Co-ordinatively Unsaturated Acetylene Complexes of Molybdenum and Tungsten: Reactions of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) * with Octacarbonyldicobalt leading to Binuclear Metallacyclopentadiene Complexes

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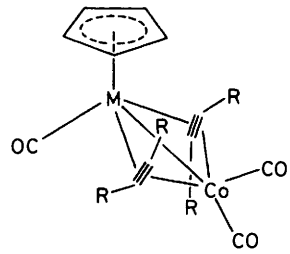
Reactions of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) with $[Co_2(CO)_8]$ gave the bis(μ-alkyne) complexes $[MCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and small amounts of the complexes $[M(CO)_2\{\eta^3\text{-}C_4(CF_3)_3CF_2CO\}(\eta^5\text{-}C_5H_5)]$. The former react with CO to give metallacyclopentadiene derivatives $[MCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ as a result of CO addition to the metal whereas reactions with PEt_3 give carbonyl substitution products $[MoCo(CO)_2(PEt_3)(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ and $[WCo(CO)(PEt_3)_2(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$.

The ability of alkynes to utilise both sets of filled π orbitals in bonding to two, three, or four metal atoms simultaneously and thus stabilise bi- and poly-nuclear clusters is well known.[1] Complexes of this type are usually obtained from reactions of metal complexes with alkynes [1] although mono(alkyne) complexes can also be employed in reactions with other metal complexes to construct polynuclear species.[2] As part of an investigation into the chemistry of co-ordinatively unsaturated bis(hexafluorobut-2-yne) complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (1) (M = Mo or W) in which both sets of acetylenic π orbitals are thought to be involved in bonding to a single metal [3] it was of interest to establish whether or not such species could be utilised to construct polynuclear complexes, in particular heterometallic species stabilised by bridging alkynes. I wish to report studies of the reactions of (1) with $[Co_2(CO)_8]$ the results of which have previously been communicated.[4]

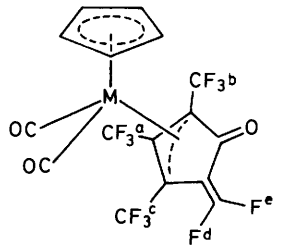
Results and Discussion

Reactions of $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ [M = Mo (1a) or W (1b)] with $[Co_2(CO)_8]$ in diethyl ether at 20 °C in an open system give red crystalline complexes $[MCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (2) and small amounts of a yellow complex $[M(CO)_2\{\eta^3\text{-}C_4(CF_3)_3CF_2CO\}(\eta^5\text{-}C_5H_5)]$ (3). The same complexes are produced in a closed reactor with short reaction times but in addition a third complex is produced, $[MCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (4), the yield of which increases with temperature and reaction time. It was subsequently found that (2a) reacts rapidly with CO (50 °C, 5 atm, diethyl ether) to give (4a) thus explaining these observations.

The structure proposed for (2) is based on spectroscopic evidence. Two terminal ν(CO) modes are observed above 2 000 cm^{-1} in the i.r. spectrum (Table 1) while the mass spectrum exhibits a molecular ion P^+ and ions $[P - CO]^+$, $[P - 2CO]^+$, and $[P - 3CO]^+$. The band at *ca.* 1 590 cm^{-1} in the i.r. spectrum assigned as the C≡C stretching mode of the bridging alkynes, compares with that of $[Co_2(CO)_6(\mu\text{-}CF_3C{\equiv}CCF_3)]$ (1 600 cm^{-1}) [5] while the lack of discernible CF_3–CF_3 coupling in the ^{19}F n.m.r. spectrum confirms that the alkynes have not undergone cyclisation. The latter feature also tends to rule out the μ-parallel bridging mode [1a] found in some alkyne complexes. It is perhaps not entirely surprising that bis(μ-alkyne) complexes of this type can be synthesised from



