Cyclo-oligomerisation Reactions of Bis(alkyne) and η^2-Vinyl Complexes of Molybdenum and Tungsten with t-Butyl Isocyanide leading to Iminocyclopentadiene Derivatives†

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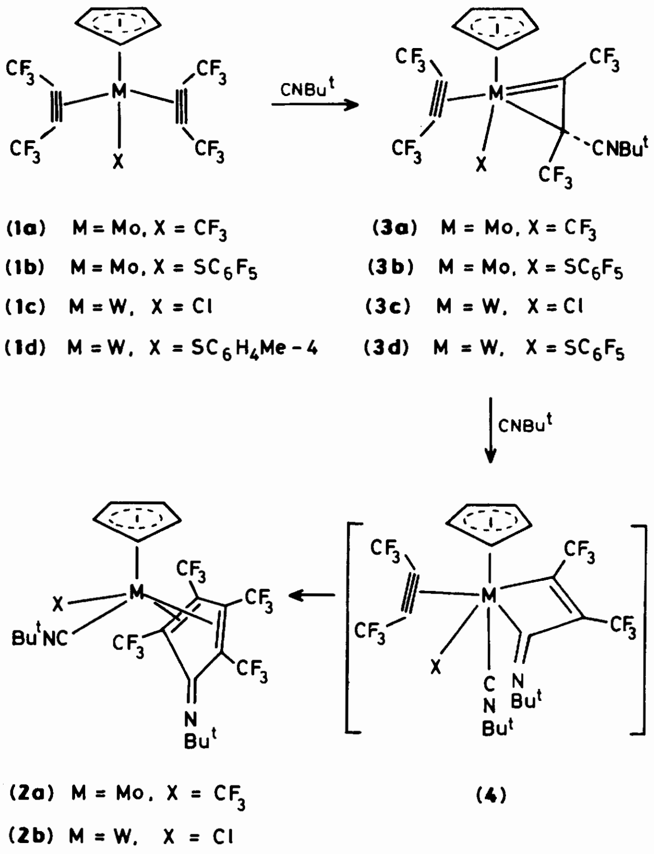
Reactions of t-butyl isocyanide with bis(alkyne) complexes [M(SR)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (M = Mo, R = C$_6$F$_5$; M = W, R = C$_6$H$_4$Me-4) and isomeric η^2-vinyl complexes [W{C(CF$_3$)C(CF$_3$)SR}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (R = Me, Pr^i, or Bu^t) give bis(isocyanide)-metallacyclic derivatives [M{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)}(SR)(CNBu^t)$_2$(η^5-C$_5$H$_5$)] (**7**), *via* η^2-vinyl, [M{η^2-C(CF$_3$)C(CF$_3$)CNBu^t}(SR)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (M = Mo, R = C$_6$F$_5$), or 16-electron monoisocyanide complexes, [W{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)}(SR)(CNBu^t)-(η^5-C$_5$H$_5$)] (**6**), isolated for M = W, R = Bu^t. Metallacyclic complexes (**6**) (R = Bu^t) and (**7**) (M = W; R = C$_6$H$_4$Me-4, Pr^i, or Bu^t) can be hydrolysed to the iminoacyl oxo complex [W{η^3-C(NBu^t)C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)H}(O)(η^5-C$_5$H$_5$)] whereas thermolysis of (**7**) (M = Mo, R = C$_6$F$_5$; M = W, R = Pr^i) gives complexes [M(SR)(CNBu^t){η^2-C$_4$(CF$_3$)$_4$CNBu^t}-(η^5-C$_5$H$_5$)] containing an iminocyclopentadiene ligand bonded in a novel η^2 manner *via* the exocyclic C–N bond to the metal.

Reactions between alkynes and transition metal carbonyls frequently lead to cyclisation of two or more alkynes with carbon monoxide giving cyclopentadienone, quinone, and tropone derivatives.[1] In some cases the free ketone is produced but normally it remains co-ordinated to the metal giving a π-complex. The mechanisms by which cyclic organic systems are constructed from the alkyne and carbon monoxide are not known with certainty although several proposals have been made, involving, for example, intermediate metallacyclobutenone or metallacyclohexadienone complexes.[1,2]

Previously we have observed that reactions of [MoX(CO)$_3$(η^5-C$_5$H$_5$)] (X = Cl, Br, or I) with CF$_3$C≡CCF$_3$ lead to cyclopentadienone complexes [MoX(CO){η^4-C$_4$(CF$_3$)$_4$CO}-(η^5 -C$_5$H$_5$)] *via* isolable carbonyl-free bis(alkyne) intermediates [MoX(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (**1**).[3] Similarly, [MX(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (M = Mo, X = CF$_3$; M = W, X = Cl) reacts with t-butyl isocyanide to give structurally related iminocyclopentadiene complexes (**2a**) and (**2b**), characterised by *X*-ray diffraction studies in the case of M = Mo, X = CF$_3$.[4] In each case an intermediate 1:1 adduct [MX(CF$_3$C$_2$CF$_3$)$_2$(CNBu^t)(η^5-C$_5$H$_5$)] was isolated which was originally assigned a bis(alkyne) structure. However [WCl(CF$_3$C$_2$CF$_3$)$_2$(CNBu^t)(η^5-C$_5$H$_5$)] was recently shown to have a novel η^2-vinyl structure (**3c**) suggesting a cyclisation mechanism involving an iminocyclobutene intermediate (**4**), Scheme 1.[3b] Previously it has been reported that cobalt iminocyclobutene complexes react with alkynes to give η^4-iminocyclopentadienes[5a] which can also be obtained from the reaction of cobalt metallacycles with isocyanides.[5b] The latter observation prompted us to extend our studies to reactions of t-butyl isocyanide with bis(alkyne) thiolate complexes (**1b**) and (**1d**) and isomeric η^2-vinyl derivatives (**5**)[6] with a view to establishing the mechanism of cyclisation reactions of this type. Some of this work has been communicated previously.[7]



Scheme 1.

Results and Discussion

The results of the present work are summarised in Scheme 2 which also provides a mechanistic rationale for the processes involved. The reactions of (**1**) and (**5**) with t-butyl isocyanide depend markedly on the molar ratio of reactants, the reaction temperature, the nature of the metal, and the thiolate substituent R. Thus the reaction of [Mo(SC$_6$F$_5$)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (**1b**) with 1 mol equiv. of CNBu^t in diethyl ether at

