Reversible Migration of a Co-ordinated Mercapto Ligand on to a Metal-bound Alkyne to give η^2-Vinyl Complexes. The Crystal and Molecular Structure of $[\overline{\mathrm{WC(CF_3){\cdot}C(CF_3)S}}\mathrm{Pr^i(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$

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Thiolato complexes $[\mathrm{W(SR)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ have been shown to exhibit two basic structures, a bis-alkyne form $[\mathrm{W(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)}]$ (R = C_6F_5, Ph, or 4-MeC_6H_4) and an η^2-vinyl form $[\overline{\mathrm{WC(CF_3){\cdot}C(CF_3)S}}\mathrm{R(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)}]$ (R = Me, Et, Pr^i, Pr^n, $PhCH_2$, or Bu^t) shown by *X*-ray diffraction studies of the isopropyl complex to result from nucleophilic attack of the SR ligand on an acetylenic carbon atom.

The mechanisms of olefin and, to a lesser extent, alkyne insertions into metal–ligand bonds have been much studied in recent years but at best they are still poorly understood. Previously we have suggested that η^2-vinyl complexes could act as intermediates in some reactions involving alkynes[1] and we now provide evidence for this proposal.

Metathetical reactions of TlSR (R = C_6F_5,[2] Ph, and 4-MeC_6H_4[3]) with the bis-alkyne complex $[\mathrm{WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)}]$ have previously been shown to give bis-alkyne-thiolates $[\mathrm{W(SR)(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)}]$ (**1**) whereas with more electron-donating organic substituents, R = Bu^t, Pr^i, Et,[3] Pr^n, $PhCH_2$, or Me, complexes of similar stoicheiometry but different spectroscopic features can be isolated {*e.g.* $[\mathrm{W(SPr^i)(C_4F_6)_2(\eta^5\text{-}C_5H_5)}]$: i.r. ($CHCl_3$) 1760 w cm^{-1} ($\nu C{\equiv}C$); n.m.r., ^1H (−50 °C, $CDCl_3$) 5.95 (s, 5H, C_5H_5), 1.50 (d, 3H, Me), 1.35 (d, 3H, Me), and 1.30 (m, 1H); ^{19}F (−30 °C, $CDCl_3$) −55.5 (qq, 3F), −57.80 (q, J_{FF} 3.0 Hz, 3F), −57.95 (m, 3F), and −58.35 p.p.m. (m, 3F)}.

A dinuclear structure with bridging thiolate groups was originally proposed for the latter type of complex.[3] However, in view of spectroscopic similarities to recently reported η^2-vinyl complexes[1,4] an *X*-ray diffraction study of the isopropyl derivative was carried out in order to establish the nature of these compounds unequivocally. This revealed the novel structure (**2a**) shown in Figure 1.†

This illustrates that a novel 6-electron-donor *trihapto* ligand

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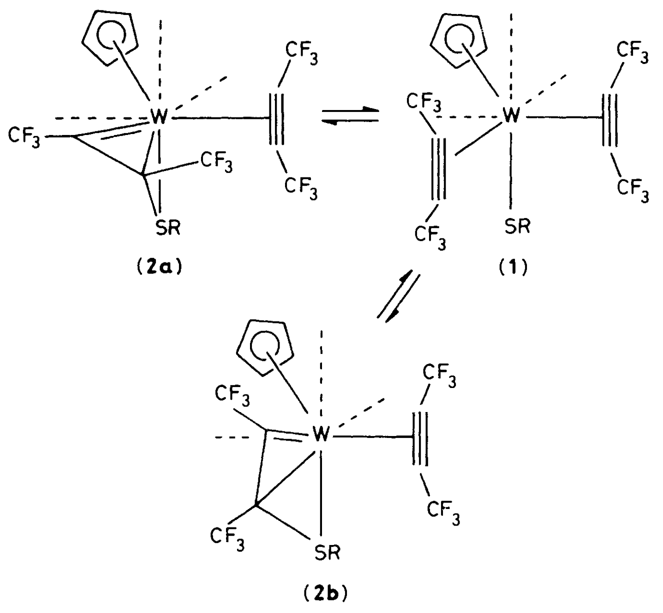
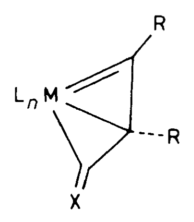
† *Crystal data:* (**2a**): $C_{16}H_{12}F_{12}SW$, M = 648.16, monoclinic, space group $C2/c$, a = 28.571(3), b = 10.430(2), c = 13.764(2) Å, β = 99.78(1)°, U = 4042 Å^3, Z = 8, D_c = 2.130 g cm^{-3}, R = 0.040, R_w = 0.065 for 4113 independent intensities with $I > 3\sigma(I)$. An Enraf Nonius CAD4F diffractometer and Mo *X*-rays were used, together with the GX program package. Atomic co-ordinates are obtainable on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. The full literature citation for this communication should accompany such requests.



