Cymantrenylmethylidyne, $\equiv C-C_5H_4Mn(CO)_3$, as a Bridging Ligand for Polymetallic Assembly

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The reaction of $[Mn(CO)_3(\eta^5\text{-}C_5H_4Li)]$ with $[M(CO)_6]$, $(CF_3CO)_2O$ and L_2 [M = W, L_2 = *N,N,N',N'*-tetramethylethylenediamine (tmen); M = Mo, L_2 = 2,2'-bipyridyl (bipy)] affords the cymantrenylmethylidyne complexes $[MMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5L_2(O_2CCF_3)]$. One manganese-bound carbonyl ligand in the alkylidynetungsten complex is photolabile in tetrahydrofuran leading to $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_4(thf)(tmen)(O_2CCF_3)]$. Treating the molybdenum complex with $NaC_5H_5\cdot MeOC_2H_4OMe$ or $K[HB(pz)_3]$ (pz = pyrazol-1-yl) provides the complexes $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5L']$ [L' = $\eta\text{-}C_5H_5$ or $HB(pz)_3$]. Reactions of the former with $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) or $[Co_2(CO)_8]$ give the penta- and tetra-metallic compounds $[Mo_2Mn_2Ni(\mu_3\text{-}\sigma:\sigma':\eta^5\text{-}CC_5H_4)_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ and $[MoMnCo_2(\mu_4\text{-}\sigma:\sigma':\sigma'':\eta^5\text{-}CC_5H_4)(CO)_{11}(\eta\text{-}C_5H_5)]$. Treatment of $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(tmen)(O_2CCF_3)]$ with $[NH_2Et_2][S_2CNEt_2]$ provides a complex $[WMn(\mu\text{-}\eta^2:\eta^5\text{-}SCHC_5H_4)(CO)_4(S_2CNEt_2\text{-}S,S')(\eta^2\text{-}SCNEt_2)]$ bearing the unusual $S{=}CHC_5H_4$ ligand.

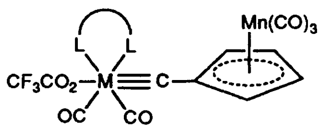
The chemistry of heteropolymetallic compounds with alkylidyne ligands which bridge exclusively through the alkylidyne carbon has been extensively developed by Stone and co-workers.[1,2] Complexes wherein the alkylidyne substituent also participates in the bridging are less well studied but include complexes of the cymantrenylmethylidyne $\equiv C-C_5H_4Mn(CO)_3$,[3] ferrocenylmethylidyne[4] and ruthenocenylmethylidyne[5] moieties.

Recently polymetallic ensembles supported by the 1,1'-ferrocenediyl di(methylidyne)[6] and chromium tricarbonyl anisylmethylidyne[7] bridges have been described. Reactions of the latter class of complexes were hampered by the facile elimination of the $Cr(CO)_3$ group, however in general cyclopentadienyl co-ordination is less labile than that of simple neutral arenes. Accordingly, we turn our attention in this paper to the use of fulvenylidene (CC_5H_4) as a support for heteropolymetallic assembly.

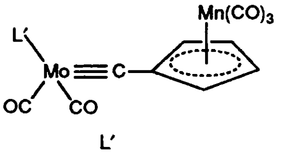
Results and Discussion

Cymantrene, $[Mn(CO)_3(\eta\text{-}C_5H_5)]$, is readily lithiated by *n*-butyllithium providing $[Mn(CO)_3(\eta^5\text{-}C_5H_4Li)]$.[8] This reagent was found by Fischer *et al.*[3] to react with $[W(CO)_6]$ leading to the bimetallic acylate $[WMn\{\mu\text{-}\sigma:\eta^5\text{-}C(OLi)C_5H_4\}(CO)_8]$. Ethylation with $[OEt_3]BF_4$, followed by treatment with aluminium bromide provided the cymantrenylmethylidyne tungsten complex $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_7Br]$ **1** in 26% yield. We required a more convenient and higher yielding entry into alkylidyne tungsten complexes bearing cymantrenyl substituents and have developed one based on methods described by Mayr *et al.*[9] for simple alkyl- and aryl-methylidynes.

