 °C in hexane. However, in all cases the sole isolable product was the previously reported bis alkyne derivative $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with increasing amounts of decomposition being observed at higher temperatures. In one reaction (110 °C, 48 h) the IR spectrum of the crude product showed weak ν(CO) modes similar to those of $[Mo(CO)_2(\eta^4\text{-}C_4(CF_3)_4CO)(\eta^5\text{-}C_5H_5)]$ (**3a**) at 2070 cm^{-1} (co-ordinated CO) and 1730, 1720 (ketonic CO). However the species responsible for these bands could not be isolated in a pure form, the main product being $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2d**). Reactions of $[WX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = Br, I) with $CF_3C{\equiv}CCF_3$ were also carried out (hexane ca. 110 °C) and gave yellow crystalline derivatives $[WX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (X = Br, **2e**; X = I, **2f**). On the basis of comparable spectroscopic data to the structurally characterised chloro derivative **2d** [3] similar structures can be assigned. As with the last derivative the ^{19}F NMR data are temperature dependent showing two CF_3 resonances at low temperatures which collapse to a single peak above 0 °C (**2e**) and −6 °C (**2f**). This can be attributed to the well known phenomenon of alkyne 'propeller' rotation about the metal alkyne bond axis. At the slow exchange limit the alkynes presumably adopt the solid-state conformation in which the C≡C axes lie parallel to the M–X bond so as to render each end of the symmetry related alkynes inequivalent [3].

The results described herein, when taken in conjunction with those obtained previously [3,4] demonstrate that cyclisation of $CF_3C{\equiv}CCF_3$ in reactions with halides $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W; X = Cl, Br, I) depends on both the metal and the halide. With tungsten complexes cyclisation clearly does not occur readily and bis alkyne complexes are the only products isolated. However, when M = Mo these derivatives react further with liberated CO to give cyclobutadiene or cyclopentadienone derivatives **4** and **3**. These differences may be related to the



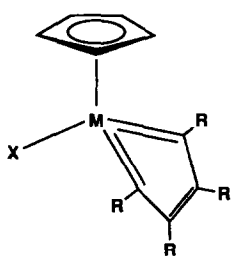
Scheme 1

mechanism of cyclisation which possibly proceeds via intermediate metallacyclopentadiene complexes **6** and **7** illustrated in Scheme 1. In support of this it has previously been demonstrated that bis alkyne → metallacyclopentadiene transformations can occur in reactions of **2** with $[Co_2(CO)_8]$ and the metallacyclic products have been structurally characterised [25]. Moreover, cyclisation of alkynes with an isocyanide to give iminocyclopentadiene products related to **3** proceeds via formal

16- and 18-electron metallacycles similar to **6** and **7** supporting the proposed reaction sequence **2** → **5** → **6** → **7** → **3** + **4** [26]. Metallacycles are also known to play a key role in alkyne cyclisations promoted by other transition metals [2,27].

In the present case it appears that the amount of CO present in the system plays a role in promoting cyclisation. This was confirmed by treating a hexane solution of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ with carbon monoxide (ca. 3.5 atm) at 70 °C when the cyclopentadienone complex **3a** was obtained as the sole isolable product. CO coordination to the metal in **2** presumably promotes metallacyclisation via an 18 electron bis alkyne intermediate **5** of a type proposed previously to explain alkyne insertion and cyclisation reactions [28,29]. Subsequent metallacyclisation to give **6** followed by ring closure gives the cyclobutadiene product **4** in the case X = I. Alternatively **6** can react with a second mole of CO to give **7** prior to CO insertion → **8** and this is followed by cyclopentadienone formation → **3** (X = Cl, Br, I). The effect of the halogen may therefore be to alter the stability of the formally 16 electron intermediate **6** relative to the 18-electron species **8**. This could occur via a steric effect which would destabilise **8** when X = I thus explaining why a cyclobutadiene complex **4** is only formed when the halogen is bulky. Alternatively, formation of **4** when X = I but not when X = Cl or Br may reflect differences in the amount of π-donation from the filled $p\pi$ orbitals on X to an empty $d\pi$ orbital on the metal in the intermediate **6**. This will also affect the relative stabilities of the two metallacycles **6** and **7**. The stability of the 16 electron metallacycle **6** may also explain the absence of cyclisation products in reactions of $CF_3C{\equiv}CCF_3$ with tungsten complexes $\{WX(CO)_3(\eta^5\text{-}C_5H_5)\}$. The transformation **5** → **6** involves a formal increase in the oxidation state of the metal by two units, i.e. $M^{II} \rightarrow M^{IV}$. Since we have previously observed a greater reluctance of cyclopentadienyl W^{II} derivatives to undergo oxidation compared with Mo^{II} [30], the absence of cyclisation products in reactions of $\{WX(CO)_3(\eta^5\text{-}C_5H_5)\}$ is perhaps explicable. It should also be noted that the reactions described herein compare closely with those involving cyclopentadienyl carbonyl derivatives of the group 5 metals $[M(CO)_4(\eta^5\text{-}C_5H_5)]$ (M = V, Nb, Ta) with alkynes reported by Nesmeyanov [31].

