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Synthetic, spectroscopic and structural studies of metallacyclopentadiene complexes of tungsten; the crystal structure of $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(4\text{-}MeC_6H_4NC)_2(\eta^5\text{-}C_5H_5)]$

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Abstract

Reactions of the η^2-vinyl complex $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ with isocyanides RNC give metallacyclopentadiene derivatives $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(CNR)_2(\eta^5\text{-}C_5H_5)]$ (R = Me, Ph or 4-MeC_6H_4) via coordinatively unsaturated intermediates $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(CNR)(\eta^5\text{-}C_5H_5)]$ isolated and characterised in the case R = 4-MeC_6H_4. The crystal structure of the d^2 complex $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)\text{-}4\text{-}MeC_6H_4NC)_2(\eta^5\text{-}C_5H_5)]$ has been determined by X-ray methods. The $WC_4(CF_3)_4$ ring system is approximately planar, with single W–C bonds, mean length 2.210(4) Å, and localised C=C double bonds.

Introduction

A recurring feature of transition metal-alkyne chemistry is the formation of metallacyclopentadiene complexes resulting from oxidative cyclisation of two alkynes with the metal [1]. In some cases the metallacycle is kinetically stable, whereas in others it functions as an intermediate in the formation of cyclobutadiene, cyclopentadienone, benzene and other organic ligands [2]. Moreover metallacyclopentadienes are thought to be key intermediates in metal-catalysed trimerisation of alkynes to give free benzenes [3]. Recently we reported that the isocyanide promoted cyclisation of alkynes in bis-alkyne $[W(4\text{-}MeC_6H_4S)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1**) and η^2-vinyl complexes $[M(\eta^3\text{-}C(CF_3)C(CF_3)SR)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (**2a,2b,2c**)

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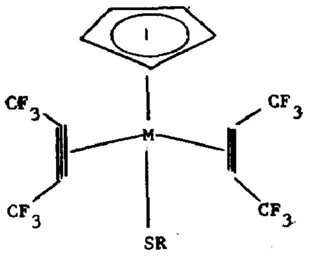
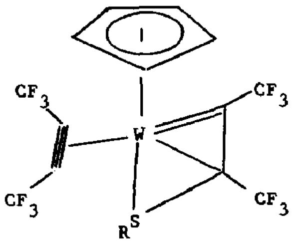
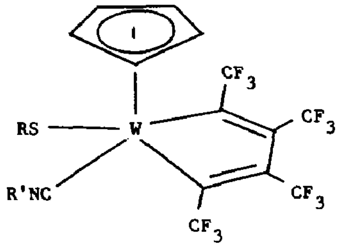


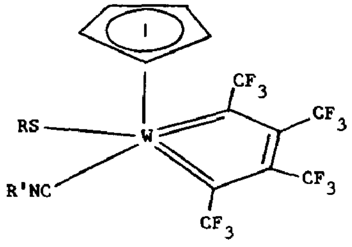
(1 : M = W , R = 4-MeC$_6$H$_4$)



(**2a** : R = Me ;
2b : R = Pr^i ;
2c : R = Bu^t)



(3i)

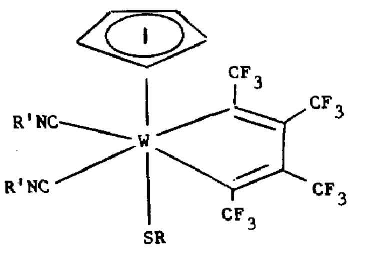


(3ii)

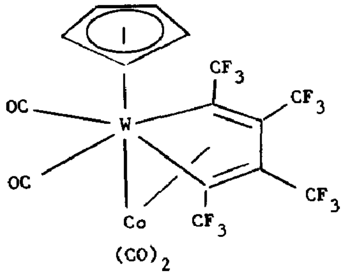
to give iminocyclopentadiene derivatives, proceeds via 16- and 18-electron complexes, which were assigned metallacyclic structures **3i** and **4** (R′ = Bu^t) on the basis of spectroscopic data [4]. However, isolation of [RuBr(η^2-C$_4$Ph$_2$H$_2$)(η^5-C$_5$H$_5$)] from the reaction of [RuBr(COD)(η^5-C$_5$H$_5$)] (COD = 1,5 cyclooctadiene) with phenylacetylene, and its structural characterisation, provided the first known example of a metallacyclopentatriene mode of bonding [5]. This raises the possibility that the 16-electron complex could also have a metallacyclopentatriene structure (**3ii**) which would confer an 18-electron configuration on the metal. Unfortunately all attempts to grow single crystals of this complex (R = R′ = Bu^t) for X-ray diffraction studies were unsuccessful, and we therefore turned our attention to derivatives containing other isocyanides. The results of these studies are now reported.

Results and discussion

Slow addition of diethyl ether solution of isocyanide RNC (R = Me, Ph or 4-MeC$_6$H$_4$) to [W(η^3-C(CF$_3$)C(CF$_3$)SPr^i)(CF$_3$C≡CCF$_3$)(η^5-C$_5$H$_5$)] (**2b**) in diethyl ether at −10 °C results in the formation of a dark green solution which subsequently turns orange. Work up of these solutions afforded orange crystalline complexes (**4a,4b,4c**) which exhibit similar spectroscopic properties to the t-butyl isocyanide derivatives (**4**) reported previously.