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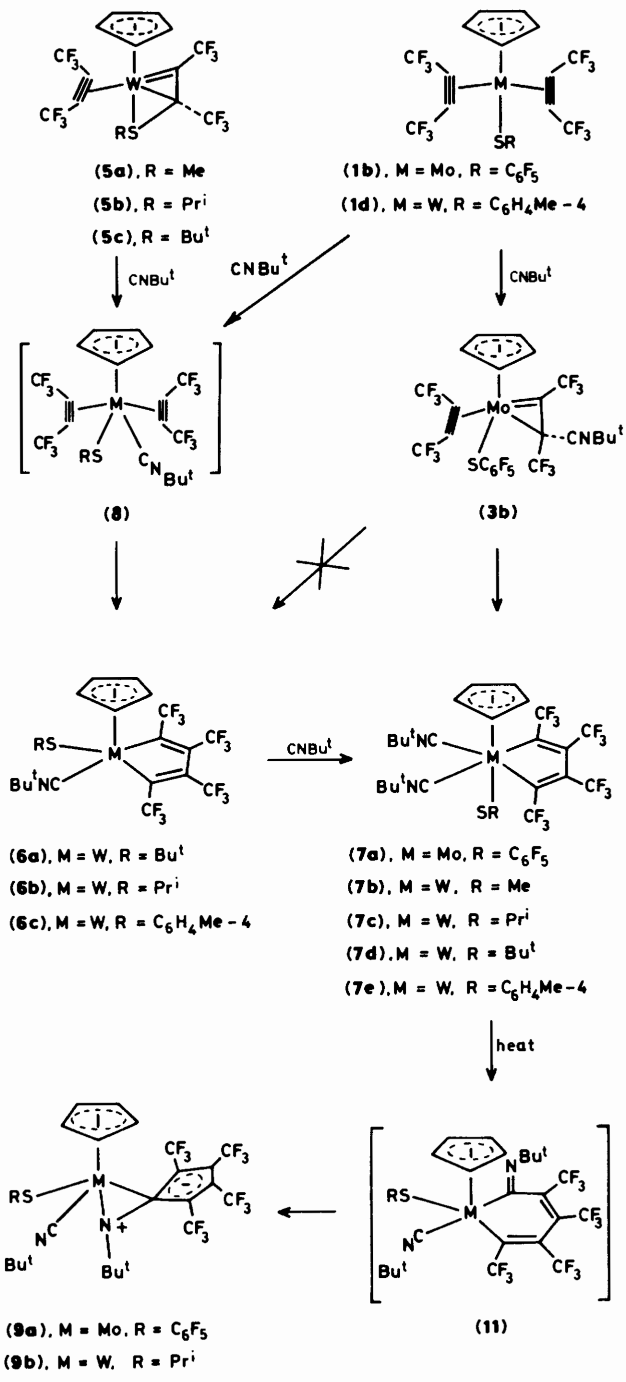
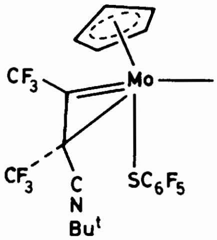
† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.



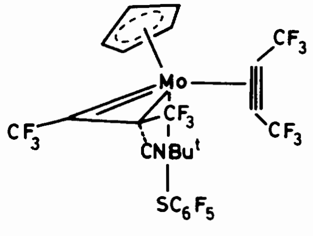
Scheme 2.

-20 °C affords moderate yields of a pale yellow microcrystalline solid which analyses as a 1:1 adduct, (**3b**). The spectroscopic features of the complex are very similar to those of the tungsten analogue (**3d**) and the chloro complex (**3c**)[4] obtained previously by similar means. *X*-Ray diffraction studies of the latter established that the isocyanide had attacked an alkyne carbon to give the η^2-vinyl structure illustrated.[3b] On the basis of comparable spectroscopic properties we also assign such a structure to (**3b**) and the previously reported tungsten analogue (**3d**).[4a] In both cases two sets of resonances are observed in the ^{1}H and ^{19}F n.m.r. spectra suggesting two isomeric forms.

The structurally related η^2-vinyl complex [Mo{η^2-C(CF$_3$)C(CF$_3$)PEt$_3$}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] also exists in two isomeric forms, a kinetic form which has a similar ^{19}F n.m.r. spectrum to the minor isomer of (**3**) (M = Mo or W, X = SC$_6$F$_5$) and a thermodynamically more stable form with similar features to the major isomer. *X*-Ray diffraction studies of the isomers reveal differences in both the orientation and the stereochemistry of the chiral carbon of the η^2-vinyl ligand.[8] The 'thermodynamic' isomer is structurally analogous to (**3c**) and this in conjunction with n.m.r. data enables us to assign structures (**3**)(**i**) and (**3**)(**ii**) to the minor and major isomers of (**3b**) and (**3d**).

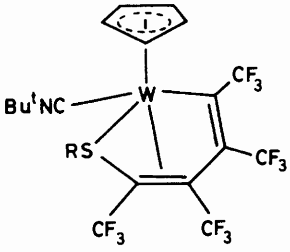


(3)(i)



(3)(ii)

The reaction of [W{η^3-C(CF$_3$)C(CF$_3$)SBu^t}(CF$_3$C≡C-CF$_3$)(η^5-C$_5$H$_5$)] (**5c**) with 1 mol equiv. of CNBu^t at -50 °C in diethyl ether gave a deep green solution from which a dark green microcrystalline solid (**6a**) was obtained on crystallisation from diethyl ether–hexane. Elemental analysis is in accord with a 1:1 adduct of stoicheiometry [W(SBu^t)(CF$_3$C$_2$CF$_3$)$_2$(CN-Bu^t)(C$_5$H$_5$)] and the i.r. spectrum indicates the presence of a co-ordinated isocyanide ligand which gives rise to a single C≡N stretching mode at 2 161 cm^{-1}. However n.m.r. data and the absence of a band near 1 800 cm^{-1} rule out an η^2-vinyl structure similar to (**3**). The ^{19}F n.m.r. data are particularly revealing since four peaks are observed, two quartets, δ_1 -45.25, $J_{1,4}$ = 16.5, δ_2 -52.66, $J_{2,3}$ = 15.5, and two quartets of quartets δ_3 -54.19, $J_{3,2}$ = 15.5, $J_{3,4}$ = 15.7, and δ_4 -57.49, $J_{4,1}$ = 16.5, $J_{4,3}$ = 15.7 (Table). *cis* CF$_3$C=CCF$_3$ groups usually exhibit coupling constants in the region 11—18 Hz[9] and on this basis an all-*cis* CF$_3$=C(CF$_3$)–C(CF$_3$)=C(CF$_3$) moiety resulting from the condensation of two alkynes is indicated. Moreover the similarity of the three CF$_3$–CF$_3$ coupling constants suggests a planar fluorocarbon chain and consequently structure (**6**) containing a metallacyclopentadiene ring is proposed. An alternative structure (**6′**), in which the C–S bond of the original η^2-vinyl complex is retained, is rejected on the basis that the analogous phosphine complex [Mo{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)SPr^i}(PEt$_3$)(η^5-C$_5$H$_5$)], obtained from the reaction of the molybdenum analogue of (**5**) with PEt$_3$ and which has been structurally characterised by *X*-ray diffraction methods, exhibits significantly different CF$_3$–CF$_3$ coupling constants.[10]



(6′)

In the present case co-ordination of CNBu^t to the metal apparently results in C–S bond fission within the η^2-vinyl ligand