Scheme 1

has been formed by nucleophilic attack of the co-ordinated sulphur atom on C(11), originally one of the central carbon atoms of a co-ordinated hexafluorobut-2-yne ligand. No metal–ligand bonds are broken during this process and the bonding of the resulting *trihapto* ligand can best be described in terms of a W–S linkage supported by an adjacent η^2-vinyl arrangement of a type now well established.[1,4,5] However, the significance of the present structure is that it provides a clear insight into the mechanism by which a ligand can migrate on to a co-ordinated alkyne, in this case to produce an η^2-vinyl derivative. It now seems conceivable that with ligands devoid of lone-pair electrons, *e.g.* H, alkyl, or aryl, complexes related to (**2a**) may be transient intermediates in the insertion reactions of alkynes into metal–hydrogen and metal–carbon bonds, while analogous species, *e.g.* (**3**), may be implicated in metal-promoted cyclisation reactions of alkynes with carbon monoxide (X = O) and isocyanides (X = NR).[4a]

The migration process involving the mercapto complexes, *i.e.* (**1**) → (**2a**), appears to be promoted by electron-releasing substituents on sulphur. Thus structure (**1**) is found with R = C_6F_5, Ph, and 4-MeC_6H_4[2,3] whereas (**2a**) is formed exclusively with R = Pr^i and Bu^t. Previously dynamic ^1H and ^{19}F n.m.r. studies[3] of $[W(SEt)(C_4F_6)_2(\eta^5\text{-}C_5H_5)]$ revealed the presence of two interconverting isomeric forms. The true nature of one of these isomers (**2a**) prompted a reinvestigation of the n.m.r. spectra at higher field strength (^1H, 200 MHz) and of a wider range of complexes. This confirmed that two isomeric forms exist when R = Me, Et, Pr^n, or $PhCH_2$, one exhibiting features consistent with structure (**2a**), *e.g.* R = Me, −50 °C, ^1H n.m.r. (CD_3COCD_3), 5.65 (s, 5H, C_5H_5) and 3.30 (s, 3H, CH_3); ^{19}F n.m.r. (CD_3COCD_3–toluene, 1:1) −53.30 (qq, 3F), −55.90 (m, 6F), and −56.25 p.p.m. (q, 3F); the other, (**2b**), exhibited a single ^{19}F n.m.r. signal (δ −55.30 p.p.m.) indicating fluxional behaviour and originally assigned structure (**1**). At higher temperatures rapid exchange is observed between both isomers leading to a single set of n.m.r. resonances while at lower temperatures the single ^{19}F n.m.r. peak due to (**2b**) broadens and at −100 °C separates into four distinct CF_3 peaks similar to those of (**2a**), *e.g.* R = Me, −100 °C, −53.80, (br., 3F), −54.65, (br., 3F), −54.80, (br., 3F), and −56.75 p.p.m. (br., 3F). This eliminates the bis-alkyne structure (**1**) originally proposed for (**2b**). Previously we have shown that related η^2-vinyl complexes $[MCl\{C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo or W; L = tertiary phosphine or phosphite) can exist in two isomeric forms owing to distinct orientational preferences of the η^2-vinyl ligand.[1b] It is therefore possible to explain the low-temperature limiting ^{19}F n.m.r. spectra of $[\overline{W\{C(CF_3)\cdot C(CF_3)\}S}R(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (R = Me, Et, $PhCH_2$, and Pr^n) in terms of two isomeric forms, one with the η^2-vinyl orientated as in the solid-state structure (**2a**), the other more structurally mobile form having the alternative orientation (**2b**).