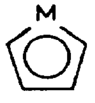
(**4a**: R = Pr^i, R' = Me ;
4b: R = Pr^i, R' = Ph
4c: R = Pr^i, R' = 4-MeC_6H_4)



(**8**)

Until recently metallacyclopentadiene MC_4R_4 complexes were believed always to contain localised C=C bonds, as indicated in structure **5**. The only significant excep-

(**5**)



(**6**)

(**7**)

tions to this rule were found in binuclear complexes in which a second metal η^5-bonded to the MC_4R_4 ring could accept electrons from the π_2 orbital and populate the $\pi_3^\star$ orbital of the butadiene-like fragment, thereby giving a system more aptly described by **6** [6]. However, the observation that the metallacyclopentatriene system **7** occurs in d^4 ruthenium and, also, in a d^2 tantalum species [5,7] indicates that the nature of the bonding in MC_4R_4 rings can depend subtly upon the electronic state of the metal, and this prompted us to determine by X-ray analysis the structure of the d^2 complex $[W\{C(CF_3)C(CF_3)C(CF_3)C(CF_3)\}(SPr^i)(4\text{-}MeC_6H_4NC)_2(\eta^5\text{-}C_5H_5)]$ (**4c**) in order to probe the bonding in the $WC_4(CF_3)_4$ ring. We also considered that a structural comparison of **4c** and $[W(\eta^5\text{-}C_5H_5)\{C(CF_3)C(CF_3)C(CF_3)C(CF_3)\}(CO)_2Co(CO)_2]$ (**8**) [8] would be of interest.

Crystals of **4c** are built up of well-separated molecules (Fig. 1) which display approximate mirror symmetry; the non-crystallographic symmetry plane passes through the midpoint of the C(11)–C(13) bond and contains the atoms W and S. The coordination of the 18-electron tungsten(IV) ion is best described as octahedral, with the centroid of the η^5-C_5H_5 ring occupying a single coordination vertex *trans* to the thiolato sulphur atom. An equatorial plane around the metal is formed by the donor carbon atoms of mutually *cis*-RNC ligands (R = 4-MeC_6H_4) and of the chelating $C_4(CF_3)_4{}^{2-}$ unit. The metal atom is displaced from the equatorial plane towards the η^5-C_5H_5 ring centroid, so that the S–W–C angles are on average some 15° below 90° (Table 1). Both **4c** and **8** contain similar $(\eta^5\text{-}C_5H_5)WC_4$ piano-stool units with an additional donor atom (S or Co) *trans* to the η^5-C_5H_5 ring. In **4c**, however, the sulphur atom does not interact with the equatorial ligands (the shortest S...equatorial contact is that of 2.774(6) Å to C(18)) whereas in **8** the Co atom is η^5-bonded to the WC_4 ring.

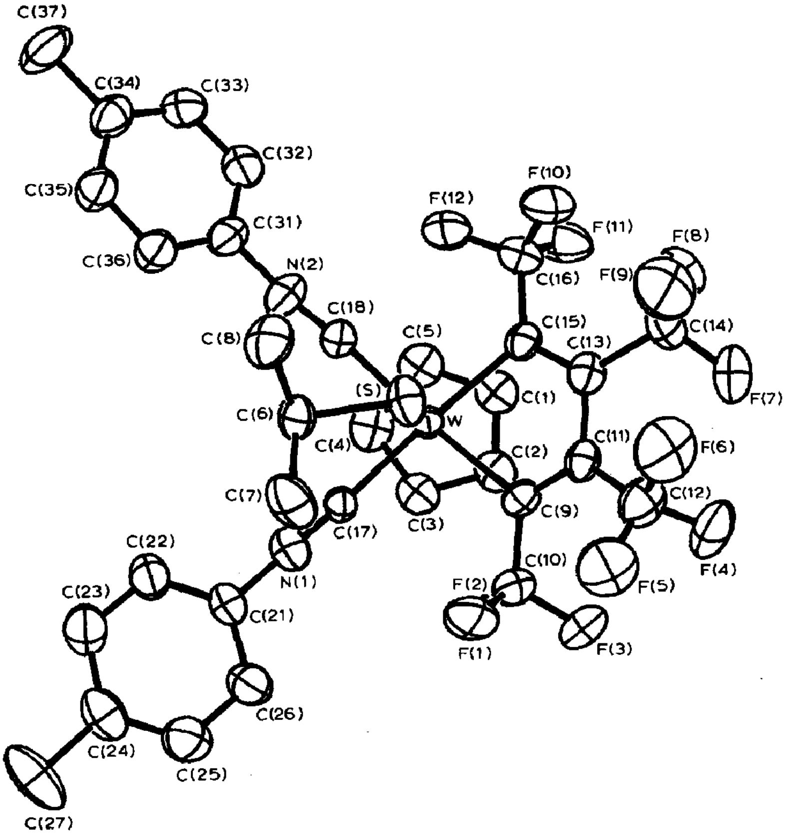


Fig. 1. A view of a molecule of $[\overline{W\{C(CF_3)C(CF_3)C(CF_3)C}(CF_3)\}(SPr^i)(4\text{-}MeC_6H_4NC)(\eta^5\text{-}C_5H_5)]$ showing the atom numbering. Hydrogen atoms are omitted and 50% probability ellipsoids are displayed.