(2a; M = Mo)
(2b; M = W)
R = CF_3



(3a; M = Mo)
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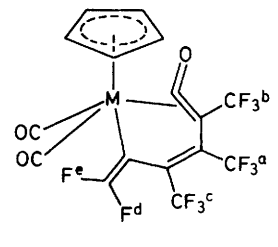
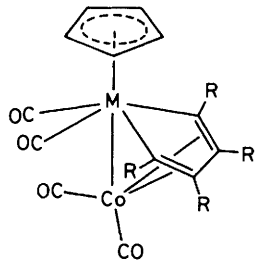


(3a'; M = Mo)
(3b'; M = W)



(4a; M = Mo)
(4b; M = W)
R = CF_3

(1) since a related binuclear species $[Mo_2Cl_2(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)_2]$ has been obtained from the photolysis of (1) [6] while related bis(alkyne) complexes of the Group 5 metals readily dimerise in a similar fashion.[7]

The co-ordination geometry at the Group 6 metal in (2) presumably resembles that in the precursor (1) [8] with an octahedral site occupied by CO instead of Cl, while diamagnetism of the complexes requires the presence of a metal–metal bond. The fact that co-ordination of CO is required for

* Chloro(η^5-cyclopentadienyl)bis(η^2-hexafluorobut-2-yne)-molybdenum and -tungsten.

Non-S.I. unit employed: 1 atm = 101 325 N m^{-2}.

Table 1. Analytical [a] and i.r. data (cm^{-1}) for the complexes

Compound	ν(CO)	ν(≥=O)	ν(C≡C)	C	H	F
(2a) $[MoCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$	2 096mw, 2 065mw, 2 040vs		1 601mw	30.3 (30.6)	0.7 (0.8)	35.8 (36.3)
(2b) $[WCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$	2 099mw, 2 063mw, 2 035vs		1 586mw	26.3 (26.8)	0.8 (0.7)	
(3a) $[Mo(CO)_2\{\eta^3\text{-}C_4(CF_3)_3CF_2CO\}(\eta^5\text{-}C_5H_5)]$	2 068s, 2 026m	1 748m	1 686mw [b]	34.8 (34.9)	1.0 (0.9)	37.5 (38.0)
(3b) $[W(CO)_2\{\eta^3\text{-}C_4(CF_3)_3CF_2CO\}(\eta^5\text{-}C_5H_5)]$	2 060s, 2 009m	1 746m	1 685mw [b]	29.7 (30.1)	0.6 (0.8)	
(4a) $[MoCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$	2 078vs, 2 036s, 2 022s, 1 989w			31.5 (31.1)	0.9 (0.8)	34.5 (34.8)
(4b) $[WCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$	2 074vs, 2 031s, 2 020s, 1 988w			28.0 (27.4)	0.7 (0.7)	29.4 (30.6)
(5) $[MoCo(CO)_2(PEt_3)(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$	2 052vs, 2 015s		1 560mw	34.9 (35.1)	3.0 (2.8)	4.0 (4.3) [c]
(6) $[WCo(CO)(PEt_3)_2(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$	1 962s		1 528mw	34.4 (34.8)	4.2 (3.9)	6.6 (6.9) [c]

[a] Calculated values in parentheses. [b] ν(C=C). [c] P analyses.

Table 2. N.m.r. data for the complexes [a]

