Co-ordinatively Unsaturated Alkyne Complexes of Molybdenum and Tungsten. Reactions of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) with Heterocyclic Thiolates leading to η^2-Vinyl Complexes

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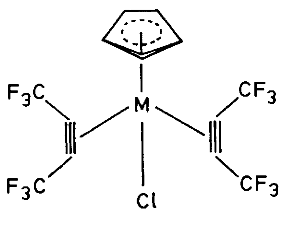
Reactions of Tl(SR) (SR^- = pyridine-2-thiolate, pyrimidine-2-thiolate, or thiazoline-2-thiolate) with the bis(hexafluorobut-2-yne) complex $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ give products $[Mo\{C(CF_3)\text{-}C(CF_3)RS\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ containing a novel η^2-vinyl ligand resulting from nucleophilic attack of nitrogen on a co-ordinated alkyne. The same pyridine-2-thiolate complex is obtained from the reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ with the thallium(I) salt of 2-mercaptopyridine *N*-oxide, in addition to $[Mo\{C(CF_3){=}C(CF_3)C(CF_3){=}C(CF_3)SC_5H_4NO\}(\eta\text{-}C_5H_5)]$. The complex $[WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ reacts with thallium(I) pyridine-2-thiolate to give the η^2-vinyl complex $[W\{C(CF_3)\text{-}C(CF_3)NC_5H_4S\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$, whereas with $Tl(SC_5H_4NO)$ cyclopentadienyl-ligand displacement is also observed giving the co-ordinatively unsaturated bis(hexafluorobut-2-yne) complexes $[W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2]$ and $[W(SC_5H_4N)(SC_5H_4NO)(CF_3C{\equiv}CCF_3)_2]$

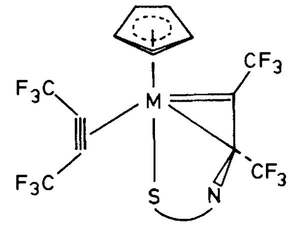
In general, unactivated acetylenes and olefins do not readily undergo nucleophilic addition unless they are co-ordinated to a transition metal, particularly one bearing a positive charge.[1,2] In contrast, activated alkynes $RC{\equiv}CR$ (*e.g.* R = CF_3 or CO_2Me) are readily attacked by nucleophiles [3] but on co-ordination they become susceptible to electrophilic attack.[2] Recently we have been carrying out a study of the reactivity of bis(hexafluorobut-2-yne) complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (1a, M = Mo; 1b, M = W)[4] in which both sets of π orbitals on the alkyne ligands are thought to be involved in bonding to the metal.[5] Since multiple-electron donation to a metal might be expected to result in re-activation of the co-ordinated alkynes towards nucleophiles, particularly with CF_3 groups attached to the acetylenic carbons, it was of interest to carry out studies of the reactions of complexes (1) with various nucleophiles. Previously we have established that heterocyclic thiols (*e.g.* 2-mercaptopyridine) undergo nucleophilic addition to free hexafluorobut-2-yne [6] and now report reactions of anions of such heterocyclic compounds with $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W).[7]

Results and Discussion

Reactions of complex (1a) with thallium(I) salts Tl(SR) (SR^- = pyridine-2-thiolate, pyridimidine-2-thiolate, or thiazoline-2-thiolate) in tetrahydrofuran (thf) at 20 °C give orange-yellow crystalline complexes which according to elemental analysis and mass spectrometry have the formula $[Mo(SR)(CCF_3)_4(\eta\text{-}C_5H_5)]$. The i.r. spectrum in each case exhibits a single $\nu(C{\equiv}C)$ mode near 1 800 cm^{-1} unlike the bis(acetylene) precursor which shows two bands in this region. Four CF_3 multiplets are observed in the ^{19}F n.m.r. spectra indicating a low symmetry for the complexes, while ^1H n.m.r. data are consistent with the presence of one $\eta^5\text{-}C_5H_5$ group and one heterocyclic SR^- ligand. Previously one of us reported that similar dithiocarbamate complexes can be isolated from reactions of (1) with NaS_2CNR_2 (R = Me or Et) and a bis(alkyne) structure was proposed.[8] However, the recent isolation of a novel η^2-vinyl complex $[W\{\eta^2\text{-}C(CF_3)C(CF_3)C(O)SMe\}(CO)_2(\eta\text{-}C_5H_5)]$ from reactions of $[W(SMe)(CO)_3(\eta\text{-}C_5H_5)]$ with $CF_3C{\equiv}CCF_3$ and related compounds from reactions of phosphines with $[M(SC_6F_5)(CO)(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo or W)[9] suggested an alternative structure (2). This was subsequently confirmed by single-crystal *X*-ray diffraction studies of complex (2a).[7,10]