The W–C(η^5-C_5H_5) bond lengths in **4c** (2.255(7)–2.360(6) Å) are comparable with those in **8** (2.285(14)–2.352(14) Å). The W–SPr^i (2.561(2) Å) and W–CNR (2.081(6) and 2.090(6) Å) distances are longer than corresponding values for $[WSPr^i(CNBu^t)\{\eta^2\text{-}C_4(CF_3)_4CNBu^t\}(\eta^5\text{-}C_5H_5)]$ (W–S 2.374(3) Å, W–CNR 2.017(9) Å) [9]. Distances and angles within the ligands of **4c** appear unexceptionable [10].

The dimensions of the $WC_4(CF_3)_4$ ring are consistent with structure **5**: the mean W–C_α distance (2.210(4) Å) is comparable with 2.194(7) Å, the length of the W–Csp^2 single bond in $[(\eta^5\text{-}C_5H_5)W(CO)_2\{C(CO_2Me)C(CO_2Me)C(O)SMe\}]$ [11], the C–C bond lengths display marked alternation (C_α–C_β 1.354(8) and 1.359(8) Å, C_β–C_β 1.472(8) Å) and the WC_4 unit is approximately planar, with internal torsion angles 12° or less (Table 1). The corresponding unit in **8** is better described by (6): the mean W–C distance (2.140(17) Å) is slightly shorter than that in **4c**, and the C–C bonds are of nearly equal length (C_α–C_β 1.432(12) and 1.437(12) Å; C_β–C_β 1.424(12) Å). The ring is again approximately planar; indeed, corresponding torsion angles in **8** agree with those in **4c** to within 2°. Evidently the delocalisation in **8** is to be ascribed to the perturbing effect of the cobalt atom rather than to any inherent tendency for MC_4R_4 ring systems to adopt structures **6** or **7** when M is a d^2 metal.

Previous observations [4] suggest that the green colour obtained on first addition of isocyanide to **2b** is due to the formation of a 1/1 adduct **3**. However attempts to

Table 1

Distances (Å) and angles (°) in $[\overline{\mathrm{W\{C(CF_3)C(CF_3)C(CF_3)C}}\mathrm{(CF_3)\}(SPr^i)(CNC_6H_4\text{-}Me\text{-}}p)_2(\eta^5\text{-}\mathrm{C_5H_5})]$

(a) Bond lengths			
W–S	2.561(2)	W–C(1)	2.353(7)
W–C(2)	2.360(6)	W–C(3)	2.304(6)
W–C(4)	2.255(7)	W–C(5)	2.290(6)
W–C(9)	2.207(6)	W–C(15)	2.213(6)
W–C(17)	2.081(6)	W–C(18)	2.090(6)
S–C(6)	1.839(6)	F(1)–C(10)	1.334(8)
F(2)–C(10)	1.344(8)	F(3)–C(10)	1.348(8)
F(4)–C(12)	1.326(9)	F(5)–C(12)	1.331(8)
F(6)–C(12)	1.350(9)	F(7)–C(14)	1.351(9)
F(8)–C(14)	1.329(9)	F(9)–C(14)	1.322(9)
F(10)–C(16)	1.325(8)	F(11)–C(16)	1.356(8)
F(12)–C(16)	1.350(8)	N(1)–C(17)	1.147(7)
N(1)–C(21)	1.404(8)	N(2)–C(18)	1.150(8)
N(2)–C(31)	1.394(8)	C(1)–C(2)	1.401(9)
C(1)–C(5)	1.397(9)	C(2)–C(3)	1.402(9)
C(3)–C(4)	1.417(9)	C(4)–C(5)	1.398(9)
C(6)–C(7)	1.521(9)	C(6)–C(8)	1.506(9)
C(9)–C(10)	1.503(8)	C(9)–C(11)	1.354(8)
C(11)–C(12)	1.516(9)	C(11)–C(13)	1.472(8)
C(13)–C(14)	1.530(8)	C(13)–C(15)	1.359(8)
C(15)–C(16)	1.504(8)	C(21)–C(22)	1.359(9)
C(21)–C(26)	1.374(9)	C(22)–C(23)	1.380(10)
C(23)–C(24)	1.372(10)	C(24)–C(25)	1.383(10)
C(24)–C(27)	1.499(11)	C(25)–C(26)	1.383(9)
C(31)–C(32)	1.376(9)	C(31)–C(36)	1.361(9)
C(32)–C(33)	1.391(10)	C(33)–C(34)	1.369(10)
C(34)–C(35)	1.396(9)	C(34)–C(37)	1.484(10)
C(35)–C(36)	1.393(9)		
(b) Bond angles			
S–W–C(CP) [a]	176.1	S–W–C(9)	76.6(2)
S–W–C(15)	73.4(2)	S–W–C(17)	76.7(2)
S–W–C(18)	72.4(2)	C(CP)–W–C(9)	106.3
C(CP)–W–C(15)	104.7	C(CP)–W–C(17)	105.7
C(CP)–W–C(18)	104.5	C(9)–W–C(15)	74.4(2)
C(9)–W–C(17)	90.3(2)	C(9)–W–C(18)	148.8(2)
C(15)–W–C(17)	148.7(2)	C(15)–W–C(18)	93.2(2)
C(17)–W–C(18)	86.0(3)	W–S–C(6)	115.2(2)
C(17)–N(1)–C(21)	175.5(6)	C(18)–N(2)–C(31)	172.3(6)
S–C(6)–C(7)	110.3(5)	S–C(6)–C(8)	108.2(5)
C(7)–C(6)–C(8)	111.3(6)	W–C(9)–C(10)	122.0(4)
W–C(9)–C(11)	116.1(4)	C(10)–C(9)–C(11)	121.4(5)
F(1)–C(10)–F(2)	104.3(5)	F(1)–C(10)–F(3)	107.0(5)
F(1)–C(10)–C(9)	113.9(6)	F(2)–C(10)–F(3)	103.2(5)
F(2)–C(10)–C(9)	112.7(5)	F(3)–C(10)–C(9)	114.8(6)
C(9)–C(11)–C(12)	124.0(6)	C(9)–C(11)–C(13)	116.2(5)
C(12)–C(11)–C(13)	119.2(5)	F(4)–C(12)–F(5)	106.1(6)
F(4)–C(12)–F(6)	106.7(6)	F(4)–C(12)–C(11)	115.5(6)
F(5)–C(12)–F(6)	104.0(6)	F(5)–C(12)–C(11)	112.7(6)
F(6)–C(12)–C(11)	111.0(6)	C(11)–C(13)–C(14)	121.3(5)
C(11)–C(13)–C(15)	116.1(5)	C(14)–C(13)–C(15)	122.3(6)
F(7)–C(14)–F(8)	103.9(6)	F(7)–C(14)–F(9)	107.0(6)
F(7)–C(14)–C(13)	110.6(6)	F(8)–C(14)–F(9)	108.3(6)
F(8)–C(14)–C(13)	114.3(6)	F(9)–C(14)–C(13)	112.1(6)
W–C(15)–C(13)	116.2(4)	W–C(15)–C(16)	122.3(4)