Although these explanations are reasonable and logical we cannot dismiss the possible role of recently isolated complexes containing the novel metallacyclopen-



		M	X	R
(9)	a	Mo	Cl	Ph
	b	Mo	Cl	CF_3
	c	Mo	SC_6F_5	CF_3
	d	W	Cl	CF_3

tatriene moiety [32,33] in the cyclisation reactions. For example, Curtis has synthesised a complex of this type **9a** by thermolysis of the bis alkyne complex $[MoCl(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5H_5)]$ of type **2** [33]. A second product of this reaction is the cyclobutadiene derivative $[MoCl_2(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5H_5)]$ related to complexes **4a** and **4b**. A related rhodium metallacyclopentatriene has also been found to react with isocyanides and CO to give iminocyclopentadiene and cyclopentadienone complexes possibly via intermediate metallacyclopentadienes [33]. Interestingly the perfluoromethyl derivative equivalent of **9a**, i.e. **9b** was isolated several years ago by photolysis of **2a** in the presence of excess $CF_3C{\equiv}CCF_3$ but not recognised as such [34]. I have also recently isolated and characterised related derivatives $[Mo(SC_6F_5)\text{-}\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**9c**) and $[WCl\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (**9d**) [35] and current investigations of the chemistry of these will hopefully establish or eliminate a role for such species in cyclisation reactions of bis-alkyne complexes such as **2**.

Experimental

NMR spectra were recorded on a Bruker WP 200SY spectrometer at 200.13 MHz (^{1}H) and 188.13 MHz (^{19}F). Coupling constant are in hertz and chemical shifts are referenced to Me_4Si (^{1}H: $\delta = 0$ ppm) and CCl_3F (^{19}F: $\delta = 0$ ppm). IR spectra were recorded as solutions on a Perkin–Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on an Vacuum Generators updated A.E.I. MS 9. Reactions were carried out under dry oxygen-free nitrogen by standard Schlenk techniques. Solvents were dried by refluxing over P_2O_5 (CH_2Cl_2), calcium hydride (hexane, diethyl ether) and distilled just before use. t-butyl isocyanide [36] and complexes $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo, W; X = Cl, Br, I) [37] were prepared by standard literature methods. $CF_3C{\equiv}CCF_3$ was obtained commercially.

*Reaction of $[MoBr(CO)_3(\eta^5\text{-}C_5H_5)]$ (**1b**) with $CF_3C{\equiv}CCF_3$*

600 mg of complex and 40 cm^3 of hexane were transferred to a thick glass tube fitted with a Westef stopcock and the solution degassed by the freeze thaw method. 2 g of hexafluorobut-2-yne were condensed in at −196 °C and the tube sealed. The mixture was heated to 100 °C for 15 h when red orange crystals formed. On cooling to 0 °C orange crystals separated out. Unreacted hexafluorobut-2-yne was removed *in vacuo*, solvent decanted off, and the orange solid extracted with diethyl ether leaving large crystals behind. The ether extract was filtered, concentrated *in vacuo*, treated with hexane and cooled to −15 °C to give orange crystals. Two more crystallisations from dichloromethane/hexane gave 230 mg, 22% of $[MoBr(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**2b**) identified by comparison with an authentic sample [4]. The residual large red-orange crystals were recrystallised twice from dichloromethane/hexane to give orange micro crystals of $[MoBr(CO)\{\eta^4\text{-}C_4(CF_3)_4CO\}(\eta^5\text{-}C_5H_5)]$ (**3b**) (340 mg, 30%). (Found: C, 29.2; H, 0.6. $BrC_{15}H_5F_{12}MoO_2$ calc.: C, 28.99; H, 0.80%.) IR (CCl_4): ν(C≡O) 2094wm, 2067m, ν(C=O) 1734sh, 1720wm, 1705m cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$]: δ 6.45, 6.38, 6.04, 6.03 (s, 5H, C_5H_5). ^{19}F NMR [$(CD_3)_2CO$]: δ −49.76 (br, overlapping peaks); −50.18 (sept, 3F); −51.82 (overlapping multiplets); −53.35 (sept, 3F); −53.60 (q, J 11.3, 3F); −54.1 (overlapping multiplets); −54.69 (br. q, J 11.0, 3F); −55.37 (q, J 12.2, 3F).