M	
(1a)	Mo
(1b)	W



	M	S⌒N
(2a)	Mo	SC_5H_4N
(2b)	Mo	$SC_4H_3N_2$
(2c)	Mo	SC_3H_4NS
(2d)	W	SC_5H_4N

An interesting feature in the structure of complex (2a) is the presence of a novel η^3 ligand $C(CF_3)C(CF_3)SC_5H_4N$ resulting from nucleophilic attack of the pyridine-2-thiolate nitrogen at an acetylenic carbon. This ligand is attached to molybdenum *via* sulphur and a novel η^2-vinyl linkage of the fluorocarbon moiety. The 18-electron configuration of the metal is attained by further attachment to the $\eta^5\text{-}C_5H_5$ ring and a two-electron $CF_3C{\equiv}CCF_3$ ligand. Attack of the pyridine nitrogen appears to occur exclusively at the alkyne since only one isomeric form of the complex was detected. Nucleophilic addition to free hexafluorobut-2-yne and other activated alkynes is well known [2] but on co-ordination to metals deactivation is normally observed and only addition reactions with electrophiles are possible.[3] Nucleophilic addition to co-ordinated alkynes is observed infrequently and usually requires the presence of a positive charge on the metal. We attribute the electrophilic nature of the alkynes in complex (1) to the involvement of both sets of $C{\equiv}C$ π orbitals in bonding with the metal atom since this would be expected to reduce the electron density in the region of the acetylenic carbon atoms. Evidence for this effect has also been found in the co-ordinatively unsaturated alkyne complex $[Mo(SBu^t)_2$-

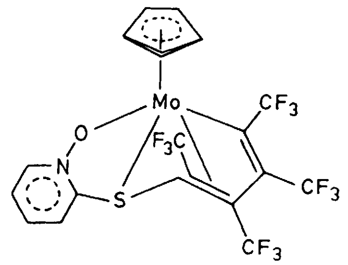
$(CNBu^t)_2(PhC{\equiv}CPh)]$[11] which reacts with $NaBH_4$ to give a mixture of *cis*- and *trans*-stilbene.

The structure of complex (2a) throws new light on the structures of $[M(SC_6F_5)(CO)(CF_3C_2CF_3)L(\eta\text{-}C_5H_5)]$ and $[M(S_2CNR_2)(CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W, L = phosphine) since it now seems probable that they also contain η^2-vinyl ligands resulting from attack of nucleophiles on co-ordinated $CF_3C{\equiv}CCF_3$ rather than on the metal as originally thought.[8,9b] Recently Green and co-workers[12] have isolated η^2-vinyl complexes from reactions of anionic nucleophiles with related cationic alkyne complexes of molybdenum and tungsten. Interestingly however, evidence for direct attack at the metal was also presented[12c] which illustrates that the nature of the alkyne and the reacting nucleophile affect the site of attack. Previously we have isolated cyclopentadiene and pyrazole derivatives from reactions of complex (1) with $Tl(C_5H_5)$ and $KHB(C_3H_3N_2)_3$[13] respectively and it now seems probable that these complexes result from initial attack of the nucleophile on the alkyne to give an intermediate η^2-vinyl derivative. This is further supported by our recent observation that phosphines and isocyanides readily add to an alkyne ligand in (1) to give η^2-vinyl complexes related to (2).[4] A number of these complexes has been found to exist in two isomeric forms, a kinetic isomer which on heating rearranges to a thermodynamically more stable isomeric form.[14] *X*-Ray diffraction studies of both forms of $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)PEt_3\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ have established that the isomers differ in the orientation of the η^2-vinyl ligand and in the configuration of the asymmetric carbon on the η^2-vinyl ligand.[10] A comparison of (2a) with this complex reveals that the former has features in common with the thermodynamic isomer.[4]