Table 1 (continued)

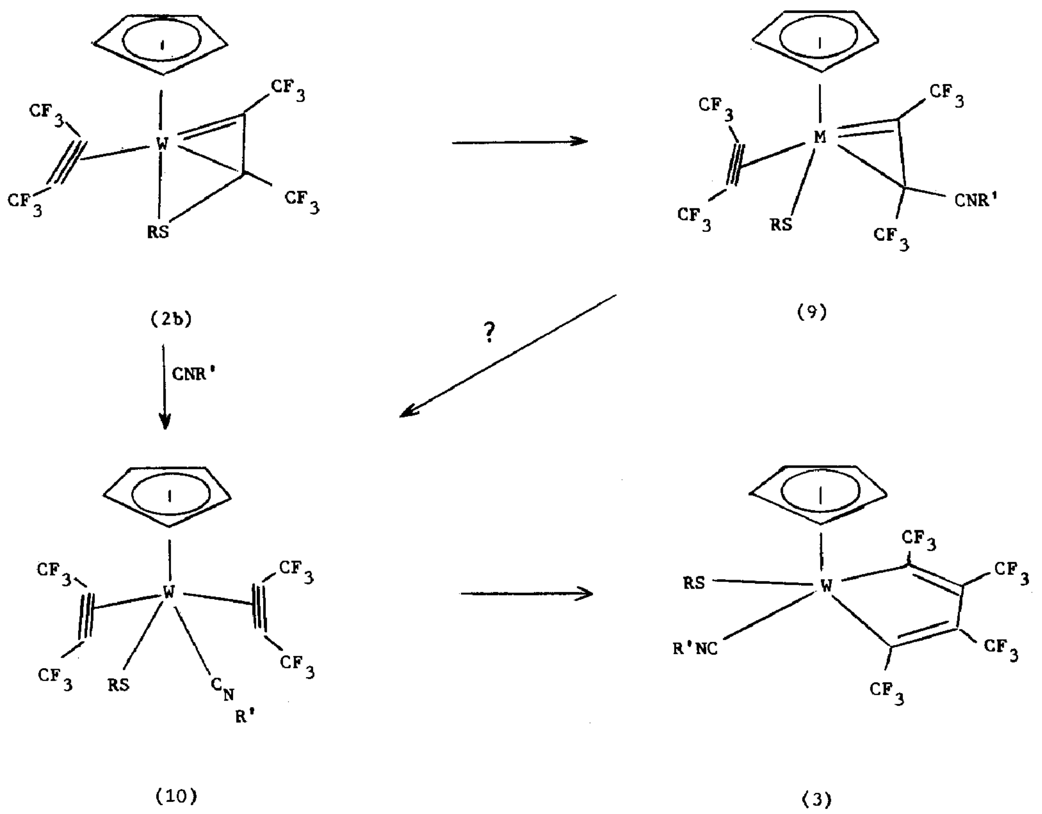
(b) Bond angles			
C(13)–C(15)–C(16)	121.5(5)	F(10)–C(16)–F(11)	106.6(5)
F(10)–C(16)–F(12)	104.2(6)	F(10)–C(16)–C(15)	115.2(5)
F(11)–C(16)–F(12)	103.7(5)	F(11)–C(16)–C(15)	112.9(6)
F(12)–C(16)–C(15)	113.2(5)	W–C(17)–N(1)	178.1(5)
W–C(18)–N(2)	175.9(5)	N(1)–C(21)–C(22)	120.0(6)
N(1)–C(21)–C(26)	119.7(6)	C(22)–C(21)–C(26)	120.2(6)
C(21)–C(22)–C(23)	121.1(6)	C(22)–C(23)–C(24)	119.4(7)
C(23)–C(24)–C(25)	119.5(6)	C(23)–C(24)–C(27)	121.6(7)
C(25)–C(24)–C(27)	118.9(7)	C(24)–C(25)–C(26)	120.6(6)
C(21)–C(26)–C(25)	119.2(6)	N(2)–C(31)–C(32)	119.6(6)
N(2)–C(31)–C(36)	119.3(6)	C(32)–C(31)–C(36)	121.1(6)
C(31)–C(32)–C(33)	118.5(6)	C(32)–C(33)–C(34)	121.7(6)
C(33)–C(34)–C(35)	118.8(6)	C(33)–C(34)–C(37)	123.2(6)
C(35)–C(34)–C(37)	118.1(6)	C(34)–C(35)–C(36)	119.6(6)
C(31)–C(36)–C(35)	120.2(6)		
(c) Torsion angles			
C(15)–W–C(9)–C(11)	8.9(4)	C(9)–W–C(15)–C(13)	−4.6(4)
W–C(9)–C(11)–C(13)	−11.8(4)	W–C(15)–C(13)–C(11)	0.2(4)
C(9)–C(11)–C(13)–C(15)	7.7(5)		