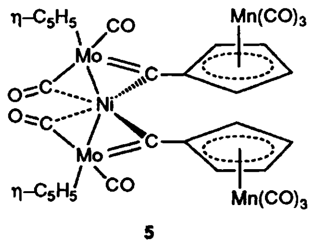
Successive treatment of $[W(CO)_6]$ with $[Mn(CO)_3(\mu\text{-}C_5H_4Li)]$, trifluoroacetic anhydride and *N,N,N',N'*-tetramethylethylenediamine (tmen) in diethyl ether provides an air and thermally stable bimetallic complex $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(tmen)(O_2CCF_3)]$ **2a**. The complex precipitates from solution as bright yellow needles in analytically pure form and in yields of approximately 67–73%; however chromatographic work-up of the supernatant liquor provides yields in excess of 90%. Spectroscopic data for **2a** and the other new complexes described herein are collected in Tables 1 and 2. The presence of an alkylidyne ligand in **2a** is indicated by the appearance of a singlet resonance in its $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 259.8.



	L L	M
2a	tmen	W
2b	bipy	Mo



L'
4a $\eta\text{-}C_5H_5$
4b $HB(pz)_3$



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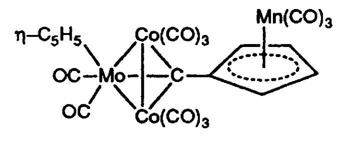

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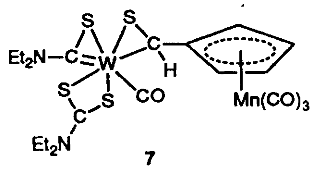

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Table 1 Analytical * and physical data for the complexes

Compound	Colour	IR(CH_2Cl_2)	Analyses (%)	
		$\nu_{max}(CO)/cm^{-1}$	C	H
2a $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(tmen)(O_2CCF_3)]$	Yellow	2025s, 1991s, 1940vs, 1903s	32.9 (33.4)	3.1 (3.0)
2b $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(bipy)(O_2CCF_3)]$	Orange	2028s, 2003s, 1941vs, 1925 (sh)	43.1 (43.4)	1.6 (1.9)
4a $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(\eta\text{-}C_5H_5)]$	Orange	2029s, 1997s, 1948vs, 1927 (sh)	44.0 (44.5)	2.4 (2.1)
4b $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5\{HB(pz)_3\}]$	Salmon	2027vs, 1996s, 1947vs, 1914s	41.0 (41.4)	2.8 (2.4)
5 $[Mo_2Mn_2Ni(\mu_3\text{-}\sigma:\sigma':\eta^5\text{-}CC_5H_4)(CO)_{10}(\eta\text{-}C_5H_5)_2]$	Bronze	2022vs, 1987m, 1971m, 1942vs, 1818m (br)	41.7 (41.6)	2.0 (2.0)
6 $[MoMnCo_2(\mu_4\text{-}\sigma:\sigma':\sigma'':\eta^5\text{-}CC_5H_4)(CO)_{11}(\eta\text{-}C_5H_5)]$	Green	2083w, 2072w, 2056w, 2032vs, 2020vs, 1933s, 1859w (br)	37.4 (36.8)	1.6 (1.3)
7 $[WMn(\mu\text{-}\eta^2:\eta^5\text{-}SCHC_5H_4)(CO)_4(S_2CNEt_2\text{-}S,S')(\eta^2\text{-}SCNEt_2)]$	Green	2020s, 1941vs (br)	33.2 (33.2)	3.0 (3.5)

* Calculated values given in parentheses.