Table. N.m.r. data for the complexes at room temperature

Complex	^{1}H			^{19}F
	C_5H_5	Bu^t	SR	
(**3b**) (major)	5.81 (s, 5 H)	1.66 (s, 9 H)	—	−54.51 (br s, 3 F), −55.23 (q, J = 3.0, 3 F), −55.41 (br s, 3 F), −57.60 (br s, 3 F)
(minor)	*a*	1.79 (s, 9 H)		−54.06 (br s, 3 F), −55.83 (br s, 3 F), −58.46 (br s, 3 F)[a]
(**6a**)[b]	5.19 (s, 5 H)	1.60 (s, 9 H)	1.50 (s, 9 H)	−45.25 (q, $J_{1,4}$ = 16.5, 3 F), −52.66 (q, $J_{2,3}$ = 15.5, 3 F), −54.19 (qq, $J_{3,2}$ = 15.5, $J_{3,4}$ = 15.7, 3 F), −57.49 (qq, $J_{4,1}$ = 16.5, $J_{4,3}$ = 15.7, 3 F)
(**6b**)[b]				−45.02 (q, $J_{1,4}$ = 15.5, 3 F), −52.85 (q, $J_{2,3}$ = 14.7, 3 F), −54.04 (qq, $J_{3,2}$ = 14.7, $J_{3,4}$ = 14.6, 3 F), −57.4 (qq, $J_{4,3}$ = 14.6, $J_{4,1}$ = 15.5, 3 F)
(**6c**)[b]				−45.58 (q, J = 15.3, 3 F), −52.88 (q, J = 15.0, 3 F), −53.67 (septet, J = 14.8, 3 F), −57.72 (septet, J = 15.2, 3 F)
(**7a**)	5.17 (s, 5 H)	1.49 (s, 18 H)	—	−49.65 (m, 6 F), −55.46 (m, 6 F)
(**7e**)	4.77 (s, 5 H)	1.37 (s, 18 H)	7.25 (d), 7.10, (d, 4 H), 2.29 (s, 3 H)	−50.37 (m, 6 F), −56.47 (m, 6 F)
(**7b**)	4.75 (s, 5 H)	1.50 (s, 18 H)	2.36 (s, 3 H)	−50.05 (m, 6 F), −55.75 (m, 6 F)
(**7c**)[c]	4.98 (s, 5 H)	1.56 (s, 18 H)	3.63 (m, 1 H), 1.19 (d, J = 6.5, 6 H)	−49.36 (m, 6 F), −55.10 (m, 6 F)
(**7d**)	4.72 (s, 5 H)	1.50 (s, 18 H)	1.40 (s, 9 H)	−48.95 (m, 6 F), −56.15 (m, 6 F)
(**10**)	6.29 (s, 5 H)	1.53 (s, 9 H)	2.82 (q, J_{HF} = 9.0, 1 H)	−54.17 (dq, $J_{F,H}$ = 9.5, $J_{1,2}$ = 9.75, 3 F), −55.33 (qq, $J_{1,2}$ = 9.67, $J_{2,3}$ = 4.5, 3 F), −59.28 (qq, $J_{3,2}$ = 4.5, $J_{3,4}$ = 10.5, 3 F), −59.92 ($J_{4,3}$ = 10.5, 3 F)
(**9a**)	5.01 (s, 5 H)	1.54 (s, 9 H), 1.33 (s, 9 H)		−47.27 (q, J = 11.5, 3 F), −47.41 (q, J = 11.0, 3 F), −54.04 (septet, J = 12.0, 3 F), −55.02 (septet, J = 12.0, 3 F)
(**9b**)	4.84 (s, 5 H)	1.59 (s, 9 H), 1.50 (s, 9 H)	3.17 (m, 1 H), 1.33 (d, J = 7.0, 3 H), 1.28 (d, J = 7.0, 3 H)	−47.25 (app. quintet, 6 F), −54.25 (septet, J = 11.0, 3 F), −54.48 (septet, J = 11.0, 3 F)

[a] Obscured by major isomer resonance. [b] In CD_2Cl_2 at −15 °C. [c] In $(CD_3)_2CO$.

followed by oxidative cyclisation of the two alkynes with the metal. This not only oxidises the metal to W^{IV} but also generates a 16-electron configuration at the metal centre. Although the isolation of such a species is somewhat unexpected in view of the electronic unsaturation of the tungsten atom we note that stable 16-electron cyclopentadienyl molybdenum and tungsten complexes $[MX_2(NO)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, X = alkyl)[11] and $[Mo(SR)_2(NO)(\eta^5\text{-}C_5H_5)]$[12] (R = alkyl or aryl) are known while the tris(thiolate) complex $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$ has recently been synthesised in these laboratories and structurally characterised by *X*-ray diffraction studies.[13]

The fact that species such as (**6**) have not been isolated previously may reflect their kinetic reactivity rather than thermodynamic instability. This derives from our observation that bis(isocyanide) complexes (**7**) are obtained from the reactions of excess (3 mol equiv.) of CNBu^t with bis(alkyne) and η^2-vinyl complexes (**1**) and (**5**). When carried out in diethyl ether at room temperature these reactions initially produce a green solution and this rapidly turns orange-yellow before precipitating orange-yellow crystals of (**7**). In the case of (**1d**), (**5b**), and (**5c**) the reactions were also studied at low temperature by ^{19}F n.m.r. spectroscopy where it was established that in each case on addition of 1 mol equiv. of CNBu^t at −50 °C the green colour is due to formation of a 1:1 adduct, (**6**). Addition of a second mol equiv. of the isocyanide at this temperature has little effect but at higher temperatures the green solutions turn orange-yellow as the 2:1 adducts are formed. Similar studies of the reaction between (**1b**) and CNBu^t revealed that the η^2-vinyl complex (**3b**) is formed initially but on addition of a second mole of CNBu^t (**7a**) is obtained.

Although complexes (**7**) share some common spectral features with iminocyclopentadienes (**2**), important differences are apparent consistent with the metallacyclic structure illustrated. The i.r. spectrum in each case exhibits two $\nu_{C\equiv N}$ modes in the co-ordinated isocyanide region at *ca.* 2 150 cm^{-1} suggesting the presence of two metal-co-ordinated isocyanide ligands. The absence of an imine ligand which this implies is further supported by the lack of a $\nu_{C=N}$ mode which in (**2**) is observed near 1 700 cm^{-1}. The ^{1}H n.m.r. spectra confirm the presence of an $\eta^5\text{-}C_5H_5$ ligand giving a singlet near 5 p.p.m. Interestingly the isopropyl methyls of (**7c**) give rise to a doublet instead of the two doublets which might be expected for a structure such as (**2**) where the chiral metal centre would render the methyl groups diastereotopic. This and the observation of only one tertiary butyl resonance provides evidence for a plane of symmetry in the molecule in accord with the presence of only two complex multiplets in the ^{19}F n.m.r. spectra. Significantly the appearance of these multiplets is virtually identical to that of the two resonances observed with metallacyclic complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}Co(CO)_2]$ obtained from the octacarbonyldicobalt-induced cyclisation of the two alkynes in $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W).[14]

The proposed structure of (**7**) is based upon a '4 × 3 piano stool' with the two isocyanides and the fluorocarbon unit forming the square base and this is capped by a thiolate ligand. The n.m.r. data exclude the alternative isomeric structure where one isocyanide occupies the capping position. *X*-Ray diffraction studies show that the cobalt atom occupies this position in $[(\eta^5\text{-}C_5H_5)(CO)_2W\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}Co(CO)_2]$ while two equivalent tungsten-co-ordinated carbonyls occupy *cis* positions on the basal plane.[15] This illustrates that although the formation of (**7**) from the co-ordinatively unsaturated precursor (**6**) presumably involves initial co-ordination of the isocyanide at the vacant axial site, rearrangement must occur to give the more symmetrical isomeric form (**7**) with an axial mercapto ligand.