[a] C(CP) is the centroid of the cyclopentadienyl carbon atoms C(1)–C(5).

isolate pure samples of such species by addition of one molar equivalent of isocyanide were only partly successful owing to their instability. In the case of the *p*-tolylisocyanide derivative **3a** a sample of ca. 85% purity (NMR) was obtained by carrying out the reaction at −78 °C. Interestingly at this temperature the reaction solution turned red on slow addition of isocyanide and a red solid precipitated. On warming, the solid turned green (ca. −50 °C) and the dark green microcrystalline complex **3** ($R = Pr^i$, $R' = 4\text{-}MeC_6H_4$) was isolated at room temperature. The spectroscopic properties are consistent with the proposed structure and, e.g. the IR spectrum exhibits a single ν(C≡N) peak at 2130 cm^{-1}. The ^{19}F NMR spectrum contains two quartets *J* 15.2 and 14.4 Hz due to the two CF_3 groups on the terminal carbons C(1) and C(4) of the diene and two septets (quartet of quartets) due to the internal CF_3 groups. This is consistent with the absence of a plane of symmetry in the molecule and accordingly the isopropyl methyls, which are diastereotopic, give rise to two doublets in the ^1H NMR spectrum.

Since all attempts to obtain single crystals of **3a** for X-ray diffraction studies were unsuccessful the structure was further probed by $^{13}C\{^{19}F\}$ NMR spectroscopy. For comparison the spectrum of the bis isocyanide derivative **4c** was also recorded. The spectrum of the latter shows two CF_3 signals δ 129.83, and 122.09 and, more significantly, two metallaring peaks δ 146.18 and 174.58. The presence of ^{183}W satellites *J*(C–W) 84.5 Hz establishes that the highest frequency signal is due to the metallated carbons in the 1 and 4 positions of the ring. The less symmetric complex **3a** gives rise to four metallaring peaks two at δ 139.51 and 131.71 which we assign to C(2) and C(3), whereas the C(1) and C(4) carbons resonate at δ 188.70 and 180.57. In contrast the C(1) and C(4) carbons of the metallacyclopentatriene complex $[RuBr(\eta^2\text{-}C_4Ph_2H_2)(\eta^5\text{-}C_5H_5)]$ give rise to a peak at δ 271.1 consistent with their carbenoid character [5]. On this basis we conclude that, despite the electron deficient nature of the complex, the mode of bonding in the metallaring of **3** is very similar to that in the 18-electron bis isocyanide derivative **4**. Clearly there is no evidence for any significant contribution from the metallacyclopentatriene mode of bonding in **7** despite the electron deficient nature of the 16-electron configuration. Conceivably the formal lack of electron density in the metal is relieved partially by sulphur → metal π-donation, evidence for which we have reported previously in alkyne thiolate complexes $[MSC_6F_5(CO)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [12]. Moreover an increasing number of group 6 metal cyclopentadienylmetal complexes reported in recent years can formally be considered electron deficient, including, for example, thiolate derivatives $[W(SC_6F_5)_3(CO)(\eta^5\text{-}C_5H_5)]$, $[MTl(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) [13] and $[Mo(SR)_2(NO)(\eta^5\text{-}C_5H_5)]$ [14].

It is of interest to speculate on the nature of the red intermediate formed in the initial stages of the reaction between complex **2b** and *p*-tolylisocyanide. Attempts to characterise the complex at low temperatures by NMR spectroscopy were unsuccessful but the following observations are pertinent. Since the complex thermally rearranges to the metallacyclopentadiene derivative **3a** in the solid state in the absence of other reagents, it must be isomeric with **3a**. From consideration of previous reactions of complexes **1** and **2**, the two most probable structures are **9** and **10** (see Scheme 1), containing respectively a carbon-coordinated or a metal-coordinated isocyanide ligand.