Table 2 Hydrogen-1 and carbon-13 data [a] for the complexes

Compound	$^1H(\delta)$	$^{13}C(\delta)$ [b]
2a	2.70, 2.89, 3.16 (s × 3, 16 H, tmen), 4.59, 4.94 (s × 2, 4 H, C_5H_4)	259.8 (W≡C), 224.5 (br, MnCO), 220.2 [*J*(WC) 177, WCO], 160.5 [q, *J*(FC) 36, CO_2], 115.9 [q, *J*(FC) 292, CF_3] 107.5 (C^1 of C_5H_4), 86.1, 80.4 (C^{2-5} of C_5H_4), 60.6, 56.7, 50.6 (tmen)
2b	4.50, 4.96 [br s × 2, 4 H, C_5H_4], 7.56, 8.09, 8.17, 9.18 [m × 4, 8 H, bipy]	275.0 (Mo≡C), 223.9 (br, MnCO), 223.5 (MoCO), 154.4, 153.9, 139.8, 126.0, 122.1 (bipy), 103.1 (C^1 of C_5H_4), 86.3, 80.7 (C^{2-5} of C_5H_4)
4a	4.56, 5.11 (s × 2, 4 H, C_5H_4), 5.58 (s, 5 H, C_5H_5)	295.5 (Mo≡C), 227.4 (MoCO), 222.9 (br, MnCO), 102.7 (C^1 of C_5H_4), 92.9 (C_5H_5), 82.4, 81.1 (C^{2-5} of C_5H_4)
4b	3.78 [br s, 1 H, BH], 4.60, 5.15 (s × 2, 4 H, C_5H_4), 6.15, 6.23, 7.26, 7.60, 7.66, 7.88 [br s × 6, 9 H, $C_3H_3N_2$]	279.1 (Mo≡C), 224.8 (MoCO), 224.0 (br, MnCO), 144.2, 142.9 (2:1, C^3 of $C_3N_2H_3$), 135.4, 105.3 ($C^{4,5}$ of $C_3N_2H_3$), 102.7 (C^1 of C_5H_4), 86.5, 80.6 (C^{2-5} of C_5H_4)
5	4.57, 4.68, 4.91, 5.00 (s × 4, 8 H, C_5H_4), 5.64 (s, 10 H, C_5H_5)	317.3 (μ-*C*R), 239.9 (μ-CO), 226.3 (MoCO), 224.0 (br, MnCO), 109.5 (C^1 of C_5H_4), 93.1 (C_5H_5), 88.4, 87.5, 82.4, 80.6 (C^{2-5} of C_5H_4)
6	4.54, 4.95 (s × 2, 4 H, C_5H_4), 5.26 (s, 5 H, C_5H_5)	258.8 (μ_3-*C*R), 225.0 (br, MnCO), 208.3 [vbr, $MoCo_2(CO)_8$], 127.4 (C^1 of C_5H_4), 91.7 (C_5H_5), 85.6, 79.5 (C^{2-5} of C_5H_4)
7	1.14–1.30 (m, 12 H, NCH_2CH_3), 3.30–3.98 (m × 3, 8 H, NCH_2), 4.41, 4.59, 4.66, 4.88, 4.99 (s × 5, 5 H, C_5H_4 and CHS)	256.0 [*J*(WC) 112, SCN], 225.7 (br, MnCO), 225.4 (S_2CN), 216.7 [*J*(WC) 146, WCO], 214.7 [*J*(WC) 73, CHS], 115.5 (C^1 of C_5H_4), 81.7, 81.2, 81.0, 80.9 (C^{2-5} of C_5H_4), 51.7, 50.3, 45.8, 44.6 (NCH_2), 14.2, 13.8, 12.7, 12.1 (CH_3)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at room temperature in $CDCl_3$. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$.

Two resonances are observed in the carbonyl region, one of which is slightly broader and to lower field (δ 224.5) which may be assigned to the $Mn(CO)_3$ group. That to higher field shows tungsten-183 satellites [δ 220.2, *J*(WC) 177 Hz] and considered in combination with the appearance of four infrared-active ν(CO) bands {tetrahydrofuran: 2023, 1937 [$Mn(CO)_3$], 1990, 1904 cm^{-1} [$W(CO)_2$]} confirms the anticipated *trans* disposition of the trifluoroacetate and alkylidyne ligands.

Much of the derivative chemistry of the thermally substitution-inert complex $[Mn(CO)_3(\eta\text{-}C_5H_5)]$ relies on the facile photoextrusion of carbon monoxide in donor solvents, in particular tetrahydrofuran (thf) wherein the ether complex $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$ is obtained in virtually quantitative spectroscopic (IR) yield.[10] The effect of substituting a cyclopentadienyl ring proton on cymantrene for a $-C{\equiv}W(CO)_2(tmen)(O_2CCF_3)$ group has virtually no effect on the electron density at the manganese centre {$[Mn(CO)_3(\eta\text{-}C_5H_5)]$: ν(CO) 2021, 1934 cm^{-1} (thf)} and so it is not surprising that irradiation of a yellow thf solution of **2a** leads to the formation of a deep burgundy solution and the development of new infrared bands at 1983m, 1927s, 1894vs and 1857m cm^{-1}. The solvent-stabilised complex $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$ generated under similar conditions has infrared activity at 1928 and 1852 cm^{-1} and thus it would appear that a similar reaction has occurred to provide solutions of $[WMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_4(thf)(tmen)(O_2CCF_3)]$ **3**. As in the case of $[Mn(CO)_2(thf)(\eta\text{-}C_5H_5)]$, attempts to isolate **3** from solution have so far been unsuccessful, however the reaction is spectroscopically quantitative (IR).