The formation of a metallacyclic species from a bis(alkyne) precursor, although widely postulated in the literature, has only rarely been demonstrated in practice. The first reported example involved the bis(alkyne)iron cluster complex $[Fe_3(CO)_3\text{-}(PhC{\equiv}CPh)_2]$ which has been observed to undergo thermal rearrangement to an isomeric metallacyclic form.[16] The reactions of monoalkyne complexes $[Co(PPh_3)(RC{\equiv}CR)(\eta^5\text{-}$

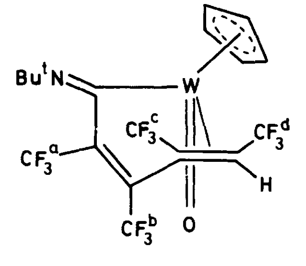
C$_5$H$_5$)] with alkynes to give metallacyclic derivatives [Co{C(R)=C(R)C(R)=C(R)}(PPh$_3$)(η^5-C$_5$H$_5$)] proceed *via* bis(alkyne) intermediates according to kinetic studies.[17] Of more relevance in the present case are the previously mentioned reactions of [MCl(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] (M = Mo or W) with [Co$_2$(CO)$_8$] which give bis(μ-alkyne) complexes [(η^5-C$_5$H$_5$)(CO)M(μ-CF$_3$C≡CCF$_3$)$_2$Co(CO)$_2$] initially and these react with carbon monoxide to produce metallacyclic species [(η^5-C$_5$H$_5$)(CO)$_2$M{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)}-Co(CO)$_2$].[14]

Metallacyclisation to give (**6**) followed by (**7**) is similarly induced by co-ordination of CNBu^t to the metal centre of (**1**) and (**5**). This can either occur *via* direct attack on the metal (Scheme 2) or *via* initial attack on an alkyne of η^2-vinyl to give an intermediate of structure (**3**). ^{19}F N.m.r. studies of reactions between η^2-vinyls (**5b**) and (**5c**) and 1 mol equiv. of CNBu^t at −50 °C did not detect η^2-vinyl intermediates (**3**), the metallacycles (**6b**) and (**6c**) being the first observed reaction products. Interestingly this observation also applies to the reaction of the bis(alkyne) complex (**1d**) with CNBu^t where attack at an alkyne carbon is more probable. This may indicate that initial attack at the alkyne to give an η^2-vinyl intermediate (**3**) is followed by very rapid transfer to the metal thus promoting metallacyclisation. In this connection we have observed that the bis(alkyne) complex (**1b**) reacts with PMe$_2$Ph to give an η^2-vinyl complex similar to (**3**), but on heating phosphine transfer to the metal results in cyclisation to give the cyclobutadiene complex [Mo(SC$_6$F$_5$)(PMe$_2$Ph){η^4-C$_4$(CF$_3$)$_4$}(η^5-C$_5$H$_5$)], possibly *via* a metallacyclic intermediate related to (**6**).[10] However, we note that (**3b**) does not undergo metallacyclisation to (**6**) at 20 °C; instead metallacyclisation at this temperature only occurs on addition of a second mole of isocyanide when complex (**7a**) is obtained. This reveals that, unlike reactions involving (**1d**) and η^2-vinyls (**5**), metallacyclisation only occurs *after* addition of the second mole of isocyanide. This is further emphasised by the observation that heating (**3b**) in hexane at 65 °C did not give (**6**), the only product isolated being the iminocyclopentadiene (**9a**), which again illustrates that two moles of isocyanide are required before alkyne condensation occurs (see below).

We therefore conclude that two independent mechanisms are involved in the formation of metallacycles (**7**), the first involving initial attack on the alkyne, *i.e.* (**1**) ⟶ (**3**) ⟶ (**7**), which is observed with [Mo(SC$_6$F$_5$)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)]. However reactions of [W(SC$_6$H$_4$Me-4)(CF$_3$C≡CCF$_3$)$_2$(η^5-C$_5$H$_5$)] and η^2-vinyls [W{C(CF$_3$)C(CF$_3$)SR}(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] apparently proceed *via* initial attack at the metal, *i.e.* (**1d**)/(**5**) ⟶ (**6**) ⟶ (**7**). In this respect it is interesting to note that nucleophilic attack on cationic alkyne complexes [Mo(RC≡CR′){P(OMe)$_3$}$_2$(η^5-C$_5$H$_5$)][BF$_4$] (R = Ph, R′ = Ph or CH$_2$Ph; R = Bu^t, R′ = Me) apparently occurs at either the alkyne or the metal depending on the nature of the alkyne and the nucleophile.[18]

Co-ordination of an isocyanide to the metal centre of (**1**) or (**5**) presumably leads initially to a co-ordinatively saturated 18-electron bis(alkyne) complex (**8**) which functions as a precursor to the 16-electron metallacycle (**6**). The formation of a 1,3-diene complex [Mo(NCMe)(η^4-MeCH=CMeCH=CHC$_6$H$_4$PPh$_2$-4)(η^5-C$_5$H$_5$)][BF$_4$] by acetonitrile-induced linking of MeC≡CMe and the alkene moiety in [Mo(η^2-dpps)(MeC≡CMe)(η^5-C$_5$H$_5$)][BF$_4$] (dpps = *o*-diphenylphosphinostyrene) can be explained similarly[19] as can co-ordination-promoted metallacyclisations in rhodium chemistry.[20] It may be significant that in a wide range of studies involving nucleophilic additions to co-ordinatively unsaturated bis(alkyne) complexes of molybdenum and tungsten related to and including (**1**),[4,6,7,8,21] co-ordinatively saturated species such as (**8**) have never been isolated or even detected. This may reflect instability due to steric interactions in a crowded co-ordination sphere. However we also note that the alkynes in (**8**) only function as two-electron donors, whereas in stable co-ordinatively unsaturated bis(alkyne) complexes (**1**) both sets of filled alkyne π orbitals can participate in bonding with the metal, *i.e.* the alkynes are formally three-electron donors. It is therefore conceivable that on conversion to two-electron donation the alkynes become activated and in the case of (**8**) metallacyclisation occurs to give (**6**).[10] In other cases ligand-substitution,[21,22] ligand-migration,[10] and alkyne-oligomerisation[23] reactions have been observed which can also be explained in this way.

During n.m.r. spectral studies of the t-butyl metallacyclic complexes (**6a**) and (**7d**) the formation of another complex, (**10**) was observed as the signals due to (**6a**) and (**7d**) disappeared. The same species was also observed in n.m.r. studies of 1:1 reactions between CNBu^t and (**5b**) or (**5c**). It was subsequently established that this was due to the presence of moisture in the n.m.r. solvent, CDCl$_3$, and consequently a sample of (**10**) was isolated by stirring a solution of (**7d**) in moist CDCl$_3$ at room temperature. Complex (**10**) has the stoicheiometry [W(O)(C$_8$F$_{12}$H)(CNBu^t)(C$_5$H$_5$)] according to elemental analysis and mass spectrometry. The i.r. and n.m.r. data are consistent with the illustrated structure in which one terminal carbon of the metallacycle has been protonated while an isocyanide has inserted into the other tungsten–carbon bond. This is apparently promoted by the co-ordination of an oxygen atom to the metal centre, thus maintaining the oxidation state of the metal (W^{IV}) following loss of the thiolate ligand.