Scheme 1

In previous reactions of tertiary phosphines with the η^2-vinyl complexes **2** we have observed that nucleophilic attack occurs preferentially at a coordinated carbon atom, to yield η^2-vinyl complexes $[WSR\{\eta^2\text{-}C(CF_3)C(CF_3)PR'_3\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Bu^t, PR$'_3$ = PEt$_3$, PMe$_2$Ph; R = Pr^i, PR$'_3$ = PMe$_2$Ph) [15]. Structurally related η^2-vinyl complexes $[M\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(X)(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, X = CF_3, SC_6F_5; M = W, X = Cl, SC_6F_5) [4,16] have also been obtained as a result of isocyanide attack at an alkyne carbon of bis alkyne derivatives of type **1**, and in one case, that with M = W and X = Cl, the complex was structurally characterised by X-ray diffraction [16]. In contrast triethylphosphine addition to the molybdenum derivatives $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ gives $[MoC(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SPr^i(PEt_3)(\eta^5\text{-}C_5H_5)]$ containing a metal-coordinated phosphine ligand [17]. Moreover the low temperature NMR spectra of the reaction mixture provided evidence for an intermediate metallacyclic species similar to **3**. Although in the present case isocyanide attack on **2b** could occur initially at carbon followed by transfer to the metal, as shown (see Scheme 1), an η^2-vinyl structure (**9**) for the red intermediate seems unlikely in view of the fact that all η^2-vinyl complexes isolated so far are very pale yellow or white, including the isocyanide derivatives $[MSC_6F_5\{\eta^2\text{-}C(CF_3)C(CF_3)CNBu^t\}(CF_3C{\equiv}CCF_3)](\eta^5\text{-}C_5H_5)$ (M = Mo, W) [15,16]. We therefore tentatively propose structure **10** containing a metal-coordinated phosphine, and suggest that this undergoes oxidative metallacyclisation readily to form the 16-electron complex **3**. We have postulated the intermediacy of bis-alkyne intermediates of this type previously in cyclisation and oligomerisation reactions of bis alkyne and η^2-vinyl complexes **1** and **2**, but no evidence or their existence was ever found [4,17]. This was attributed to the fact that in such species the alkynes merely function as two-electron donors, whereas in their precursors both C≡C π-orbitals are apparently involved in bonding with metal. Since multiple electron donation in Mo^{II} and W^{II} alkyne chemistry is the rule rather than the exception [18], it can be inferred that two-electron donor alkyne complexes of these metals are either thermodynamically unstable or, more likely, are kinetically reactive.

Experimental

NMR spectra were recorded in $CDCl_3$ solution (unless stated otherwise) on a Bruker WP 200 SY spectrometer at 200.13 (^{1}H) and 188.31 MHz (^{19}F); chemical shifts are referred to $SiMe_4$ and CCl_3F ($\delta = 0$). IR spectra were recorded as solutions on a Perkin–Elmer 580 and mass spectra on an Vacuum Generators updated AEI MS9 instrument at 70 eV. Reactions were carried out under nitrogen by standard Schlenk techniques. Solvents were dried over powdered calcium hydride (Et_2O, hexane) or P_2O_5 (dichloromethane) and distilled under nitrogen before use. $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ [15] and isocyanide [19] were prepared by standard literature methods.

Reactions of $[W\text{-}\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ with MeNC 1/3 molar ratio

A solution of MeNC (8.3 mg, 0.2 mmol) in 5 cm^3 diethyl ether was added slowly to a stirred solution of the complex (44 mg 0.068 mmol) in 10 cm^3 diethyl ether at $-10\,°$C. The yellow solution turned green and then orange. 10 cm^3 hexane was added, and cooling to $-20°C$ gave orange crystals. Recrystallisation from dichloromethane/hexane gave 40 mg (81%) of $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(MeNC)_2(\eta^5\text{-}C_5H_5)]$ (**4a**). Found: C, 32.2; H, 2.6%. $C_{20}H_{18}F_{12}N_2SW$ calcd.: C, 32.9; H, 2.6%. IR (KBr) $\nu(C\equiv N)$ 2200(s), 2180(s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.83 (s, 5H, C_5H_5), 3.63 (s, 6H, MeNC), 3.00 (sept, J 6.8 Hz, 1H, Pr^i), 1.49 (d, J 6.8 Hz, 6H, Pr^i), ^{19}F NMR ($CDCl_3$) δ -50.86 (m, 6F); -56.43, (m, 6F); mass spectrum m/z 648 $[M^+-(MeNC)_2]$.

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with PhNC, 1/3 molar ratio

A solution of phenyl isocyanide (21.5 mg, 0.02 mmol) in 2 cm^3 of diethyl ether was added to a stirred solution of the complex (44 mg, 0.068 mmol) in diethyl ether (10 cm^3) at $-10°C$, giving a green solution which slowly turned orange. 10 cm^3 of hexane was added, and cooling to $-20°C$ gave orange plates. Recrystallization from dichloromethane/hexane gave 34 mg (59%) of $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(CNPh)_2(\eta^5\text{-}C_5H_5)]$ (**4b**). Found: C, 41.8; H, 2.6. $C_{30}H_{22}F_{12}N_2SW$ calcd.: C, 42.2; H, 2.6%. IR (KBr) $\nu(C\equiv N)$ 2150(s), 2100(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45 (m, 10H, Ph); 5.10 (s, 5H, C_5H_5); 3.20 (sept, J 7.5 Hz, 1H, Pr^i), 1.17 (d, J 7.5 Hz, 6H, CH_3). ^{19}F NMR ($CDCl_3$) δ -50.71 (m, 6F); -56.52 (m, 6F). Mass spectrum $m/z = 854$, $[M^+]$.