Reaction of [MoI(CO)$_3$(η^5-C_5H_5)] (1c) with $CF_3C{\equiv}CCF_3$

500 mg of the complex and 40 cm^3 of hexane were transferred to a thick glass tube fitted with a Westef stopcock and the mixture degassed using the freeze-thaw technique. 2 g of hexafluorobut-2-yne were condensed in and the tube sealed. The contents were reacted at 100 °C for 48 h and then allowed to cool to room temperature when an orange powder settled out. The excess of $CF_3C{\equiv}CCF_3$ was removed, the supernatant liquid filtered off and concentrated *in vacuo*. On cooling to −15 °C orange crystals were obtained. The orange powder left behind was extracted with several portions of warm hexane and these were filtered and concentrated to give a second batch of orange crystals. The two batches were combined and recrystallised twice from diethyl ether hexane at −15 °C to give [MoI(CO){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] (4a) (180 mg, 21%). (Found: C, 26.6; H, 0.9; F, 35.4; I, 19.8. $C_{14}H_5F_{12}IMoO$ calc.: C, 26.25; H, 0.8; F, 35.63; I, 19.84%.) MS: m/z 640 = M^+. IR (CCl_4): ν(CO) 2069s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.96 (s, C_5H_5). ^{19}F NMR [$(CD_3)_2CO$, −60 °C]: δ 50.25 (sept, 3F); −51.09 (sept, 3F); −54.77 (sept, 3F); −56.74 (sept, 3F).

The residue from the ether extract was recrystallised twice from dichloromethane/hexane at −20 °C to give an orange microcrystalline solid [MoI{CO){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (**3c**), (224 mg, 25%). (Found: C, 26.6; H, 0.9. $C_{15}H_5F_{12}IMoO_2$ calc.: C, 26.95; H, 0.75%.) IR ($CHCl_3$): ν(CO) 2080sh, 2063m, ν(C=O) 1702br. m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.01, 5.97, 5.69, 5.62 (s, 5H, C_5H_5) ratio 20 : 4 : 46 : 3. ^{19}F NMR [$(CD_3)_2CO$]: Isomer A: δ −50.01 (sept, 3F); −52.06 * (m, 3F); −53.53 (q, *J* 11.4, 3F); −54.24 (q, *J* 12.4, 3F). Isomer B: δ −50.49 (sept, 3F); −52.06 * (m, 3F); −54.07 (q, *J* 12.3, 3F); −54.48 (q, *J* 11.4, 3F).

Reaction of [MoI(CO){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] (4a) with CN^{t}Bu

30 mg of complex in diethyl ether (20 cm^3) was treated with 3 drops of CN^{t}Bu at 60 °C in a sealed tube for 3 h. The solution was cooled, filtered and treated with 10 cm^3 hexane. Concentration *in vacuo* followed by cooling to −15 °C gave orange crystals (18 mg, 55%) of [MoI(CN^{t}Bu){η^4-$C_4(CF_3)_4$}(η^5-C_5H_5)] (**4b**). (Found: C, 30.6; H, 1.9; N, 1.9. $C_{18}H_{14}F_{12}IMoN$ calc.: C, 31.08; H, 2.01; N, 2.01%.) IR ($CHCl_3$): ν(C≡N) 2192s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.75 (s, 5H, C_5H_5); 1.50 (s, 9H, ^{t}Bu). ^{19}F NMR [$(CD_3)_2CO$, −50 °C]: δ −50.48 (br. sept. 3F); −50.89 (br.sept, 3F); −53.64 (br. sept, 3F); −56.64 (br. sept, 3F).

Reaction of [MoI(CO){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (3c) with CN^{t}Bu

50 mg of the complex in CH_2Cl_2 (30 cm^3) was treated with 4 drops of CN^{t}Bu at room temperature and the mixture stirred for 6 h. 10 cm^3 of hexane was added and the solution concentrated *in vacuo* and on cooling to −15 °C orange crystals were obtained. A second crystallisation from CH_2Cl_2/hexane gave [MoI(CN^{t}Bu){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (**3e**) (21 mg, 39%). (Found C, 31.6; H, 2.0; N, 1.8. $C_{19}H_{14}F_{12}IMoNO$ calc.: C, 31.54; H, 1.94; N, 1.94%.) IR ($CHCl_3$): ν(C≡N) 2212s, ν(C=O) 1703s cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$]: δ 5.75, 5.72, 5.42, 5.40 (s, 5H, C_5H_5); 1.59, 1.57, 1.55 (s, 9H, ^{t}Bu). ^{19}F NMR [$(CD_3)_2CO$, −10 °C]. Isomer A: δ −50.23 (sept, 3F); −51.77 ** (3F); −53.88 (q, *J* 11.4, 3F); −55.31 (q, *J* 12.4, 3F). Isomer

* Two overlapping peaks.