(10)

The ^{1}H n.m.r., in addition to η^5-C$_5$H$_5$ and Bu^t singlets, contains a quartet (J_{HF} = 9.0 Hz) at δ 2.82 due to the single proton on the fluorocarbon ligand. The chemical shift indicates attachment to a co-ordinated alkene in agreement with the proposed structure. The ^{19}F n.m.r. spectrum contains four CF$_3$ resonances and homo- and hetero- (^{19}F–^{1}H) decoupling experiments established the coupling constants J_{ab} = 8.8, J_{bc} = 4.5, J_{cd} = 10.4, and J_{dH} = 10.0 Hz. These data are similar to those of [Ru{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)H}(PPh$_3$)(η^5-C$_5$H$_5$)] where a structurally related *cis*-tetrakis(trifluoromethyl)butadienyl ligand is present.[24]

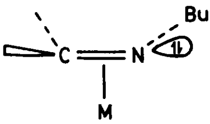
A wide variety of σ-acyl complexes have been obtained from the insertion of CO into a metal–carbon bond[25] including [Mo{C(O)C(CF$_3$)=C(CF$_3$)C(O)SR}(CO)(η^5-C$_5$H$_5$)][26] which is structurally related to (**10**). In view of the fact that CO and CNR are isoelectronic it is not surprising to find numerous examples of analogous iminoacyl–metal derivatives.[27] The presence of a metal-co-ordinated iminoacyl moiety in (**10**) is suggested by the i.r. spectrum where instead of a $\nu_{C\equiv N}$ mode near 2 200 cm^{-1} due to a co-ordinated isocyanide, a band at 1 610 cm^{-1} is observed attributable to a σ-iminoacyl C=N stretching mode.[28]

Previously we have reported that oxo complexes [M(SR)(O)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] are obtained from the air oxidation of carbonyls [M(SR)(CO)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)]

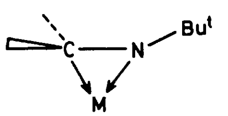
($M = Mo$, $R = CF_3$ or C_6H_5; $M = W$, $R = C_6H_5$).[29] *X*-Ray diffraction studies of $[Mo(SC_6F_5)(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[30] have established that the co-ordination geometry about the metal is approximately octahedral with the C_5H_5 ligand occupying a face and the other three ligands corners of the octahedron. Of some significance is the alkyne orientation since the C≡C axis lies perpendicular to the M–O bond. Since the metal has a d^2 configuration the alkyne adopts this orientation so as to facilitate π back donation from the filled $d\pi$ type metal orbital to a π^* orbital on the alkyne. A similar situation is found in the structure of $[Mo\{C(CF_3){=}C(CF_3)SC_6F_5\}(O)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ obtained by air oxidation of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.[10] We anticipate a comparable bonding situation in (**10**) in which the co-ordinated $(CF_3)C{=}C(CF_3)H$ moiety will be perpendicular to the W–O axis in order to maximise back donation from the metal. This leaves two empty metal π orbitals orientated along the M–O axis with which the oxygen can π bond, thus acting as a four-electron donor and allowing the metal to reach a formal 18-electron configuration.

As described earlier (Scheme 1) the isolation of η^2-vinyl intermediates (**3**) from bis(alkyne) complexes (**1**) originally led us to postulate a cyclisation mechanism involving iminocyclobutene intermediates (**4**). Alkyne(cyclopentadienyl)cobalt complexes $[Co(PhC{\equiv}CR)(PPh_3)(\eta^5\text{-}C_5H_5)]$ (R = Ph, CO_2Me, CN, or H) in reactions with 1 mol equiv. of isocyanides give iminocyclobutene complexes analogous to (**4**),[31] whereas metallacyclic derivatives $[Co\{C(Ph){=}C(R)C(R){=}C(Ph)\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ give iminocyclopentadiene complexes $[Co(\eta^4\text{-}C_4Ph_2R_2CNR')(\eta^5\text{-}C_5H_5)]$ (R = Ph, CO_2Me, or Me; $R' = Bu^t$ or aryl).[5] Consequently the isolation of metallacycles (**7**) presented an opportunity to establish their possible mechanistic role in the formation of iminocyclopentadienes (**2**). Thermolysis of (**7a**) and (**7c**) was therefore investigated in a number of solvents and at different temperatures. In both cases only one product, (**9a**) or (**9b**), was obtained but reactions were found to proceed more cleanly and rapidly and at lower temperatures in polar solvents such as dichloromethane or diethyl ether compared to non-polar sovents such as hexane.

The spectroscopic properties of (**9**) are fairly similar to those of (**2**) but two important differences are apparent. The first is the absence of a C=N stretching mode near 1 700 cm^{-1} in the i.r. spectra and the second the existence of only one isomeric form in solution, whereas complexes (**2**) exhibit *exo–endo* isomerism. This prompted *X*-ray diffraction studies of (**9b**), the results of which have been reported previously in note form.[7] These studies established that as with $[Mo(CF_3)(CNBu^t)\{\eta^4\text{-}C_4(CF_3)_4CNBu^t\}(\eta^5\text{-}C_5H_5)]$ an iminocyclopentadiene ligand has been formed by condensation of two $CF_3C{\equiv}CCF_3$ groups and one $CNBu^t$ molecule. However unlike in (**2**) this is unexpectedly attached to the metal in an η^2 fashion *via* the exocyclic C–N bond, thus accounting for the absence of a C=N stretching mode in the i.r. spectra. Of particular interest is the nature of the metal–imine linkage since the geometry of the co-ordinated ligand is not consistent with conventional π donation from a C=N double bond, *i.e.* as described by the Dewar–Chatt–Duncanson bonding scheme, (**I**). Instead, several features, *viz.* (*i*) the coplanarity of the C_5 ring with the exocyclic nitrogen (± -0.04 Å), (*ii*) the extensive delocalisation of the ring C–C bonds, (*iii*) the planarity of the co-ordination sphere around nitrogen, and (*iv*) the long N–C bond of the imine function, are more consistent with the presence of a zwitterionic cyclopentadienyl ligand as illustrated in (**II**). Thus the metal–imine linkage can be described in terms of donation of a lone pair of electrons from both carbon and nitrogen to the metal and this is complemented by back donation from the metal to the empty *p* orbital on nitrogen. Interestingly, broadly similar conclusions have been reached concerning the bonding of the imine ligand in $[W(\eta^2\text{-}Me_2CNBu^t)(Me)(NBu^t)\{N(Bu^t)CMe{=}CMe_2\}]$ where comparable structural features have been found.[32]



(**I**)



(**II**)

The spectroscopic properties of (**9**) can be explained in terms of the solid-state structure. Thus a single $\nu_{C\equiv N}$ mode is observed in the i.r. spectra near 2 150 cm^{-1} due to the co-ordinated isocyanide. In addition to one $\eta^5\text{-}C_5H_5$ and two $CNBu^t$ singlets, the ^1H n.m.r. spectrum of (**9b**) exhibits an isopropyl CH multiplet and significantly two doublets reflecting the diastereotopic nature of the two methyl groups resulting from the asymmetry of the metal centre. The ^{19}F n.m.r. spectra exhibit two septets (quartet of quartets) and two quartets due to the 1,4- and 2,3-CF_3 substituents respectively although in the isopropyl derivative the two quartets are almost coincident.