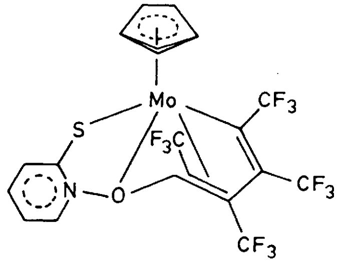
The reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (1b) with $Tl(SC_5H_4N)$ (20 °C, thf) is more complex than that of (1a) but with short reaction times (<4 h) complex (2d) is formed in addition to another complex which has not been obtained in a pure form. With longer reaction times at least three other species are also formed in varying amounts according to ^{19}F n.m.r. monitoring of the reaction. Further studies of this and related reactions of the tungsten complex (1b) are currently in progress.

Unsubstituted heteroaromatic *N*-oxides, *e.g.* quinoline *N*-oxide, react with hexafluorobut-2-yne in a primary process of 1,3-dipolar cycloaddition,[15] whereas we have shown that 2-mercaptopyridine *N*-oxide forms a product of nucleophilic addition from sulphur, $ONC_5H_4SC(CF_3){=}C(CF_3)H$.[6] It was therefore of interest to compare the reactivity of this thiolate group with co-ordinated hexafluorobut-2-yne, and reactions of complex (1) with the thallium(I) salt of 2-mercaptopyridine *N*-oxide were also carried out.

Complex (1a) reacts (20 °C, diethyl ether) to give (2a) in 57% yield indicating that deoxygenation of the anion $SC_5H_4NO^-$ occurs readily. A small quantity (12%) of a second product was also isolated which has the stoicheiometry $[Mo\{C_4(CF_3)_4SC_5H_4NO\}(\eta\text{-}C_5H_5)]$ according to elemental analysis and mass spectrometry. The latter, in addition to a molecular ion, exhibits peaks due to fragmentation of $C_4(CF_3)_4SC_5H_4NO$ indicating that condensation of both alkynes and the thiolato-group has occurred. This is supported by the absence of ν(C≡C) modes in the i.r. spectrum while the ^{19}F n.m.r. spectrum exhibits four separate CF_3 multiplets: ^{19}F decoupling experiments gave $\delta_1 = -52.94$ (qqq) ($J_{12} = 11.80$, $J_{13} = 3.46$, and $J_{14} = 11.54$), $\delta_2 = -55.58$ (qq) ($J_{21} = 11.80$ and $J_{23} = 2.19$), $\delta_3 = -56.82$ (qq) ($J_{32} = 2.19$ and $J_{33} = 3.46$), and $\delta_4 = 66.78$ (q) ($J_{41} = 11.54$ Hz). These data are consistent with an $MoC(CF_3){=}C(CF_3){-}C(CF_3){=}C(CF_3){-}SC_5H_4NO$ group, and on the basis that *cis*-$C(CF_3){=}C(CF_3)$ moieties exhibit $J_{FF} = 10$—15 Hz whereas *trans*-CF_3 substituents give $J_{FF} = 1$—3 Hz[16] two possible structures (3) and (3′) are tentatively suggested. However the data do not allow us to distinguish between these possibilities. It appears that complex (3) results from both *cis* and *trans* insertion reactions of the co-ordinated alkyne ligands. Other examples of sequential *cis–trans* alkyne insertions have been reported previously[17] although *cis–cis* insertions are generally more common.[18] At present it is not apparent which factors control the preference for a particular stereochemical mode of reaction.