** Two overlapping peaks.

B: δ −50.68 (sept, 3F); −51.19 (m, 3F); −54.37 (br. q, *J* 12.3, 3F); −55.56 (q, *J* 11.4, 3F). Isomer C: δ −53.16 (sept, 3F); −54.18 (q, *J* 12.3, 3F); −54.84 (q, *J* 12.2, 3F).

*Reaction of [MoBr(CO){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (**3b**) with CN^tBu*

40 mg of complex in CH_2Cl_2 (20 cm^3) were treated with 4 drops of CN^tBu at room temperature and the mixture was stirred for 16 h. 10 cm^3 of hexane was added, the solution concentrated *in vacuo*, and on cooled to −20 °C to give orange crystals. A second crystallisation from CH_2Cl_2/hexane gave [MoBr(CN^tBu){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (**3d**) (26 mg, 60%). (Found: C, 33.3; H, 2.0; N, 1.9. $C_{19}H_{14}BrF_{12}MoNO$ calc.: C, 33.73; H, 2.07; N, 2.07%.) IR ($CHCl_3$): ν(C≡N) 2210s, ν(C=O) 1702s cm^{-1}. ^1H NMR [$(CD_3)_2CO$]: δ 6.05, 6.02, 5.63, 5.62 (s, 5H, C_5H_5); 1.59, 1.57, 1.55 (s, 9H, ^tBu). ^{19}F NMR [$(CD_3)_2CO$]. Isomer A: δ −50.14 (sept, 3F); −51.82 (sept, 3F); −53.89 (q, *J* 11.4, 3F); −55.06 (q, *J* 12.2, 3F). Isomer B: δ −50.35 (br. sept, 3F); −51.25 (br. sept, 3F); −54.22 (br. q, *J* 12.2, 3F); −55.5 (q, *J* 11.1, 3F). Isomer C: δ −52.90 (sept, 3F); −54.20 (q, *J* 12.5, 3F); −54.81 (q, *J* 12.1, 3F).

*Reaction of [$WBr(CO)_3(\eta^5$-$C_5H_5)$] (**1e**) with $CF_3C{\equiv}CCF_3$*

300 mg of complex and 2 g of $CF_3C{\equiv}CCF_3$ in 30 cm^3 hexane were heated at 110 °C in a sealed glass tube for 30 h. The mixture was allowed to cool to room temperature, the excess of $CF_3C{\equiv}CCF_3$ was removed *in vacuo*, and the solvent decanted off. The impure residue was extracted with diethyl ether (40 cm^3) and filtered, and hexane was added. Concentration followed by cooling to −20 °C gave an impure light brown solid. this was recrystallised twice from CH_2Cl_2/hexane to give yellow crystals of [$WBr(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] (**2f**) (56 mg, 12%). (Found: C, 23.4; H, 0.8. $C_{13}H_5BrF_{12}W$ calc.: C, 23.89; H, 0.77%.) IR (CCl_4): ν(C≡C) 1778m, 1759wm cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.28 (s, 5H, C_5H_5). ^{19}F NMR ($CDCl_3$): δ −57.48 (s, CF_3).

*Reaction of [$WI(CO)_3(\eta^5$-$C_5H_5)$] (**1f**) with $CF_3C{\equiv}CCF_3$*

A mixture of 300 mg of complex and 2 g of $CF_3C{\equiv}CCF_3$ was kept at 120 °C for 48 in hexane. Work up as for **2f** yellow crystals of [$WI(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] (**2g**) 43 mg, 9%. (Found: C, 22.2; H, 0.9. $C_{13}H_5F_{12}IW$ calc.: C, 22.3; H, 0.71%.) IR ($CHCl_3$); ν(C≡C) 1785wm, 1766wm cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.10 (s, 5H, C_5H_5). ^{19}F NMR ($CDCl_3$): δ −57.28 (s, CF_3).

*Reaction of [$MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] (**2a**) with CO*

170 mg of complex and 20 cm^3 of hexane was transferred under nitrogen to a 100 cm^3 autoclave, which was then sealed, purged with CO four times and pressurised to 3.5 atmospheres with CO. The mixture was then kept at 70 °C and the reaction followed by IR spectroscopy of samples extracted at intervals. After 72 h no starting material remained. As the solution cooled slowly to room temperature an orange powder separated and this was recrystallised from dichloromethane/hexane to give [MoCl(CO){η^4-$C_4(CF_3)_4CO$}(η^5-C_5H_5)] (**3a**) (43 mg, 23%), identified by comparison with an authentic sample [3].

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