These spectroscopic data indicate that only one isomeric form of the complex exists in solution, presumably that found in the solid state for (**9b**) in which the imine ligand adopts an orientation with the C–N bond approximately parallel to the W–S axis, the torsion angle S–W–CN being $-23.45°$. This contrasts with the orientation of alkyne ligands in complexes with similar co-ordination spheres, *e.g.* $[Mo(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$[30] and $[Mo(SC_6H_4NO_2\text{-}4)\{P(OMe)_3\}(MeC{\equiv}CMe)(\eta^5\text{-}C_5H_5)]$[21c] where the four-electron donor alkyne ligands lie approximately perpendicular to the M–S bond and parallel to the M–L axis where L is a π-acceptor ligand. This difference presumably reflects the fact that the metal–alkyne bonding, unlike the metal–imine interaction, is based upon Dewar–Chatt–Duncanson type interactions.

A feature of alkyne complexes of this type is the ability of the alkynes to undergo propeller rotation about the metal–alkyne bond and with asymmetric alkynes, *e.g.* low-temperature n.m.r. studies of PhC≡CMe have established the existence of two alkyne orientations which presumably differ by *ca.* 180°.[3a] In principle two orientations should also be possible for the imine ligand in (**9**), that found in the solid state and one in which the imine has rotated by *ca.* 180°. As mentioned earlier, η^4-imine complexes (**2**) exhibit *exo–endo* isomerism in which the η^4-imine ligand adopts two orientations which also differ by *ca.* 180°. However, variable-temperature ^{19}F n.m.r. spectra recorded over the temperature range 20 to −80 °C did not reveal extra peaks which could be attributed to a second isomer. Molecular graphics studies established that steric constraints do not preclude the existence of a second isomer and consequently we assume that electronic factors are responsible. Interestingly the low-temperature ^{19}F n.m.r. spectra were not totally invariant since one of the CF_3 quartets was observed to broaden and at −80 °C disappear completely into the baseline. We[19] and others[33] have observed this phenomenon in a variety of complexes containing fluorocarbon chains resulting from condensation of two or more hexafluorobut-2-yne ligands and attribute it to restricted rotation of the CF_3 group.

The structure of (**9**) in which the iminocyclopentadiene ligand co-ordinates in an η^2 fashion through the C–N bond to the metal contrasts with that of (**2**) where co-ordination occurs *via* four of the carbon atoms of the C_5 ring. This could reflect a thermodynamic effect, *i.e.* in (**9**), containing a sulphur ligand capable of π donation to the metal, the η^2 form is more stable whereas in (**2**) where π donation from ligand X is impossible ($X = CF_3$) or less likely (X = Cl) the η^4-bonded form is preferred. Alternatively, the different structures may reflect kinetic factors since complexes (**2**) were obtained at room temperature whereas formation of (**9**) from (**7**) required elevated temperatures. This implies that the η^4-bonded form is produced initially and this subsequently isomerises to the η^2-bonded isomer.

Whatever the rationale for the isolation of the two isomeric forms in these and earlier studies it seems probable that both are formed *via* metallacyclic intermediates (**7**) but in the case of (**2**) these are too unstable to be detected. The conversion of (**7**) into (**9**) or (**2**) presumably involves initial insertion of one of the isocyanides into a metal–carbon bond of the metallacycle to give an intermediate iminometallacyclohexadiene (**11**), Scheme 2. This mechanism has been proposed previously[4b] and is supported by the fact that isocyanide insertion into the M–C bond of a metallacycle is involved in the transformation of (**7**) into (**10**). Reductive cyclisation in (**11**) subsequently produces the iminocyclopentadiene complex in η^2- or η^4-bonded form, (**9**) or (**2**).

Conclusions

Initial studies showed that reactions of t-butyl isocyanide with bis(alkyne) complexes $[MX(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ give η^4-iminocyclopentadiene complexes (**2**) *via* 1:1 adducts $[MX(CNBu^t)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.[4] Later work established an η^2-vinyl structure (**3**) for the 1:1 complexes[3b] illustrating that initial attack by the isocyanide is directed at an alkyne carbon, thus implicating iminocyclobutenes in the cyclisation mechanism (Scheme 1). However the present work illustrates that the crucial carbon–carbon bond-forming process between the alkynes and an isocyanide occurs at a later stage *via* intermediate metallacyclopentadiene complexes (**7**). Thus the overall reaction involves condensation of the two alkynes *before* the isocyanide becomes involved in the cyclisation process (Scheme 2). It also appears that metallacycles (**7**) are formed *via* two distinct mechanistic pathways. The first involves initial attack by the isocyanide at an alkyne carbon to give η^2-vinyls (**3**) and cyclometallation only takes place after co-ordination of the second molecule of isocyanide has occurred. The alternative route involves initial attack at the metal by isocyanide to give 16-electron metallacycles (**6**), *i.e.* in this case only one isocyanide is required to promote cyclometallation.

Finally we note that cyclisation of two alkynes and one isocyanide gives an iminocyclopentadiene ligand which can co-ordinate either *via* the exocyclic C–N bond in an η^2 manner to the metal or alternatively as an η^4 ligand *via* the cyclopentadiene ring.

Experimental

N.m.r. spectra were recorded in $CDCl_3$ solution (unless stated otherwise) on a Bruker WP 200 SY spectrometer at 200.13 (^1H) and 188.31 MHz (^{19}F); chemical shifts are referred to $SiMe_4$ and CCl_3F ($\delta = 0$). I.r. spectra were recorded as solutions on a Perkin-Elmer 580 and mass spectra on an updated Vacuum Generator AEI MS9 instrument at 70 eV. Reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried over powdered calcium hydride (Et_2O, hexane) or P_2O_5 (dichloromethane) and distilled under nitrogen just before use. Complexes $[M(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$[6] and t-butyl isocyanide[34] were synthesised according to literature methods.

Reaction of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1b**) *with* $CNBu^t$ (1:1 *molar ratio*).—t-Butyl isocyanide (6 mg) in diethyl ether (2 cm^3) was added dropwise to a stirred solution of the complex (50 mg) in diethyl ether (20 cm^3) held at −20 °C; the colour turned pale yellow-brown. Hexane (15 cm^3) was added, the solution concentrated and on cooling to −15 °C a yellow–buff microcrystalline solid was obtained. This was crystallised a second time from diethyl ether–hexane to give $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**); yield 32 mg (57%) (Found: C, 37.6; H, 1.9; N, 1.8. Calc. for $C_{24}H_{14}F_{17}MoNS$: C, 37.55; H, 1.80; N, 1.80%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 210s, $\nu_{C\equiv C}$ 1 825wm cm^{-1}.