The synthesis of a molybdenum derivative $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5(bipy)(O_2CCF_3)]$ **2b** (bipy = 2,2′-bipyridyl) proceeds in a manner completely analogous to that described above for **2a** with the exception that **2b** is somewhat more light- and air-sensitive in the solid state than the tungsten complex **2a**. Characteristic data for **2b** are collected in Tables 1 and 2 and suggest that the complex has a similar structure to **2a**.

We find that using bipy as the diamine chelate rather than tmen provides complexes more amenable to conversion to half-sandwich derivatives than those bearing tmen ligands. Thus whilst we have been unable to replace the tmen and trifluoroacetate ligands in **2a** with either of the facially capping cyclopentadienyl or hydrotris(pyrazol-1-yl)borato groups, the reactions of salts of these anions with **2b** lead in high yield to the derivatives $[MoMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5L']$ [L′ = $\eta\text{-}C_5H_5$ **4a** or $HB(pz)_3$ **4b** (pz = pyrazol-1-yl)]. The orange cyclopentadienyl derivative **4a** is sufficiently volatile for electron impact mass spectrometry and a molecular ion is observed which shows the correct isotope cluster in addition to peaks due to $[M - n\mathrm{CO}]^+$ (n = 3, 4 or 5) and $[M - 5\mathrm{CO} - \mathrm{Mn}]^+$. Apparently the loss of three carbonyl ligands is more facile than that of the remaining two, suggesting an increased lability for the carbonyls bound to manganese, consistent with the photochemical results obtained for **2a**. The ion resulting from the loss of the manganese atom is followed by a series of ions corresponding to the degradation of the $\mathrm{CC_5H_4}$ ligand *via* loss of $\mathrm{C_2H_2}$, $\mathrm{C_4H_4}$, $\mathrm{C_5H_4}$ and $\mathrm{C_6H_4}$.

The cyclopentadienyl derivative **4a** is an ideal candidate for the synthesis of polymetallic species: reactions with $[\mathrm{Ni(cod)_2}]$ (cod = cycloocta-1,5-diene) or $[\mathrm{Co_2(CO)_8}]$ provide the penta- and tetra-metallic cluster compounds $[\mathrm{Mo_2Mn_2Ni(\mu_3\text{-}\sigma:\sigma':\eta^5\text{-}CC_5H_4)_2(CO)_{10}(\eta\text{-}C_5H_5)_2}]$ **5** and $[\mathrm{MoMnCo_2(\mu_4\text{-}\sigma:\sigma':\sigma'':\eta^5\text{-}CC_5H_4)(CO)_{11}(\eta\text{-}C_5H_5)}]$ **6**. The bronze nickel derivative **5** features the trimetallaspiropentadiene or 'bow-tie' configuration which has been observed in other examples of this reaction with simpler alkylidyne substituents.[1,2,6,11] The NMR data for the cluster compound **5** indicate that the two fulvenylidene bridging ligands are chemically equivalent but that the mirror symmetry present in **4a** is destroyed upon nickel complexation, the molecule having overall C_2 symmetry and diastereotopic pairs of carbon atoms in the $\mathrm{C_5H_4}$ rings. Thus five signals of equal intensity are observed at δ 109.5, 88.4, 87.5, 82.4 and 80.6 in the ^{13}C NMR spectrum of **5** compared with three signals in the spectrum of **4a** at δ 102.7, 82.4 and 81.1. In the case of simple arylmethylidyne derivatives[11] the faces and atoms of the freely rotating aryl rings are prochiral. A similar situation arises in the case of $[\mathrm{Cr_2Mo_2Ni(\mu_3\text{-}\sigma:\sigma':\eta^6\text{-}CC_6H_4OMe\text{-}2)(CO)_{10}(\eta\text{-}C_5H_5)_2}]$[7] except that whilst the faces of the anisyl group in the precursor complex $[\mathrm{CrMo(\mu\text{-}\sigma:\eta^6\text{-}CC_6H_4OMe\text{-}2)(CO)_5(\eta\text{-}C_5H_5)}]$ are prochiral in the absence of $\mathrm{Cr(CO)_3}$ substituents, the atoms are all chemically distinct because of the asymmetric *ortho* substitution of the ring. The dicobalt species **6** appears on the basis of spectroscopic and elemental microanalytical data to be isostructural with the known aryl- and alkyl-methylidyne derivatives $[\mathrm{MCo_2(\mu_3\text{-}CR)(CO)_8L''}]$ [M = Cr, Mo or W; L″ = η-$\mathrm{C_5H_5}$ or HB(pz)$_3$].[12]