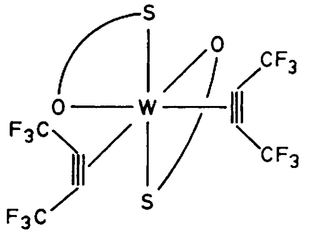


(3)



(3′)

The reaction of $[WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ with $Tl(SC_5H_4NO)$ (thf, 20 °C) is similarly more complex than that of the molybdenum derivative (1a) giving only traces of the η^2-vinyl complex (2d) the main products being unexpectedly bis(alkyne) derivatives $[W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2]$ (4) and $[W(SC_5H_4N)(SC_5H_4NO)(CF_3C{\equiv}CCF_3)_2]$ (5) resulting from displacement of both Cl and C_5H_5 ligands. The i.r. spectra of both complexes exhibit two ν(C≡C) modes near 1 800 cm^{-1} and strong ν(C–F) bands (1 100—1 300 cm^{-1}) similar to those of (1b). Only one set of SC_5H_4NO proton signals is observed in the ^1H n.m.r. spectrum of (4) indicating equivalence of both chelate rings, while two CF_3 signals are observed in the ^{19}F n.m.r. spectrum down to −60 °C. The ^{19}F n.m.r. spectrum of (5) in contrast exhibits four equal-intensity resonances at −48 °C reflecting the lower symmetry of the complex. These data are consistent with the structures



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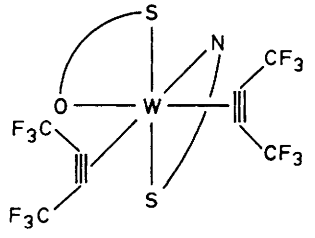


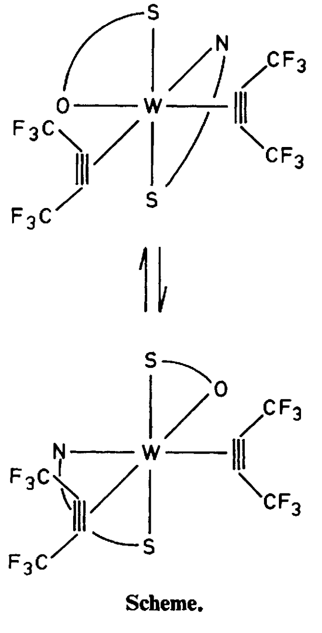
(5)

S⌒O = 2-SC_5H_4NO

S⌒N = 2-SC_5H_4N

illustrated in which the alkynes occupy *cis* positions about an octahedrally co-ordinated tungsten atom. A similar structure is found with $[Mo(S_2CNEt_2)_2(PhC{\equiv}CPh)_2]$ which has been characterised by *X*-ray diffraction studies.[19] As with $[WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$,[20] both alkynes adopt an orientation such that the C≡C axes lie parallel to each other and the ^{19}F n.m.r. spectra suggest that this is also the case in complexes (4) and (5). However the data do not distinguish between the various isomeric forms which are possible depending on the disposition of the chelate ligands except that (4) adopts a higher symmetry structure in which either two sulphur or two oxygen atoms are *trans* to each other. Extended-Hückel calculations on the model complex $[Mo(S_2CNH_2)_2(HC{\equiv}CH)_2]$ confirm that in the parallel orientation both alkyne π-perpendicular orbitals can overlap with the only empty metal $d\ \pi$ orbital and as a consequence six electrons are effectively donated from the two alkynes to the metal.[21]