	δ(^{1}H)/p.p.m.		δ(^{19}F)/p.p.m.	
Compound	$\eta^5\text{-}C_5H_5$	PEt_3	CF_3	CF_2
(2a)	5.87 (s)		−48.34 (s,br), −49.27 (s,br)	
(2b)	5.88 (s)		−48.68 (s,br), −49.56 (s,br)	
(3a)	5.32 (s)		−48.82 (qq, J_{FF} = 8.9, 9.9), −55.71 (q, J_{FF} = 8.9), −56.26 (dq, J_{FF} = 26.6, 9.8)	−75.84 (dq, J_{FF} = 26.6, 8.5), −81.58 (d, J_{FF} = 8.5)
(3b)	5.40 (s)		−48.97 (qq, J_{FF} = 9.5, 10.1), −55.50 (q, J_{FF} = 9.5), −56.10 (dq, J_{FF} = 26.6, 10.1)	−75.05 (dq, J_{FF} = 26.7, 11.3), −79.68 (d, J_{FF} = 11.5)
(4a)	5.62 (s)		−44.77 (m), −52.28 (m)	
(4b)	5.24 (s)		−44.05 (m), −51.26 (m)	
(5) [b]	5.61 (d, J_{PH} = 1.6)	2.06 (m, 6 H) 1.26 (m, 9 H)	−45.70 (s,br), −48.30 (m)	
(6) [b]	5.55 (d, J_{PH} = 1.7)	2.07 (m, 6 H) 1.80 (m, 6 H) 1.21 (m, 9 H) 1.02 (m, 9 H)	−44.39 (m), −45.05 (s,br)	

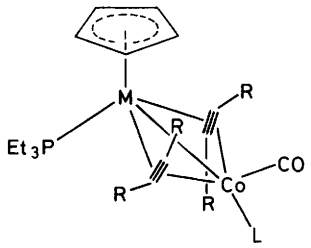
[a] ^{1}H, δ ($SiMe_4$) = 0 p.p.m.; ^{19}F, δ (CCl_3F) = 0 p.p.m., ^{31}P, δ (H_3PI_4) = 0 p.p.m. Chemical shifts are positive to high frequency (q = quartet, throughout). Coupling constants in Hz. [b] ^{31}P-{^{1}H} n.m.r.: (5) 24.12 (s) and (6) −9.06 (s, ^{183}W satellites J_{PW} = 191.7).

the metal to attain an 18-electron configuration when the alkynes can only act as two-electron donors to each metal provides further evidence that in complexes of type (1) the 18-electron configuration of the metal is achieved by participation of both sets of filled π-orbitals on the alkyne ligands.[9]

The spectroscopic features of complexes (4), in particular the two complex multiplets in the ^{19}F n.m.r. spectra (Table 2) indicated that alkyne cyclisation had occurred and this was confirmed by single-crystal *X*-ray diffraction studies of (4b).[4] The two bridging alkynes in (2b) have undergone cyclisation to produce a metallacyclopentadiene ring apparently as a result of CO co-ordination to tungsten. The tungsten co-ordination in (4b) can be described in terms of an $(\eta^5\text{-}C_5H_5)WC_4$ ' piano stool ' with a cobalt atom added *trans* to the C_5H_5 ring. A similar geometry is found in the Mo^{IV} complex $[MoI_3(CO)_2(\eta^5\text{-}C_5H_4Me)]$ where an iodo-ligand lies *trans* to the $\eta^5\text{-}C_5H_4Me$ ligand.[10]

The formation of metallacyclopentadiene rings in reactions of alkynes with metal complexes is well documented [11] but intimate mechanistic details have rarely been reported. The ability of binuclear bis(μ-alkyne) complexes such as (2) to undergo transformation into a metallacyclic species clearly illustrates one particular mechanism which finds precedent in iron cluster chemistry, *viz.* the isomerism of $[Fe_3(CO)_8(PhC{\equiv}CPh)_2]$ (violet isomer) into $[Fe_3(CO)_8(C_4Ph_4)]$ (black isomer).[1b] Bis(alkyne) intermediates are also implicated in the formation of cobaltacyclopentadiene derivatives $[Co(CR^1{=}CR^2{-}CR^3{=}CR^4)(PPh_3)(\eta^5\text{-}C_5H_5)]$ from the reaction of alkynes $R^1C{\equiv}CR^2$ with mono(alkyne) complexes $[Co(R^2C{\equiv}CR^4)(PPh_3)(\eta^5\text{-}C_5H_5)]$.[12] Previously we have observed that co-ordination of CO to the bis(hexafluorobut-2-yne) complex $[MoI(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ results in complete cyclisation of the two alkynes to give a tetrakis(trifluoromethyl)cyclobutadiene complex $[MoI(CO)\{\eta^4\text{-}C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ possibly *via* a metallacyclopentadiene intermediate.[13] The cyclisation (2) ⟶ (4) clearly supports such a proposal, the second metal Co effectively trapping and stabilising such a species before full cyclisation can occur. Moreover, it has been proposed that metals can promote the symmetry-forbidden $\pi_{2s} + \pi_{2s}$ cyclisation of two acetylenes to cyclobutadiene provided an intermediate bis(μ-alkyne) complex related to (2) is accessible.[14] The significance of the reaction (2) ⟶ (4) is that stepwise oxidative routes to cyclobutadienes *via* metallacycles may provide alternative lower energy pathways.