Mayr *et al.*[13] have reported an unusual reaction of the compounds $[\mathrm{W(\equiv CR)(CO)_2(py)_2Br}]$ (R = Me or Ph, py = pyridine) with $[\mathrm{NH_2Et_2}][\mathrm{S_2CNEt_2}]$ which leads to the thioaldehyde complexes $[\mathrm{W(\eta^2\text{-}SCNEt_2)(S_2CNEt_2\text{-}}S,S')\mathrm{(CO)(\eta^2\text{-}SCHR)}]$. We find that a similar reaction ensues with **2a** providing the related complex $[\mathrm{WMn(\mu\text{-}\eta^2:\eta^5\text{-}SCHC_5H_4)(CO)_4(S_2CNEt_2\text{-}}S,S')\mathrm{(\eta^2\text{-}SCNEt_2)}]$ **7**. As expected for the tmen chelated complex **2a** the reaction time is considerably slower (1 week) than for the bis(pyridine) derivatives.

Experimental

All manipulations were carried out using conventional Schlenk-tube techniques under an atmosphere of oxygen-free nitrogen. Light petroleum refers to that fraction of b.p. 40–60 °C. All solvents were dried and deoxygenated prior to use. Spectroscopic data were obtained using Perkin Elmer 1720-X (FT-IR), and JEOL JNM-EX 270 (^{1}H and ^{13}C NMR) instruments. The reagent $[\mathrm{Mn(CO)_3(\eta^5\text{-}C_5H_4Li)}]$ was prepared according to a published procedure.[8] Chromatography was performed using Brockman activity 2 alumina. All compounds described were mildly air- and light-sensitive and were stored under nitrogen in the dark (−20 °C) but could be handled briefly as solids in air.

Synthesis of Compounds $[\mathrm{MMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5L_2(O_2CCF_3)}]$ (M = W, L$_2$ = *tmen* **2a**; M = Mo, L$_2$ = *bipy* **2b**).—*Compound* **2a**. A solution of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ (6.40 g, 31 mmol) in tetrahydrofuran (110 cm^3) and diethyl ether (16 cm^3) was cooled to −80 °C and treated with a solution of LiBu in hexane (1.60 mol dm^{-3}, 20.0 cm^3, 32.0 mmol) and stirred for 1 h. Solid $[\mathrm{W(CO)_6}]$ (11.0 g, 31.3 mmol) was then added and the mixture allowed to warm slowly to −10 °C and stirred at this temperature for 1 h. The yellow solution was then re-cooled to −80 °C and treated with a solution of trifluoroacetic anhydride in tetrahydrofuran (4.50 cm^3 in 50 cm^3). Neat tmen (20 cm^3) was then added and the mixture allowed to warm to room temperature and freed of volatiles under reduced pressure. The residue was extracted with dichloromethane (3 × 60 cm^3) and the combined extracts were chromatographed on a water-cooled column (8 × 25 cm) eluting with dichloromethane. The major yellow band was collected and concentrated *in vacuo* to *ca.* 40 cm^3 and then diluted with light petroleum (100 cm^3) and cooled to −80 °C overnight. The bright yellow crystalline product was isolated by decantation, washed with light petroleum (2 × 50 cm^3) and dried *in vacuo*. Yield 19.5 g (91%).

Compound **2b**. A solution of $[\mathrm{Mn(CO)_3(\eta\text{-}C_5H_5)}]$ (5.00 g, 24.5 mmol) in tetrahydrofuran (100 cm^3) and diethyl ether (15 cm^3) was treated with LiBu (15.3 cm^3, 1.60 mol dm^{-3}, 24.5 mmol) at −80 °C as in (*i*) above to provide a solution of $[\mathrm{Mn(CO)_3(\eta^5\text{-}C_5H_4Li)}]$. This was treated with solid $[\mathrm{Mo(CO)_6}]$ (6.50 g, 24.5 mmol) at −80 °C and allowed to warm to −10 °C and stirred at that temperature for 1 h. The resulting acylate solution was then cooled to −80 °C and treated dropwise with a solution of trifluoroacetic anhydride in tetrahydrofuran (3.8 cm^3 in 50 cm^3) and then allowed to warm to −10 °C and treated with solid 2,2′-bipyridyl (4.20 g, 27 mmol, 1.1 equivalents). Upon warming to room temperature a copious orange precipitate of the desired product formed which was isolated by filtration (under air), and washed with diethyl ether (2 × 20 cm^3) and dried *in vacuo*. Yield 13.5 g (87%).