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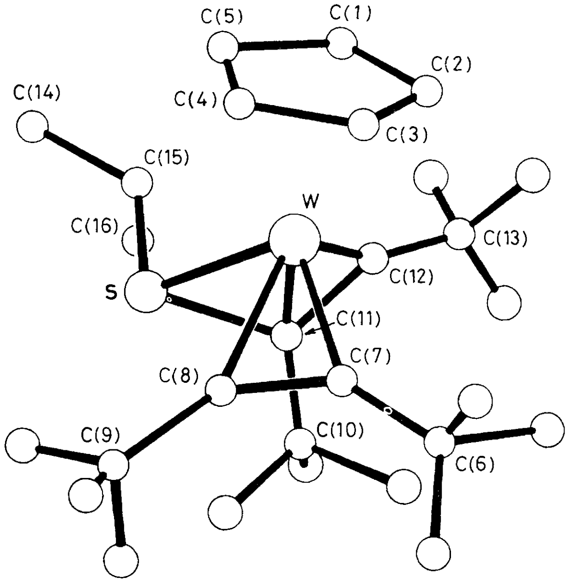

Figure 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)W(F_3CC_2CF_3)\{F_3CCC(CF_3)SPr^i\}]$ (**2a**). Selected distances in Å are: W–S 2.457(2), W–C(7) 2.062(9), W–C(8) 2.103(8), W–C(11) 2.178(8), W–C(12) 1.905(7), C(7)–C(8) 1.300(13), S–C(11) 1.764(8), and C(11)–C(12) 1.417(10). Hydrogen atoms are omitted and fluorine atoms are not numbered.

We cannot completely exclude an alternative dinuclear mercapto-bridged structure for (**2b**), *i.e.* the structure originally proposed for (**2a**), but the presence of only two νC≡C modes (*e.g.* R = Me: 1789 and 1752 cm^{-1}) in the i.r. spectra of the complexes (one for each isomer) argues in favour of the former explanation.

To account for the exchange process (**2a**) ⇌ (**2b**) and in particular total CF_3 site-exchange in (**2**) it is necessary to postulate a process (see Scheme 1) involving fission of the C–S bond between the SR and $C(CF_3)C(CF_3)$ moieties of the mercapto vinyl ligand so as to regenerate an intermediate bis-alkyne complex (**1**) containing rotating $CF_3C{\equiv}CCF_3$ ligands. This is in accord with the fact that with less basic mercapto groups (**1**) is the preferred structure whereas with more basic SR ligands the η^2-vinyl structure is more stable. In the intermediate situation migration of the SR ligand on to the alkyne appears to be a reversible process on the n.m.r. time-scale.

These observations may have implications for migratory insertion reactions involving hydrido or alkyl groups and co-ordinated alkenes or alkynes, *i.e.* the basicity of the migrating group may determine the ease with which the reaction proceeds. Interestingly in one particular case[6] evidence has been presented for an equilibrium between a hydrido ethylene and an ethyl complex $[RhH(C_2H_4)(PMe_3)(\eta^5\text{-}C_5H_5)]^+ \rightleftharpoons [RhC_2H_5(PMe_3)(\eta^5\text{-}C_5H_5)]^+$. Moreover Green *et al.* have suggested that hydride addition to $[Mo\{P(OMe)_3\}_2(R^1C{\equiv}CR^2)(\eta^5\text{-}C_5H_5)]^+$ (R^1 = Bu^t, R^2 = H or R^1 = R^2 = Ph) which gives η^1 or η^2 vinyl derivatives, depending on reaction conditions, may proceed *via* insertion of the co-ordinated alkyne into the Mo–H bond of an intermediate metal hydride.[7] The reactions reported herein are clearly in accord with such a proposal.

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