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with 4-MeC$_6$H$_4$NC, 1/3 molar ratio

A solution of $4\text{-}MeC_6H_4NC$ (30 mg. 0.026 mmol) in 5 cm^3 of diethyl ether was added to a stirred solution of the complex (56 mg, 0.086 mmol) in diethyl ether (10 cm^3), at $-10°C$, giving a green solution which turned slowly orange. 10 cm^3 of hexane was added, and cooling to $-20°C$ gave orange crystals of $[\overline{WC(CF_3)=C(CF_3)C(CF_3)=C}(CF_3)(SPr^i)(4\text{-}MeC_6H_4NC)_2(\eta^5\text{-}C_5H_5)]$ (**4c**), which were recrystallized from dichloromethane/hexane. Yield 48 mg (63%). Found: C, 43.3; H, 3.3. $C_{32}H_{26}F_{12}N_2SW$ calcd.: C, 43.6; H, 3.3%. IR (KBr): $\nu(C\equiv N)$ 2150(s), 2110(s) cm^{-1}, ^1H NMR ($CDCl_3$): δ 7.23 (m, 4H, C_6H_4) 5.05 (s, 5H, C_5H_5), 3.18 (sept., J 6.7 Hz, 1H, Pr^i) 2.38 (s, 6H, CH_3), 1.13 (d, J 6.7 Hz, 6H, Pr^i); ^{19}F NMR ($CDCl_3$), δ -50.19 (m, 6F); -55.97 (m, 6F). Mass spectrum $m/z = 882$, $[M^+]$.

Reaction of $[W\{\eta^3\text{-}C(CF_3)C(CF_3)SPr^i\}(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ with 4-MeC$_6$H$_4$NC, 1/1 molar ratio

A solution of $4\text{-}MeC_6H_4NC$ (19.9 mg, 0.17 mmol) in 10 cm^3 of hexane was added dropwise during 1 h to a stirred solution of the complex (110 mg, 0.17 mmol) in diethyl ether (10 cm^3) at $-78°C$. The solution turned red and a red solid separated. Solvent was removed at low temperature and the red solid turned green when allowed to warm to room temperature. The green solid was washed twice with cold hexane to give 45 mg of impure $[WC(CF_3)=C(CF_3)C(CF_3)=C(CF_3)(SPr^i)(4\text{-}MeC_6H_4NC)(\eta^5\text{-}C_5H_5)]$ (**3a**). IR (KBr): $\nu(C\equiv N)$ 2130(s) cm^{-1}; ^1H NMR (CD_2Cl_2, $-60°C$): δ 7.35 (m, 4H, C_6H_4); 5.30 (s, 5H, C_5H_5), 4.27 (m, 1H, Pr^i), 2.40 (s, 3H, Me), 1.40 (d, J 6.75 Hz, 3H, Pr^i), 1.325 (d, J 6.75 Hz, 3H, Pr^i). ^{19}F NMR (CD_2Cl_2, $-60°C$): δ -45.33 (q, 3F, J 15.2 Hz), -53.41 (q, J 14.4 Hz, 3F), -54.17 (sept, J· 14.8 Hz, 3F): -57.65 (sept, J 15.3 Hz, 3F).

Table 2

Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for [$\overline{W\{C(CF_3)C(CF_3)C(CF_3)C}(CF)_3)\}(SPr^i)(CNC_6H_4\text{-Me-p})_2(\eta^5\text{-}C_5H_5)$]