Further attempts to promote metallacyclisation reactions by addition of triethylphosphine to (2a) or (2b) (hexane or diethyl ether respectively, 60 °C) were unsuccessful since



(5; M = Mo, L = CO)
(6; M = W, L = PEt_3)
R = CF_3

carbonyl substitution occurred to give $[MoCo(CO)_2(PEt_3)(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (5) and $[WCo(CO)(PEt_3)_2(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (6). The presence of ν(C≡C) bands near 1 550 cm^{-1} in the i.r. spectra of both complexes suggest similar structures to (2a) and (2b). The ^1H n.m.r. spectrum of the tungsten derivative (6) contains two sets of PEt_3 signals while the $\eta^5\text{-}C_5H_5$ signal, a doublet, exhibits coupling to one other nucleus having $I = \frac{1}{2}$, presumably one of the ^{31}P nuclei (J_{PH} = 1.7 Hz). This suggests that one PEt_3 ligand is co-ordinated to tungsten, the other to cobalt. This conclusion is supported by the observation of only one ^{31}P resonance in the $^{31}P\text{-}\{^1H\}$ spectrum which is accompanied by tungsten (^{183}W) satellites (J_{PW} = 191.7 Hz) thus indicating a direct W–P bond. The other PEt_3 resonance is presumably subject to extreme line broadening as a result of co-ordination to cobalt, the nucleus of which exhibits a quadrupole moment.

A sharp singlet is observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (5) suggesting the illustrated structure in which the phosphine ligand is co-ordinated to molybdenum. In accord with this conclusion the ^1H n.m.r. resonance of the C_5H_5 group again exhibits a doublet splitting, J_{PH} = 1.6 Hz. This is further supported by the high frequency (2 052 and 2 015 cm^{-1}) of the two ν(CO) modes in the i.r. spectrum since the alternative structure containing a Co(CO)(PEt_3) moiety might be expected to result in a ν(CO) mode with a frequency similar to that of (6) (1 962 cm^{-1}). Although not isolated, small quantities of a species exhibiting two CO modes similar to those of (5) were detected during the reaction of (2b) with PEt_3 indicating that CO substitution in (2b) initially involves displacement of the carbonyl attached to tungsten. Consequently these reactions provide further illustrations of the ability of hexafluorobut-2-yne to activate carbonyl ligands towards substitution in Group 6 metal complexes.[15] The observation that the CO stretching frequency in $[WBr_2(CO)(CF_3C{\equiv}CCF_3)_2]$ is significantly higher than that of free carbon monoxide [3] suggests that this may be due to the extreme π-acceptor ability of $CF_3C{\equiv}CCF_3$ which reduces the ability of the metal to π back-donate effectively to the carbonyl ligand thus weakening the M–CO bond.