Interestingly the calculations also indicate that alkyne propeller rotation should involve a relatively high energy barrier *ca.* 170 kJ mol^{-1}. However, dynamic n.m.r. studies of complexes (4) and (5) indicate that fluxional behaviour occurs in both cases since coalescence of both CF_3 resonances of (4) is observed at 77 °C while two of the four ^{19}F n.m.r. resonances of (5) (δ_1 and δ_3) coalesce at 22 °C while δ_2 and δ_4 coalesce at 82 °C. Two types of fluxional behaviour are possible in complexes (4) and (5), alkyne rotation or a dissociative process involving interchange of the chelating ligands as found in $[MoO(S_2CNR_2)_2(alkyne)]$ (M = Mo or W, R = Me or Et).[22] Although the latter process could account for the fluxional behaviour of (4), CF_3 site exchange in (5) resulting from chelate interchange can only occur if the SC_5H_4N and SC_5H_4NO ligands exchange sites simultaneously and in a specific manner (see Scheme). Since CF_3 site exchange appears to involve two different energy barriers this process is excluded. Consequently we attribute the fluxional behaviour in complex (5) and possibly in (4) to alkyne rotation. The significant difference in coalescence temperatures in the spectra of (5) therefore indicates that the two alkynes experience different barriers to rotation. Alkyne rotation is also thought to be responsible for the temperature dependence of the n.m.r. spectra of complexes $[W(S_2CNR_2)_2(CO)(alkyne)]$, whereas the structurally related oxo-complexes mentioned previously[22] undergo preferential chelate-ligand interchange. A possible explanation for this difference is the electronic configuration of the metal in the latter (d^2) whereas the former and also (4) and (5) are d^4 complexes. A similar situation is also found in cyclopentadienyl complexes $[M(SC_6F_5)L(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo or W) which exhibit alkyne rotation when L = CO, tertiary phosphine, or phosphite, *i.e.* with a d^4 configuration, whereas the oxo-complexes (L = O) with a d^2 configuration are stereochemically rigid.[14] The existence of two different rotational barriers in complex (5) presumably results from the fact that each alkyne lies *trans* to a different donor atom and the rotational barriers will then reflect differing π-bonding abilities of the *trans* atoms. Barriers to alkyne rotation in $[MX(RC{\equiv}CR)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W: X = Cl, Br, or I; R = Me or CF_3),[23] $[M(SC_6F_5)L(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ (M = Mo or W; L = CO, tertiary phosphine, or phosphite),[14] and $[MoL(L')(MeC{\equiv}CMe)(\eta\text{-}C_5H_5)][BF_4]$ or $[MoL(L')(MeC{\equiv}CMe)(\eta^5\text{-}C_9H_7)][BF_4]$ (L and L′ = CO or tertiary phosphine)[24] exhibit wide variations depending on the nature of the ligand(s) *cis* to the alkyne(s) and a corresponding *trans* effect is to be expected.



Scheme.

The formation of complexes (4) and (5) by displacement of a cyclopentadienyl ligand is unexpected in view of the mild conditions of the reaction. Precedents for C_5H_5 displacement do exist, particularly in reactions involving nickelocene,[25] but these probably result from the open-shell configuration of the metal. Interestingly $[W(NO)(CO)_2(\eta\text{-}C_5H_5)]$ has been reported to undergo nucleophilic attack by trimethylphosphine to yield a σ-C_5H_5 complex $[W(NO)(CO)_2(PEt_3)_2(\sigma\text{-}C_5H_5)]$.[26] This suggests a mechanism for displacement of C_5H_5 from complex (1b) in which nucleophilic attack induces an $\eta^5 \longrightarrow \sigma$-$C_5H_5$ transformation followed by cleavage of the remaining tungsten–carbon σ bond. Previously reported routes to bis(chelate),bis(alkyne) complexes similar to (4) have involved conventional synthetic procedures [equation (i);

$$[Mo(CO)_2(S_2CNEt)_2] \xrightarrow{RC{\equiv}CR'} [Mo(CO)(RC{\equiv}CR')(S_2CNEt)_2] \xrightarrow{RC{\equiv}CR'} [Mo(RC{\equiv}CR')_2(S_2CNEt_2)_2] \qquad (i)$$

R,R′ = alkyl, aryl, or ester] which suffer from the disadvantage that introduction of the second alkyne ligand is frequently difficult.[19a,27] We are currently investigating this alternative route involving displacement of the cyclopentadienyl and chloro-ligands from complexes similar to (1).

