

Preliminary communication

**Ortho-metallation of η -pyrrolylmetal complexes
 with triosmium clusters**

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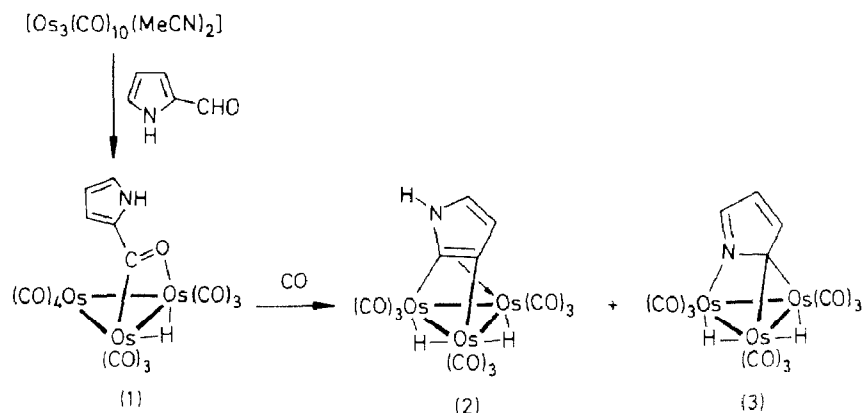
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Abstract

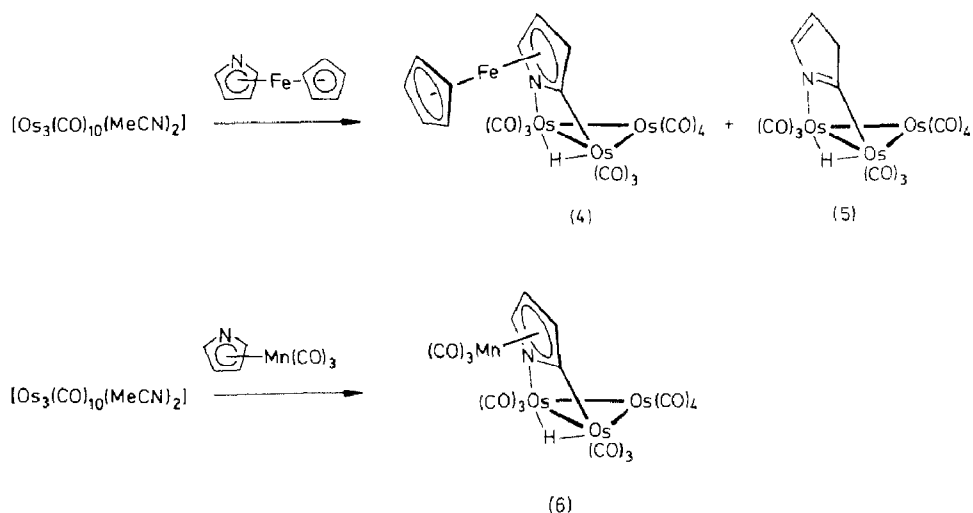
The cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts with (η -cyclopentadienyl)(η -pyrrolyl)iron [azaferrocene, $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_4\text{H}_4\text{N})$] under mild conditions to give the oxidative addition product $[\text{Os}_3\text{H}\{(\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)\}(\text{CO})_{10}]$. The group $(\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)$ acts as a three-electron donor through the *ortho*-metallated pyrrolyl ring. An analogous compounds, $[\text{Os}_3\text{H}\{(\text{C}_4\text{H}_3\text{N})\text{Mn}(\text{CO})_3\}(\text{CO})_{10}]$, is obtained by the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with $[\text{Mn}(\eta\text{-pyrrolyl})(\text{CO})_3]$.

We have previously shown that 2-formylpyrrole is useful for introducing the pyrrole ring into triosmium clusters [1]. Initially it reacts by oxidative addition of the formyl group at $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ and displacement of the acetonitrile ligands to give the corresponding acyl complex (Scheme 1). Subsequent thermal decarbonylation of the acyl derivative **1** affords the isomeric nonacarbonyl clusters **2** and **3**. X-ray structures of **1**, **3**, and the *N*-methyl substituted form of **2** have all been determined [2,3].

The fact that η -pyrrolyl is a ligand equivalent to η -cyclopentadienyl and that its complexes have appreciable stability led us to investigate their interaction with Os_3 clusters. As expected, azaferrocene and (η -pyrrole)tricarbonylmanganese [4] are much more reactive by oxidative addition with triosmium clusters than is pyrrole itself; there is an available lone-pair at nitrogen in the complexed forms for initial coordination. Oxidative addition of pyrrole with $[\text{Os}_3(\text{CO})_{12}]$ occurs at high temperatures (170 °C) whereas $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts in 2 h with azaferrocene in refluxing dichloromethane to give only two isolable products: $[\text{Os}_3\text{H}\{(\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)\}(\text{CO})_{10}]$ (**4**) (60%) and $[\text{Os}_3\text{H}(\text{C}_4\text{H}_4)(\text{CO})_{10}]$ (**5**) (23%) as shown in Scheme



Scheme 1.