The third product of the reaction of (1) with $[Co_2(CO)_8]$ has the formula $M(C_5H_5)(CO)_3(C_8F_{11})$ (3) according to elemental analysis and mass spectrometry. However, the i.r. spectra indicate that only two terminally bonded carbonyl ligands are present while two other prominent bonds are observed near 1 750 and 1 680 cm^{-1} which may be assigned respectively as ν(>C=O) and ν(C=C) modes. The ^{19}F n.m.r. spectra contain five distinct multiplets, integrated ratio 3 : 3 : 3 : 1 : 1, suggesting three distinct CF_3 environments and a CF_2 group. These data and the results of ^{19}F decoupling experiments can be explained in terms of two possible structures (3) and (3′), the $^{19}F\text{–}^{19}F$ coupling connectivities for the molybdenum complex (3a) being as follows: δ_1 – 48.82 (qq, J_{ba} = 8.9, J_{bc} = 9.9, $CF_3{}^b$); δ_2 – 55.71 (q, J_{ab} = 8.9, $CF_3{}^a$); δ_3 – 56.26 (dq, J_{cd} = 26.6, J_{cb} = 9.8, $CF_3{}^c$); δ_4 – 75.84 (dq, J_{dc} = 26.6, J_{de} = 8.5, F^d); and δ_5 – 81.58 p.p.m. (d, J_{ed} = 8.5 Hz, F^e). Complex (3) is structurally related to η^3-lactone complexes $[M\{\eta^3\text{-}CRCRCR'C(O)O\}(CO)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, R = Me, R′ = Me or CF_3;[16] M = W, R = CF_3, R′ = SMe [17]) while (3′) can be compared with $[Mo\{C(O)(CMe)_4C(CF_3)O\}(CO)(\eta^5\text{-}C_5H_5)]$,[16] both of which have been isolated from reactions of alkynes with $[MX(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = alkyl or SMe). It is not possible to distinguish between (3) and (3′) with the data available except that the mass spectra of (3) exhibit ions $[P]^{2+}$, $[P - CO]^+$, $[P - 2CO]^+$, and $[P - 2CO + F]^+$ but no ion $[P - 3CO]^+$ which might possibly be observed with structure (3′).

It appears that (3) is formed during the reaction of (1) with $[Co_2(CO)_8]$ as a result of fluorine abstraction from a CF_3 group, presumably by a cobalt carbonyl moiety. Previously CF_3 groups on hexafluorobut-2-yne have been found to undergo nucleophilic attack by metal carbonyl anions affording metallated perfluoroallenyl derivatives $[M\{CF_3\text{–}C{=}C{=}CF_2\}]$ [18] in accord with this suggestion. Thermolysis of complexes (2) and (4) did not produce (3) even at 80 °C in hexane thus eliminating two alternative mechanistic possibilities.

In conclusion it appears that binuclear units can be constructed from mononuclear bis(alkyne) complexes (1) despite the fact that both sets of π-orbitals on the alkynes are apparently involved in bonding to the metal. Moreover, the demonstration that bis(μ-alkyne) complexes can act as precursors to metallacyclopentadiene derivatives may prove to have more widespread significance in the context of metallacycle formation in reactions of alkynes with metal complexes.

Experimental

The complexes $[MCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) were synthesised by known methods [8] while $[Co_2(CO)_8]$ was obtained commercially (Strem) and recrystallised before use. Reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were refluxed over calcium hydride and distilled under nitrogen before use. Infrared spectra were recorded as solutions on a Perkin-Elmer 580 spectrometer. N.m.r. spectra were recorded on a Bruker WP 200 SY spectrometer at 200.13 (^1H), 188.31 (^{19}F), and 81.02 MHz (^{31}P) in $CDCl_3$; chemical shifts are referred to $SiMe_4$, CCl_3F, and 85% H_3PO_4 (aqueous) respectively. Mass spectra were obtained at 70 eV on a Vacuum Generators updated AEI MS 9.