Experimental

Unless otherwise stated, i.r. spectra were recorded as $CHCl_3$ solutions on a Perkin-Elmer 580 spectrophotometer. N.m.r. spectra were recorded in $CDCl_3$ (unless stated otherwise) on JEOL MH 100 and Bruker WP 200 SY spectrometers; ^1H and ^{19}F chemical shifts are measured relative to $SiMe_4$ and CCl_3F respectively. Reactions were carried out using Schlenk techniques and dried deoxygenated solvents (thf–Na, CH_2Cl_2, Et_2O, and hexane–CaH) either in an atmosphere of oxygen-free dry dinitrogen or *in vacuo*. Melting points are uncorrected. Thallium salts of heterocyclic thiolates[28] and the complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W)[23] were prepared as described previously.

Reaction of $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ *with Thallium Thiolates derived from 2-Mercapto-pyridine, -pyrimidine, and -thiazoline and 2-Mercaptopyridine N-Oxide.*—(*a*) *Thallium pyridine-2-thiolate.* The thallium salt of 2-mercaptopyridine (0.10 g, 0.31 mmol) and $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (0.15 g, 0.29 mmol) were stirred in tetrahydrofuran (40 cm^3)

under nitrogen for 4 h at room temperature. The product solution was evaporated to dryness under reduced pressure and the residue was extracted with diethyl ether and filtered. The filtrate was evaporated under reduced pressure, and the residual solid was recrystallised to give yellow $[\mathrm{Mo\{SC_5H_4NC(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)}]$ (2a) (0.10 g, 59%), m.p. 157—158 °C (from diethyl ether–hexane); i.r. ($CHCl_3$) 2 960—2 860, 1 806, 1 620, 1 540, 1 465, 1 420, and 1 270—1 100 cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 100 MHz), δ 8.3 (1 H, d, *J* 8, aryl H, H^6), 7.7 (1 H, d, *J* 8, aryl H, H^3), 7.5 (1 H, 5, *J* 8, aryl H, H^4 or H^5), 6.9 (1 H, t, *J* 8 Hz, aryl H, H^4 or H^5), and 5.9 (5 H, s, C_5H_5); ^{19}F ($CDCl_3$, 188 MHz), δ −53.46 (3 F, spt), −54.43 [3 F, q, *J*(FF) 3.4], −55.49 [3 F, q, *J*(FF) 3.6 Hz], and −56.14 (3 F, spt). Mass spectrum: *m/e* 595 $[P]^+$; also $[P - C_4F_6]^+$, $[P - C_4F_6 - C_5H_5]^+$, $[P - C_8F_{11}]^+$, and $[P - C_8F_{12}]^+$.

(*b*) *Thallium pyrimidine-2-thiolate*. The thallium salt of 2-mercaptopyrimidine (0.12 g, 0.38 mmol) and $[\mathrm{MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)}]$ (0.19 g, 0.37 mmol) were stirred in tetrahydrofuran (20 cm^3) for 24 h at room temperature. Work-up as above gave yellow $[\mathrm{Mo\{SC_4H_3N_2C(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)}]$ (2b) (0.08 g, 14%), m.p. 180—182 °C (from diethyl ether–hexane). N.m.r.: ^1H ($CDCl_3$, 100 MHz), δ 8.72 (1 H, dd, *J* 2 and 5, aryl H, H^4 or H^6), 8.60 (1 H, d, *J* 8, aryl H, H^4 or H^6), 7.30 (1 H, dd , *J* 4 and 6 Hz, aryl H, H^5), and 6.08 (4 H, s, C_5H_5); ^{19}F ($CDCl_3$, 188 MHz), δ −53.52, (3 F, spt), 54.66 [3 F, q, *J*(FF) 2.9 Hz], and 55.95 (6 F, m, 2 × CF_3). Mass spectrum: *m/e* 596 $[P]^+$; also $[P - F]^+$, $[P - C_4F_6]^+$, $[P - C_4F_6 - C_5H_5]^+$, and $[P - C_8F_{11}]^+$ (Found: C, 34.35; H, 1.50; N, 5.05. $C_{17}H_8F_{12}MoN_2S$ requires C, 34.2; H, 1.35; N, 4.70%).