Thermolysis of $[Mo(SC_6F_5)\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**3b**).—The complex (25 mg) in hexane (20 cm^3) was transferred to a thick glass tube and the mixture deoxygenated with four freeze–thaw cycles. The tube was sealed and heated at 70 °C for 2.5 h when a brown solution was obtained. On cooling to room temperature this was filtered and concentrated to *ca.* 5 cm^3. On cooling to −15 °C dark green crystals were obtained. These were recrystallised a second time from diethyl ether–hexane to give $[Mo(SC_6F_5)(CNBu^t)\{\eta^2\text{-}C_4(CF_3)_4CNBu^t\}(\eta^5\text{-}C_5H_5)]$ (**9a**).

Reaction of $[W\{C(CF_3)C(CF_3)SBu^t\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5c**) *with* $CNBu^t$ (1:1 *molar ratio*).—t-Butyl isocyanide (9 mg) in diethyl ether (2 cm^3) was added dropwise to a vigorously stirred solution of the complex (70 mg) in diethyl ether (20 cm^3) held at −50 °C; the yellow-orange solution turned deep green. Ice-cold hexane (20 cm^3) was added slowly and the solution concentrated *in vacuo* when a green microcrystalline solid was obtained contaminated with small quantities of orange-yellow crystals of (**7d**). Recrystallisation twice from diethyl ether–hexane at −10 °C gave the dark green complex $[W\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}(SBu^t)(CNBu^t)(\eta^5\text{-}C_5H_5)]$ (**6a**); yield 30 mg (38%) (Found: C, 35.3; H, 3.0; N, 1.9. Calc. for $C_{22}H_{23}F_{12}NSW$: C, 35.4; H, 3.1; N, 1.9%). I.r. (Nujol): $\nu_{C\equiv N}$ 2 161s, $\nu_{C=C}$ 1 522w cm^{-1}.

Reaction of $[Mo(SC_6F_5)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1b**) *with* $CNBu^t$ (1:3 *molar ratio*).—t-Butyl isocyanide (55 mg) in diethyl ether (2 cm^3) was added slowly to a stirred solution of the complex (150 mg) in diethyl ether (15 cm^3) when the purple solution turned orange. The solution was concentrated *in vacuo* to *ca.* 80 cm^3, hexane (10 cm^3) added, and on cooling to −15 °C orange crystals were obtained. A second crystallisation from dichloromethane–hexane gave $[Mo\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}(SC_6F_5)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7a**); yield 120 mg (65%) (Found: C, 40.6; H, 2.6; N, 3.2. Calc. for $C_{29}H_{23}F_{17}MoN_2S$: C, 40.9; H, 2.70; N, 3.30%). I.r. (CH_2Cl_2): $\nu_{C\equiv N}$ 2 186s, 2 166s cm^{-1}.

Reaction of $[W(SC_6H_4Me\text{-}4)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1d**) *with* $CNBu^t$ (1:3 *molar ratio*).—t-Butyl isocyanide (36 mg) in diethyl ether (2 cm^3) was added to a stirred solution of the complex (100 mg) in diethyl ether (15 cm^3) giving initially a dark green solution which turned orange. Hexane (10 cm^3) was added and on concentration *in vacuo* and cooling to −15 °C orange crystals were obtained. Recrystallisation from dichloromethane–hexane gave $[W\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}(SC_6H_4Me\text{-}4)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7e**); yield 85 mg (69%) (Found: C, 41.4; H, 3.5; N, 3.0. Calc. for $C_{30}H_{30}F_{12}N_2SW$: C, 41.75; H, 3.50; N, 3.25%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 182s, 2 154s cm^{-1}.

Reaction of $[W\{C(CF_3)C(CF_3)SMe\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5a**) *with* $CNBu^t$ (1:3 *molar ratio*).—t-Butyl isocyanide (16 mg) in diethyl ether (2 cm^3) was added slowly to a stirred solution of the complex (40 mg) in diethyl ether (15 cm^3); the orange-red solution rapidly turned dark green and then orange. Hexane (10 cm^3) was added, and the solution concentrated *in vacuo* and cooled to −15 °C to give orange crystals. A second recrystallisation from dichloromethane–hexane gave $[W\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)\}(SMe)(CNBu^t)_2(\eta^5\text{-}$

$C_5H_5)]$ (**7b**); yield 36 mg (71%) (Found: C, 36.4; H, 2.8. Calc. for $C_{24}H_{26}F_{12}N_2S$: C, 36.65; H, 2.95%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 158s, 2 130s cm^{-1}.

Reaction of $[W\{C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5b**) *with* $CNBu^t$ (1:3 *molar ratio*).—t-Butyl isocyanide (58 mg) in hexane (2 cm^3) was added slowly to a stirred solution of the complex (150 mg) in diethyl ether (20 cm^3); orange crystals began to form and hexane (10 cm^3) was added slowly and the solution cooled to −15 °C. The orange crystals obtained were recrystallised from dichloromethane–hexane to give $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SPr^i)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7c**); yield 128 mg (60%) (Found: C, 38.3; H, 3.7; N, 3.4; S, 4.0. Calc. for $C_{26}H_{30}F_{12}N_2SW$: C, 38.5; H, 3.70; N, 3.45; S, 3.95%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 160s, 2 132s cm^{-1}.

Reaction of $[W\{C(CF_3)C(CF_3)SBu^t\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ (**5c**) *with* $CNBu^t$ (1:3 *molar ratio*).—t-Butyl isocyanide (38 mg) in diethyl ether (2 cm^3) was added to a stirred solution of the complex (100 mg) in diethyl ether (15 cm^3), giving a green solution which slowly turned orange. Hexane (10 cm^3) was added and on cooling to −15 °C orange crystals were obtained. Recrystallisation from dichloromethane–hexane gave $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SBu^t)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7d**); yield 69 mg (55%) (Found: C, 39.3; H, 3.7; N, 3.6. Calc. for $C_{27}H_{32}F_{12}N_2SW$: C, 39.15; H, 3.85; N, 3.40%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 160s, 2 132s cm^{-1}.

Hydrolysis of $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SBu^t)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7d**).—The complex (30 mg) was dissolved in $CDCl_3$ (5 cm^3) and one drop of water added. The mixture was then stirred for 3 h after which time volatiles were removed *in vacuo* and the residue extracted with diethyl ether (10 cm^3). Hexane (10 cm^3) was added, the solution concentrated *in vacuo* and on cooling to −15 °C impure yellow-orange crystals were obtained. A second crystallisation from diethyl ether–hexane gave $[W\{C(NBu^t)C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)H\}(O)(\eta^5\text{-}C_5H_5)]$ (**10**); yield 14 mg (57%) (Found: C, 32.6; H, 2.4; N, 2.2. Calc. for $C_{18}H_{15}F_{12}NOW$: C, 32.1; H, 2.2; N, 2.1%). I.r. ($CHCl_3$): $\nu_{C=C}$ 1 647w, $\nu_{C=N}$ 1 610wm cm^{-1}. Mass spectrum: m/z 671 (M^+).