Synthesis of the Complexes $[\mathrm{MMn(\mu\text{-}\sigma:\eta^5\text{-}CC_5H_4)(CO)_5L'}]$ [L′ = η-$\mathrm{C_5H_5}$ **4a** *or* HB(pz)$_3$ **4b**].—*Complex* **4a**. A suspension of **2b** (1.00 g, 1.58 mmol) and $\mathrm{NaC_5H_5\cdot MeOC_2H_4OMe}$ (0.36 g, 2.01 mmol) in diethyl ether (50 cm^3) was stirred for 20 min during which time the alkylidyne complex slowly dissolved followed by precipitation of NaCl. The latter was removed by filtration through a pad of alumina (3 × 3 cm) and the filtrate freed of volatiles *in vacuo*. The residue was extracted with diethyl ether (2 × 20 cm^3) and the combined extracts concentrated under reduced pressure to *ca.* 10 cm^3 and chromatographed on a cryostatically cooled column loaded with alumina (−30 °C, 3 × 30 cm). The orange zone was collected, freed of solvent *in vacuo* and the residue crystallised from a mixture of light petroleum (10 cm^3) and diethyl ether (5 cm^3) at −78 °C to provide orange *microcrystals* of **4a**. Yield 0.56 g (82%).

Complex **4b**. A solution of **2b** (0.13 g, 0.20 mmol) and K[HB(pz)$_3$] (0.055 g, 0.22 mmol) in diethyl ether (15 cm^3) was stirred for 1 h and then freed of volatiles *in vacuo*. The residue was treated as above to provide salmon *microcrystals* of **4b**. Yield 0.090 g (78%).

Synthesis of Polynuclear Complexes.—*Complex* **5**. A solution of **4a** (0.10 g, 0.23 mmol) and $[\mathrm{Ni(cod)_2}]$ (0.035 g, 0.12 mmol) in tetrahydrofuran (15 cm^3) was stirred for 12 h and then freed of volatiles *in vacuo*. The residue was extracted twice with a mixture of dichloromethane (5 cm^3) and light petroleum (5 cm^3) and the combined extracts chromatographed on a water-cooled column loaded with alumina (3.0 × 30 cm) eluting with the same solvent combination. The major orange zone was collected and the solvent volume reduced *in vacuo* to *ca.* 5 cm^3. Cooling the solution to −78 °C overnight provided bronze *microcrystals* of **5** which were isolated by filtration, washed with light petroleum (5 cm^3) and dried *in vacuo*. Yield 0.097 g (87%).

Complex **6**. A suspension of **4a** (0.14 g, 0.32 mmol) and $[\mathrm{Co_2(CO)_8}]$ (0.11 g, 0.32 mmol) in light petroleum (20 cm^3) was stirred for 30 min and then freed of volatiles *in vacuo*. The dark green residue was extracted with a mixture of dichloromethane (2 cm^3) and light petroleum (8 cm^3) and the extract chromatographed on a cryostatically cooled column loaded with alumina (−30 °C, 3 × 30 cm) eluting with the same solvent mixture. The major green band was collected and freed of solvent *in vacuo*. The residue was then crystallised from light petroleum (5 cm^3) at −78 °C to provide dark green microcrystals of **6**. Yield 0.16 g (68%).

Synthesis of $[WMn(\mu\text{-}\eta^2:\eta^5\text{-}SCHC_5H_4)(CO)_4(S_2CNEt_2\text{-}S,S')(\eta^2\text{-}SCNEt_2)]$ **7**.—A solution of **2a** (2.00 g, 3.00 mmol) and $[NH_2Et_2][S_2CNEt_2]$ (2.14 g, 10 mmol) in tetrahydrofuran (50 cm^3) was stirred for 7 d and then freed of volatiles under reduced pressure. The residue was extracted with dichloromethane (2 × 20 cm^3) and the combined extracts concentrated *in vacuo* to *ca.* 10 cm^3 and chromatographed on a water-cooled column loaded with alumina (3.0 × 30 cm) eluting with dichloromethane. The major green zone was collected, freed of solvent *in vacuo* and the residue crystallised from diethyl ether (5 cm^3) at −78 °C to provide dark green *microcrystals* of **7**. Yield 0.49 g (23%).

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