(*c*) *Thallium thiazoline-2-thiolate*. The thallium salt of 2-mercaptothiazoline (0.10 g, 0.31 mmol) and $[\mathrm{MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)}]$ (0.15 g, 0.29 mmol) were stirred in tetrahydrofuran (30 cm^3) for 24 h at room temperature. Work-up as above gave orange $[\mathrm{Mo\{SC_3H_4NSC(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)}]$ (2c) (0.04 g, 23%), m.p. 151—155 °C (from diethyl ether–hexane); $\nu_{max.}$ ($CHCl_3$) 2 960, 2 930, 2 870, 1 807, 1 490, 1 400, 1 260, 1 225, 1 220, and 1 180—1 070 cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 100 MHz), δ 5.88 (5 H, s, C_5H_5), 4.5 (1 H, m), and 4.1—3.7 (3 H, m); ^{19}F ($CDCl_3$, 188 MHz), δ −53.68 (3 F, spt), −54.59 [3 F, q, *J*(FF) 3.7 Hz], 55.40 (3 F, m), and −55.64 (3 F, spt). Mass spectrum: *m/e* 603 $[P]^+$, $[P - C_4F_6]^+$, $[P - C_4F_6 - C_5H_5]^+$, and $[P - C_8F_{12}]^+$.

(*d*) *Thallium salt of 2-mercaptopyridine* N-*oxide*. The thallium salt of 2-mercaptopyridine *N*-oxide (0.165 g, 0.50 mmol) and $[\mathrm{MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)}]$ (0.14 g, 0.27 mmol) were stirred in diethyl ether (20 cm^3) for 2 h. The product was filtered and the filtrate was evaporated under reduced pressure to leave a green oil. This oily product was purified chromatographically on a silica gel column [eluant: diethyl ether–light petroleum (b.p. 60—80 °C) (1 : 4)] to give complex (2a) (0.09 g. 56%), m.p. 161—162 °C, spectroscopically (i.r., n.m.r.) identical to the compound described in section (*a*) above and small amounts of a yellow crystalline complex $[\mathrm{Mo(SC_5H_4NOC_8F_{12})(\eta\text{-}C_5H_5)}]$ (3) (0.02 g, 12%); i.r. (CCl_4) 1 615, 1 588, 1 279, 1 262, 1 220, 1 204, 1 191, 1 171, 1 161, 1 149, and 1 118 cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 200 MHz), δ 7.99 (1 H, m), 7.61 (1 H, ddd), 6.98 (1 H, ddd), 6.89 (1 H, ddd), and 6.35 (5 H, s, C_5H_5); ^{19}F ($CDCl_3$, 188 MHz), see text. Mass spectrum: *m/e* 611 $[P]^+$; also $[P - F]^+$, $[SC_5H_4NOC_8F_{10}]^+$, $[SC_5H_4NOC_8F_9]^+$, $[SC_5H_4NOC_8F_8]^+$, $[P - C_8F_{12}]^+$, and $[P - C_8F_{12}O]^+$ (Found: C, 34.8; H, 1.60; N, 2.95. $C_{18}H_9F_{12}MoNOS$ requires C, 35.35; H, 1.45; N, 2.30%).