Thermal Isomerisation of $[Mo\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SC_6F_5)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7a**).—A solution of the complex (80 mg) in dichloromethane (30 cm^3) was transferred to a thick glass tube fitted with a Westef stopcock and degassed using the freeze–thaw method (four cycles). It was then heated at 90 °C for 3 h and the colour changed from orange to dark green. Volatiles were removed *in vacuo* and the residue extracted with diethyl ether (20 cm^3) and filtered. Hexane (10 cm^3) was added and the solution concentrated before cooling to −15 °C giving dark green crystals. Recrystallisation from diethyl ether–hexane gave $[Mo(SC_6F_5)(CNBu^t)\{\eta^2\text{-}C_4(CF_3)_4CNBu^t\}(\eta^5\text{-}C_5H_5)]$ (**9a**); yield 32 mg (40%) (Found: C, 41.7; H, 3.0; N, 3.2. Calc. for $C_{29}H_{23}F_{17}MoN_2S$: C, 40.9; H, 2.70; N, 3.30%). I.r. ($CHCl_3$): $\nu_{C\equiv N}$ 2 162s cm^{-1}.

Thermal Isomerisation of $[W\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}(SPr^i)(CNBu^t)_2(\eta^5\text{-}C_5H_5)]$ (**7c**).—A solution of the complex (106 mg) in dichloromethane (30 cm^3) was transferred to a thick glass tube fitted with a Westef stopcock and degassed using the freeze–thaw method. On heating to 50 °C for 72 h the orange solution turned dark green. Volatiles were removed *in vacuo* and the residue extracted with warm (50 °C) hexane (30 cm^3). The solution was filtered, concentrated to *ca.* 15 cm^3 and on cooling to −15 °C dark green crystals were obtained. A second crystallisation from diethyl ether–hexane gave $[W(SPr^i)(CNBu^t)\{\eta^2\text{-}C_4(CF_3)_4CNBu^t\}(\eta^5\text{-}C_5H_5)]$ (**9b**); yield 23 mg (22%) (Found: C, 38.2; H, 3.4; N, 3.4. Calc. for $C_{26}H_{30}F_{12}N_2SW$: C, 38.35; H, 3.70; N, 3.45%). I.r. ($CHCl_3$) $\nu_{C\equiv N}$ 2 140s cm^{-1}.

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References

1 W. Hübel, 'Organic Synthesis *via* Metal Carbonyls,' eds. I. Wender and P. Pino, Wiley-Interscience, New York, 1968, vol. 1, ch. 3; F. L. Bowden and A. B. P. Lever, *Organomet. Chem. Rev. A*, 1968, **3**, 229.
2 L. S. Liebeskind and C. F. Jewell, jun., *J. Organomet. Chem.*, 1985, **285**, 305; E. A. Kelley, G. A. Wright, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 178; P. A. Corrigan, R. S. Dickson, S. H. Johnson, G. N. Pain, and M. Yeoh, *Aust. J. Chem.*, 1982, **35**, 2203; N. C. Schore, B. E. La Belle, M. J. Knudsen, H. Hope, and X-J. Xu, *J. Organomet. Chem.*, 1984, **272**, 45; R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A.*, 1970, 2981.
3 (*a*) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1976, 738; (*b*) J. L. Davidson, G. Vasapollo, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1982, 1025.
4 (*a*) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1977, 287; (*b*) J. L. Davidson, M. Green, J. Z. Nyathi, F. G. A. Stone, and A. J. Welch, *ibid.*, p. 2246.
5 (*a*) Y. Wakatsuki, S. Maya, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1986, 1201; (*b*) H. Yamazaki and Y. Wakatsuki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1239.
6 J. L. Davidson, L. Carlton, J. C. Miller, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1984, 11; L. Carlton and J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1987, 895.
7 J. L. Davidson, W. F. Wilson, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 461.
8 J. L. Davidson, W. F. Wilson, Lj. Manojlović-Muir, and K. W. Muir, *J. Organomet. Chem.*, 1983, **254**, C6.
9 R. Fields, *Ann. Rep. N.M.R. Spectrosc.*, 1977, **7**, 1.
10 J. L. Davidson, unpublished work.
11 P. Legzdins, S. J. Rettig, L. Sanchez, B. E. Bursten, and M. G. Gatler, *J. Am. Chem. Soc.*, 1985, **107**, 1411.
12 M. T. Ashby and J. H. Enemark, *J. Am. Chem. Soc.*, 1986, **108**, 730.
13 W. A. W. A. Bakar, J. L. Davidson, W. E. Lindsell, K. J. McCullough, and K. W. Muir, *J. Organomet. Chem.*, 1987, **322**, C1.
14 J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1983, 1667.
15 J. L. Davidson, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1980, 749.
16 (*a*) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Am. Chem. Soc.*, 1965, **38**, 3; (*b*) R. P. Dodge and V. Shomaker, *Acta Crystallogr.*, 1965, **18**, 614.
17 Y. Wakutsuki, O. Nomura, K. Kitaura, K. Morokuma, and H. Yamazaki, *J. Am. Chem. Soc.*, 1983, **105**, 1907.
18 S. R. Allen, R. G. Beevor, M. Green, N. C. Norman, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1985, 435.
19 S. R. Allen, M. Green, G. Moran, A. G. Orpen, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1984, 441.
20 M. E. Howden, R. D. W. Kemmitt, and M. D. Schilling, *J. Chem. Soc., Dalton Trans.*, 1983, 2459.
21 (*a*) S. R. Allen, P. K. Buker, S. G. Barnes, M. Green, L. Trollope, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1981, 873; (*b*) S. R. Allen, M. Green, N. C. Norman, K. E. Paddick, and A. G. Orpen, *ibid.*, 1983, 1625; (*c*) S. R. Allen, T. H. Glauert, M. Green, K. A. Mead, N. C. Norman, and A. G. Orpen, *ibid.*, 1984, 1747.
22 J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 2423.
23 L. Carlton, J. L. Davidson, P. Ewing, Lj. Manojlović-Muir, and K. W. Muir, *J. Chem. Soc., Chem. Commun.*, 1985, 474.
24 T. Blackmore, M. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1974, 106.
25 J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980.

26 J. E. Guerchais, F. Le Floch-Perennou, F. Y. Petillon, A. N. Keith, Lj. Manojlović-Muir, K. W. Muir, and D. W. A. Sharp, *J. Chem. Soc., Chem. Commun.*, 1979, 410.

27 J. J. Alexander, in 'The Chemistry of the Metal–Carbon Bond,' eds. F. R. Hartley and S. Patai, J. Wiley and Sons, New York, 1985, vol. 2, ch. 5.

28 R. D. Adams and D. F. Chodosh, *J. Am. Chem. Soc.*, 1977, **99**, 6544.

29 P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1976, 241.

30 J. A. K. Howard, R. D. Stansfield, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 246.

31 Y. Wakatsuki, S. Miya, S. Ikuta, and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1985, 35; H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1975, **97**, 3546.

32 K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 2088.

33 R. S. Dickson, personal communication; J. T. Mague, *Inorg. Chem.*, 1970, **9**, 1610.

34 W. P. Weber and G. W. Gokel, *Tetrahedron Lett.*, 1972, 1637.

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