Scheme 2.

2. Clusters **4** and **5** were separated by chromatography on Florisil as air-stable orange and orange-red crystals respectively.

Cluster **5** can be accounted for by breakdown of azaferrocene but we do not know the stage at which this occurs. Pyrrole itself reacts with $[\text{Os}_3(\text{CO})_{12}]$ to give **5** but only along with compounds **2** and **3** and does not react with the bis-acetonitrile cluster in dichloromethane [1,3]. We believe that **4** and **5** are each formed from an intermediate that is formed by reaction of azaferrocene with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$.

The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with $[\text{Mn}(\text{C}_4\text{H}_4\text{N})(\text{CO})_3]$ in refluxing cyclohexane over 4 h gives yellow crystals in moderate yield (37%) of a cluster related to **4**, $[\text{Os}_3\text{H}\{(\text{C}_4\text{H}_3\text{N})\text{Mn}(\text{CO})_3\}(\text{CO})_{10}]$ (**6**). At this stage in our work clusters **4** and **6** (Scheme 2) have been characterised mainly by their IR and ^1H NMR data (Table 1). IR carbonyl spectra for **4** and **6** are very similar in pattern except for three extra absorptions at 2038, 1964, and 1960 cm^{-1} for **6**, which we assign to the $\text{Mn}(\text{CO})_3$ group. Apart from these extra peaks, the IR spectra of **4** and **6** are quite close to those of the μ -2-pyridyl cluster $[\text{Os}_3\text{H}(\text{C}_5\text{H}_3\text{N})(\text{CO})_{10}]$ and of other related *ortho*-metallated nitrogen-heterocyclic compounds [5–8]. This supports

Table 1

Some spectroscopic data for clusters $[\text{Os}_3\text{H}(\mu\text{-X})(\text{CO})_{10}]$ (**4** and **6**), where $\text{X} = (\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)$ and $(\text{C}_4\text{H}_3\text{N})\text{Mn}(\text{CO})_3$, respectively

Compound	X	$\nu(\text{CO})^a$ (cm^{-1})	$^1\text{H NMR} (\delta)^b$
(4)	$(\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)$	2103m, 2061vs, 2051s	5.76(br) 1H
		2020vs, 2011s, 2001m	4.64(dd) 1H
		1982m, 1972w	4.50(dd) 1H
			4.30(s) C_5H_5
			-13.7(s) OsH
(6)	$(\text{C}_4\text{H}_3\text{N})\text{Mn}(\text{CO})_3$	2107m, 2068vs, 2059vs	6.40(br) 1H
		2038m*, 2025vs, 2009vs	5.20(dd) 1H
		1997m, 1981m, 1964m*	4.70(dd) 1H
		1960m*	-13.9(s) OsH

^a Cyclohexane solution. The absorptions marked with * are assigned to the $\text{Mn}(\text{CO})_3$ group. ^b 60 MHz at room temperature.

the N–C mode of attachment to the osmium atoms. The IR data in Table 1 indicate that the iron group $(\text{C}_4\text{H}_3\text{N})\text{Fe}(\text{C}_5\text{H}_5)$ is a better donor and/or poorer acceptor than the corresponding Mn group in **6** since the $\nu(\text{CO})$ frequencies for the cluster are lower in the iron case.

The $^1\text{H NMR}$ spectra of **4** and **6** (Table 1) confirm *ortho*-metallation, but the hydride signals (δ -13.7 and -13.9, respectively) are somewhat shifted from those of related compounds, for example there is a signal at δ -15.1 for cluster **5**. The structures in Scheme 2 seem the most probable and we are trying to grow crystals suitable for single-crystal X-ray structure determination*. Crystal structures are needed to confirm the proposed structures and would also indicate how closely the Fe and Mn atoms approach the hydride ligands and whether or not there is any direct Fe–H or Mn–H bonding. The heterocyclic ring in **5** is at 75° to the metal plane and we would expect a similar tilt in **4** and **6**, with the Fe and Mn bent down towards the hydride as illustrated.

References

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* *Note added in proof.* The X-ray structures of **4** and **6** have now been determined (A.J. Deeming and N.I. Powell, unpublished results); the representations in Scheme 2 are correct and there are no direct Fe–H or Mn–H bonds.