	x	y	z	U [a]
W	0.13805(2)	0.27768(1)	−0.33947(1)	0.031
S	0.36550(15)	0.24149(8)	−0.26773(9)	0.049
F(1)	0.1313(4)	0.2727(2)	−0.1329(2)	0.076
F(2)	−0.0419(4)	0.3074(2)	−0.2036(2)	0.075
F(3)	−0.0432(4)	0.2005(2)	−0.1504(2)	0.078
F(4)	0.0286(4)	0.0425(2)	−0.1711(2)	0.086
F(5)	0.1675(4)	0.1235(2)	−0.1186(2)	0.086
F(6)	0.2365(5)	0.0338(2)	−0.1795(2)	0.089
F(7)	0.0885(4)	−0.0215(2)	−0.2882(2)	0.086
F(8)	0.1215(5)	−0.0038(2)	−0.3964(2)	0.094
F(9)	0.2889(4)	−0.0094(2)	−0.3102(3)	0.105
F(10)	0.3027(4)	0.0784(2)	−0.4355(2)	0.073
F(11)	0.1055(4)	0.1091(3)	−0.4869(2)	0.082
F(12)	0.2624(5)	0.1914(2)	−0.4738(2)	0.086
N(1)	0.2115(5)	0.4240(3)	−0.2342(3)	0.048
N(2)	0.3629(5)	0.3465(3)	−0.4274(3)	0.054
C(1)	−0.0478(6)	0.2404(3)	−0.4241(3)	0.051
C(2)	−0.0965(5)	0.2692(3)	−0.3629(3)	0.048
C(3)	−0.0580(5)	0.3464(3)	−0.3547(3)	0.047
C(4)	0.0166(6)	0.3651(3)	−0.4106(3)	0.054
C(5)	0.0210(6)	0.2993(4)	−0.4533(3)	0.052
C(6)	0.4796(5)	0.3224(3)	−0.2427(3)	0.044
C(7)	0.4935(7)	0.3382(4)	−0.1613(3)	0.066
C(8)	0.6121(6)	0.3028(4)	−0.2648(4)	0.066
C(9)	0.0868(5)	0.2094(3)	−0.2476(3)	0.039
C(10)	0.0356(6)	0.2460(4)	−0.1841(3)	0.053
C(11)	0.1189(5)	0.1340(3)	−0.2473(3)	0.040
C(12)	0.1347(7)	0.0837(4)	−0.1799(4)	0.062
C(13)	0.1589(5)	0.1038(3)	−0.3147(3)	0.042
C(14)	0.1666(7)	0.0174(3)	−0.3283(4)	0.066
C(15)	0.1747(5)	0.1566(3)	−0.3665(3)	0.039
C(16)	0.2116(7)	0.1332(3)	−0.4387(3)	0.056
C(17)	0.1851(5)	0.3712(3)	−0.2705(3)	0.040
C(18)	0.2839(5)	0.3193(3)	−0.3972(3)	0.042
C(21)	0.2522(6)	0.4853(3)	−0.1868(3)	0.043
C(22)	0.3424(7)	0.5370(4)	−0.2041(3)	0.057
C(23)	0.3869(7)	0.5964(4)	−0.1574(4)	0.062
C(24)	0.3415(7)	0.6023(3)	−0.0918(4)	0.057
C(25)	0.2491(7)	0.5498(4)	−0.0744(3)	0.063
C(26)	0.2052(7)	0.4906(3)	−0.1215(4)	0.058
C(27)	0.3884(9)	0.6648(5)	−0.0385(4)	0.098
C(31)	0.4624(5)	0.3695(3)	−0.4667(3)	0.045
C(32)	0.4590(6)	0.3443(4)	−0.5372(3)	0.055
C(33)	0.5598(7)	0.3677(4)	−0.5751(3)	0.061
C(34)	0.6605(6)	0.4152(3)	−0.5444(3)	0.052
C(35)	0.6618(6)	0.4400(4)	−0.4728(3)	0.054
C(36)	0.5604(6)	0.4173(4)	−0.4349(3)	0.055
C(37)	0.7700(8)	0.4408(4)	−0.5831(4)	0.082

[a] U is the mean latent root of the orthogonalised anisotropic displacement tensor.

X-Ray analysis of $[W\{C(CF_3)C(CF_3)C(CF_3)C(CF_3)\}(SPr^i)(CNC_6H_4Me\text{-}p)_2(\eta^5\text{-}C_5H_5)]$

Crystal Data. $C_{32}H_{26}F_{12}N_2SW$, $M = 882.5$. Monoclinic, a 10.163(1), b 17.418(4), c 18.577(2) Å, β 98.934(7)°, V 3248.6(7) Å^3, $Z = 4$, D_x 1.804 g cm^{-3}, $F(000) = 1720$, space group $P2_1/c$. Mo-K_α radiation, λ 0.71069 Å, μ 37.9 cm^{-1}.

Measurements. An orange plate of dimensions $0.70 \times 0.60 \times 0.25$ mm was mounted on an Enraf–Nonius CAD4F diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by a least-squares treatment of the setting angles of 23 reflections with $12 \leqslant \theta \leqslant 14°$ [20]. The intensities of 11760 reflections with $2 \leqslant \theta \leqslant 30°$ in octants $h, \pm k, \pm l$ were determined from $\omega/2\theta$ scans of 1.20° in ω. After correction for crystal decomposition (up to 10% reduction in the intensity of standard reflections), Lp and absorption effects (transmission factors on F 0.65–1.54) [21] symmetrically equivalent reflections were merged ($R_{int} = 0.059$ for 2154 duplicates) to give 9490 unique refelections. Of these 5735 with $I \geqslant 3\sigma(I)$ were used subsequently.

Structure analysis. The structure was solved by Patterson and Fourier methods. Final parameters (Table 2) were obtained from least squares minimisation of $\Sigma w(|F_0| - |F_c|)^2$ with $w^{-1} = \sigma^2 + 0.00023F^2$ (where σ is derived from counting statistics). Anisotropic displacement parameters were refined for all non-H atoms. H-atoms were allowed to ride on adjacent C atoms with C–H 0.96 Å and U(H) 0.050 Å^2. Adjustment of 433 parameters, using full-matrix blocks covering up to 350 parameters, converged at $R = 0.037$, $R_w = 0.044$. In the final difference synthesis $|\Delta\rho|$ was < 2.4 eÅ^{-3} near the W atom and < 0.7 eÅ^{-3} elsewhere. Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref. 22. All calculations were performed on a GOULD 3227 computer using the GX program package [23].

Atomic coordinates are given in Table 2. Lists of observed and calculated structure factors are available from the authors.

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