Reactions of $[\mathrm{WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)}]$ *with Thallium Thiolates*.—(*a*) *Thallium salt of 2-mercaptopyridine*. Complex (1b) (0.10 g, 0.16 mmol) and $Tl(SC_5H_4N)$ (0.12 g, 0.38 mmol) in thf (30 cm^3) were stirred for 4 h under nitrogen. Volatiles were removed and the residue extracted with diethyl ether and filtered. A succession of fractional crystallisations eventually gave small quantities (25 mg, 22%) of $[\mathrm{W\{SC_5H_4NC(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta\text{-}C_5H_5)}]$ (2d) and a second impure compound which was not characterised. I.r. (CCl_4) of (2d): 1 788, 1 608, 1 548, 1 470, 1 421, 1 410, 1 276, 1 270, 1 254, 1 232, 1 202, 1 177, 1 152, and 1 050 cm^{-1}. N.m.r.: ^1H ($CDCl_3$), δ 8.74 (1 H, ddd), 7.74 (1 H, br d), 7.48 (1 H, ddd), 6.98 (1 H, ddd), 5.98 (5 H, s, C_5H_5); ^{19}F ($CDCl_3$, 188 MHz), δ −55.14 [3 F, q, *J*(FF) 3.48 Hz], −55.46 (3 F, spt), −56.04 (3 F, m), and −57.74 (3 F, spt). Mass spectrum: *m/e* 681 $[P]^+$; also $[P - F]^+$, $[P - C_4F_6]^+$, $[P - C_4F_6 - C_5H_5]^+$, $[P - C_8F_{10}]^+$, $[P - C_8F_{11}]^+$, and $[P - C_8F_{12}]^+$ (Found: C, 31.0; H, 1.45; N, 2.20. $C_{18}H_9F_{12}NSW$ requires C, 31.65; H, 1.30; N, 2.05%).

(*b*) *Thallium salt of 2-mercaptopyridine* N-*oxide*. The thallium salt of 2-mercaptopyridine *N*-oxide (0.36 g, 1.10 mmol) and $[\mathrm{WCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)}]$ (0.46 g, 0.76 mmol) were stirred in diethyl ether (30 cm^3) for 48 h at room temperature. The solution was evaporated to dryness under reduced pressure and the residue chromatographed on a silica gel column (40 g), using light petroleum–diethyl ether (5 : 1 increasing to 1 : 1) as eluant. The first component eluted was (2d) (0.025 g, 5%) followed by $[\mathrm{W(SC_5H_4N)(SC_5H_4NO)(CF_3C{\equiv}CCF_3)_2}]$ (5) (0.16 g, 29%), m.p. 162—164 °C. I.r. ($CHCl_3$) of (5): 3 020, 1 820, 1 790, 1 467, 1 288, 1 240, and 1 150—1 140 cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 200 MHz), δ 8.29 (1 H, ddd), 8.18 (1 H, ddd), 7.93—7.77 (2 H, m), 7.59 (1 H, ddd), 7.29 (1 H, td), 7.06 (1 H, dt), and 6.87 (1 H, ddd); ^{19}F ($[^2H_8]$-toluene, 188 MHz, −48 °C), δ_1 −55.94, (3 F, m), δ_2 −56.10 (3 F, spt), δ_3 −57.08 (3 F, m), and δ_4 −57.90 (3 F, spt). Mass spectrum: *m/e* 742 $[P]^+$; also $[P - F]^+$, $[P - C_8F_{11}]^+$, and $[P - C_8F_{12}]^+$ (Found: C, 29.65; H, 1.2; N, 3.65. $C_{18}H_8F_{12}N_2O_4S_2W$ requires C, 29.05; H, 1.10; N, 3.75%). This was followed by $[\mathrm{W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2}]$ (4) (yield 20 mg, 4%) as yellow crystals, m.p. 192—195 °C; i.r. ($CHCl_3$) 3 010, 1 810, 1 790, 1 605, 1 555, 1 465, 1 278, 1 242, 1 185, 1 150, and 970 cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 100 MHz), δ 7.92 (2 H, ddd), 7.76 (2 H, ddd), 7.41 (2 H, td); ^{19}F ($[^2H_8]$toluene, 188 MHz, 17 °C), δ −56.01 [6 F, q, *J*(FF) 3.77] and −56.21 [6 F, q, *J*(FF) 3.75 Hz]. Mass spectrum: *m/e* 758 $[P]^+$; also $[P - F]^+$, $[P - C_8F_{11}]^+$, and $[P - C_8F_{12}]^+$ (Found: C, 29.15; H, 1.05; N, 3.50. $C_{18}H_8F_{12}N_2S_2O_2W$ requires C, 28.4; H, 1.05; N, 3.70%).

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