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NEW IRON–MOLYBDENUM AND IRON–TUNGSTEN ANIONIC CARBONYL CLUSTERS

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SUMMARY

The new polynuclear carbonyl complexes $[Me_4N]_2[(\pi\text{-}C_5H_5)_2M_2Fe_2(CO)_{10}]$ (M = Mo or W) have been synthesised and characterised by analysis, IR and NMR spectroscopy.

INTRODUCTION

Anionic polynuclear carbonyl complexes are, in general, more difficult to isolate and characterise than their neutral analogues[1–3]. In consequence their synthesis and properties have not been as thoroughly investigated, and mixed metal polynuclear carbonyl anions, in particular, have been relatively little studied. Known complexes of this type include $[MFe_2(CO)_{12}]^-$ (M = Mn[4–6], Tc[5] or Re[7,8]), $[MOs_2(CO)_{12}]^-$ (M = Mn or Re)[9,10], $[ReRu_3(CO)_{16}]^-$ [10], $[MCo_3(CO)_{12}]^-$ (M = Fe[11,12], Ru[12] and Os[13]), $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo or W)[14], $[Mo_2Ni_4(CO)_{14}]^{2-}$ [15], $[(\pi\text{-}C_5H_5)_2Ni_2Mn(CO)_5]^-$ [16] and $[Ni_2Co_4(CO)_{14}]^{2-}$ [17]. In this paper we report the preparation of two new complexes of the type, $[Me_4N]_2[(\pi\text{-}C_5H_5)_2M_2Fe(CO)_{10}]$ (M = Mo and W), which we have characterised by elemental analysis and by IR and NMR spectroscopy.

RESULTS AND DISCUSSION

The anion $C_5H_5(CO)_3Mo^-$ readily attacks $Fe_2(CO)_9$ at room temperature in tetrahydrofuran solution to give the complex anion, $[(C_5H_5)_2Mo_2Fe_2(CO)_{10}]^{2-}$, which was isolated as its tetramethylammonium salt. The stoicheiometry of this maroon complex was established by elemental analysis. The red-violet tungsten complex, $[Me_4N]_2[(C_5H_5)_2W_2Fe_2(CO)_{10}]$ was similarly obtained using $C_5H_5(CO)_3W^-$ in place of $C_5H_5(CO)_3Mo^-$. Both complexes are air-sensitive in the solid state and, as expected, are soluble only in polar solvents giving red solutions which are extremely air-sensitive.

Their NMR spectra show two singlet resonances, one at about τ 6.5 and the other in the region τ 4.6–4.8 which may be respectively assigned as being due to the

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methyl protons and to the equivalent protons on the cyclopentadienyl rings. The integrated intensity ratio of these two resonances is 12/5 which is as expected if the given formulation is correct, and the positions of the cyclopentadienyl proton resonances for both the molybdenum and tungsten complexes are close to those found for related complexes of these two metals, suggesting that the cyclopentadienyl rings remain bound to the Group VIA metal.

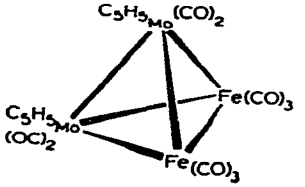
TABLE 1

INFRARED AND NMR DATA FOR THE COMPLEXES $[Me_4N]_2[(\pi\text{-}C_5H_5)_2M_2Fe_2(CO)_{10}]$ (M = Mo and W)

M	*Phase*	$\nu(CO)$ (cm^{-1})	$\tau(C_5H_5)$[a]	$\tau(CH_3)$[a]
W	nujol	1995 ms 1929 s 1888 s 1850 vs		
	CH_2Cl_2[b]	1997 w 1930 ms 1880 m(br)	4.66	6.60
	THF	1996 mw 1926 m 1884 vs 1861 ms(sh)		
Mo	nujol	1994 ms 1925 s 1887 s 1852 vs		
	CH_2Cl_2	1998 ms 1932 vs 1884 vs 1868 ms(sh)	4.74	6.54

[a] Taken in $(CD_3)_2CO$. [b] Only slightly soluble.

The infrared spectra of the complexes (Table 1) exhibit four carbonyl stretching absorptions, both in the solid state and in solution. It is reasonable to assume that bridging carbonyl groups are absent since related anionic complexes containing such groups, *e.g.* carbonylferrate anions[18], show bridging carbonyl stretching frequencies well below 1800 cm^{-1}. The relatively simple spectra obtained strongly favour a symmetrical structure, and a tetrahedral arrangement of the metal atoms as shown below seems the most probable. The symmetry of this idealised structure is C_{2v} and eight terminal carbonyl stretching absorptions $(3A_1 + 3B_1 + 2B_2)$ are expected for such a structure on the basis of group theory.



Attempted acidification of these complexes results in extensive decomposition and we were not able to isolate any neutral polynuclear carbonyl hydride complexes from the reaction mixtures.

EXPERIMENTAL

All reactions and manipulations were performed under nitrogen, and solvents were degassed before use. Infrared spectra of the complexes in the carbonyl region (2150–1600 cm^{-1}) were recorded on a Perkin–Elmer 257 grating spectrophotometer and were calibrated against carbon monoxide. NMR spectra in deuteriated acetone were taken on a Varian Associates HA-100 spectrometer operating at 100 MHz and

TMS was used as an internal reference. The starting materials were prepared by literature methods.

Reaction of $Fe_2(CO)_9$ with $C_5H_5(CO)_3Mo^-$

A solution of $C_5H_5(CO)_3Mo^-Na^+$, prepared from $[C_5H_5Mo(CO)_3]_2$ (1.00 g, 2.04 mmole) by sodium amalgam reduction in 20 ml of dry THF, was added to a suspension of $Fe_2(CO)_9$ (0.76 g, 2.1 mmole) in THF (10 ml). The mixture was stirred at room temperature in $\frac{1}{2}$ h. The residue remaining on evaporation of the solution *in vacuo* was extracted with 100 ml of water and this extract after filtration was treated with an excess of a saturated aqueous solution of $Me_4N^+Cl^-$. The precipitate was filtered, washed twice with 25 ml portions of water and dried *in vacuo* over phosphoric oxide for ca. 1 h. Extraction of this precipitate with anhydrous MeOH gave a deep red solution which, after filtration, was concentrated under a stream of nitrogen. The maroon crystalline product deposited was recrystallised from MeOH in the presence of a trace of Me_4NCl. (Yield 65%). (Found: C, 38.8; H, 3.7; N, 3.1. $C_{28}H_{34}Fe_2Mo_2N_2O_{10}$ calcd.: C, 39.0; H, 4.0; N, 3.2(5)%.)

TLC analysis of the residue left after aqueous extraction showed the presence of $[C_5H_5Mo(CO)_3]_2$ and traces of unreacted $Fe_2(CO)_9$, while $Fe(CO)_5$ was detected in the evaporated THF.

Reaction of $Fe_2(CO)_9$ with $C_5H_5(CO)_3W^-$

The reaction between $Fe_2(CO)_9$ (0.8 g, 2.20 mmole) and $C_5H_5(CO)_3W^-Na^+$, prepared from $[C_5H_5W(CO)_3]_2$ (1.34 g, 2.01 mmole) by sodium amalgam reduction, was carried out in THF (total volume 30 ml) in an analogous manner to that described above, giving reddish violet crystals of the product in 69% yield. (Found: C, 32.3; H, 3.5; N, 3.0. $C_{28}H_{34}Fe_2N_2O_{10}W_2$ calcd.: C, 32.4; H, 3.3; N, 3.7%.)

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