$[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ + $[Co_2(CO)_8]$, *Open System*.—The complex $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.5 g, 0.96 mmol) and $[Co_2(CO)_8]$ (1.0 g, 2.9 mmol) were dissolved in diethyl ether (50 cm^3) in a 150-cm^3 Schlenk tube under nitrogen. The mixture was stirred for 48 h and the volatiles removed. Excess $[Co_2(CO)_8]$ was sublimed off onto a cold-finger and the residue extracted with diethyl ether and filtered off. Recrystallisation from diethyl ether–hexane at −20 °C gave a mixture of $[MoCo(CO)_3(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (2a) and $[Co_4(CO)_{12}]$. The latter was removed by oxidation (exposure to air) leaving orange-red crystals of (2a) which were recrystallised again. Yield 0.34 g, 56%. The insoluble residue after the ether extraction was extracted with

dichloromethane, filtered, and on addition of hexane and cooling to −20 °C yellow crystals of $[Mo(CO)_2\{\eta^3\text{-}C_4(CF_3)_3CF_2CO\}(\eta^5\text{-}C_5H_5)]$ (3a) were obtained. Yield 11 mg, 2%.

$[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ + $[Co_2(CO)_8]$, *Open System.*—Complex (1b) (0.3 g, 0.49 mmol) was similarly reacted with $[Co_2(CO)_8]$ (0.6 g, 1.74 mmol), to give (2b) (0.22 g, 62%) and (3b) (5 mg, 1.6%).

$[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ + $[Co_2(CO)_8]$, *Closed System.*—Complex (1a) (0.3 g, 0.58 mmol) and $[Co_2(CO)_8]$ (0.6 g, 1.74 mmol) in diethyl ether (40 cm³) were reacted at 35 °C in a sealed tube for 20 d. Volatiles were removed and excess $[Co_2(CO)_8]$ sublimed off as before, $[Co_4(CO)_{12}]$ was allowed to oxidise and the reaction mixture extracted with diethyl ether and filtered. Addition of hexane, followed by partial removal of solvent *in vacuo*, and cooling to −20 °C gave large dark red crystals of $[MoCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (4a) (0.21 g, 56%) and small orange-red crystals of (2a) (25 mg, 7%). Extraction of the ether-insoluble residue with dichloromethane as before gave yellow crystals of (3a) (8 mg, 2.5%). Shorter reaction times gave lower yields of (4a) but higher yields of (2a), while higher reaction temperatures gave increased yields of (4a).

$[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ + $[Co_2(CO)_8]$, *Closed System.*—Complex (1b) (0.3 g, 0.49 mmol) and $[Co_2(CO)_8]$ (0.6 g, 1.74 mmol) were reacted similarly for 28 d at 35—40 °C. Work-up as before gave $[WCo(CO)_4\{C_4(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$ (4b) (0.14 g, 38%), (2b) (0.09 g, 25%), and (3b) (4 mg, 1.3%).

$[MoCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (2a) + CO.—Complex (2a) (20 mg, 0.038 mmol) in diethyl ether (30 cm³) was reacted in an autoclave (100 cm³) with carbon monoxide (5 atm) at 50 °C for 20 h. The reaction solution was filtered and hexane added. Partial removal of solvent *in vacuo* followed by cooling to −20 °C gave (4a). Yield 14 mg, 67%.

$[MoCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (2a) + PEt_3.—Complex (2a) (30 mg, 0.057 mmol) in hexane (20 cm³) was reacted with PEt_3 (30 mg, 0.25 mmol) in a sealed tube at 60 °C for 30 min. On partial removal of solvent *in vacuo* and cooling to −20 °C dark red crystals of $[MoCo(CO)_2(PEt_3)(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (5) were obtained. A further crystallisation from diethyl ether–hexane gave analytically pure crystals. Yield 22 mg, 64%.

$[WCo(CO)_3(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (2b) + PEt_3.—Complex (2a) (20 mg, 0.028 mmol) and PEt_3 (20 mg, 0.17 mmol) in diethyl ether (20 cm³) at 60 °C similarly gave dark red crystals of $[WCo(CO)(PEt_3)_2(\mu\text{-}CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (6) from diethyl ether–hexane at −20 °C. Yield 5 mg, 28%.

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