A New Type of Pyrrole Co-ordination: μ_3-Pyrrole-2,3-diyl Triosmium Complexes

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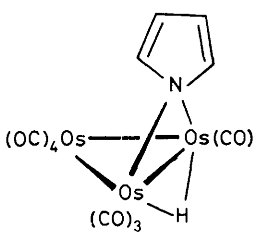
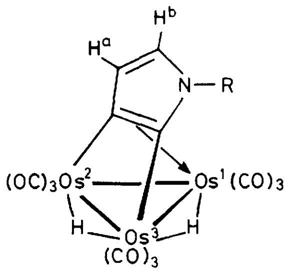
Pyrrole reacts with $[Os_3(CO)_{12}]$ in refluxing decalin to give $[Os_3H_2(CO)_9(\mu_3\text{-}C_4H_2NH)]$ (yield 54%) which is analogous to the benzene derivative $[Os_3H_2(CO)_9(\mu_3\text{-}C_6H_4)]$ and is not related to known pyrrolyl complexes such as $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)]$ in which the pyrrolyl is deprotonated at nitrogen. *N*-Methylpyrrole forms a directly related compound differing, however, in its much faster exchange of the hydrido-ligands.

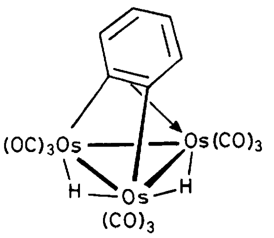
Pyrrole (5-azacyclopentadiene, C_4H_5N) forms σ-*N* and η^5-pyrrolyl complexes, which are related to cyclopentadienyl complexes. Direct reaction of pyrrole with $[Mn_2(CO)_{10}]$ or of potassium pyrrolyl with $[MnBr(CO)_5]$ gives $[Mn(CO)_3(\eta^5\text{-}C_4H_4N)]$ which is directly related to $[Mn(CO)_3(\eta^5\text{-}C_5H_5)]$.[1-3] In some ways the chemistry of η^5-pyrrolyl relates to that of η^5-cyclopentadienyl in that it may be acetylated by electrophilic substitution. In this way a bridging pyrrolyl, σ-*N*-bonded at one manganese and η^5-co-ordinated at another manganese atom, was obtained.[4] $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)]$ is known,[2,5-7] the $\eta^5\text{-}C_4H_4N$ ligand of which may be converted to $\sigma\text{-}N\text{-}C_4H_4N$ by uptake of ligands to give $[Fe(\eta^5\text{-}C_5H_5)L_2(\sigma\text{-}N\text{-}C_4H_4N)]$ (L = CO, CNMe, *etc.*).[7] *N*-Bonded titanium and zirconium compounds have also been characterised.[8] In all these reported examples the NH hydrogen atom of pyrrole has been lost as a proton. We will now describe complexes in which for the first time C–H rather than N–H bond cleavage has occurred.



(1)



(2); R = H
(3); R = Me



(4)

Results and Discussion

$[Os_3(CO)_{12}]$, or better $[Os_3(CO)_{10}(NCMe)_2]$, reacts with primary amines to give among the products μ-amido-complexes of type $[Os_3H(CO)_{10}(NHR)]$. The NHR ligand is a three-electron donor and for pyrrole to behave in this way the nitrogen would need to be tetrahedral requiring a loss of π-electron delocalisation. We expected therefore that $[Os_3H(CO)_{10}(\mu\text{-}C_4H_4N)]$ (1) would not be formed readily and that other products might be available. Indeed, the direct thermal reaction of $[Os_3(CO)_{12}]$ with pyrrole gives a compound analysing as $[Os_3(CO)_9(C_4H_5N)]$ but which is the dihydride $[Os_3H_2(CO)_9(\mu_3\text{-}C_4H_2NH)]$ (2). Observation of a ^1H n.m.r. singlet (δ 7.54 p.p.m.) and ν(NH) in the i.r. spectrum (absorptions at 3 670 and 3 600 cm^{-1}, Nujol mull) confirm that the N–H bond remains. No exchange of this hydrogen atom occurs with D_2O. Furthermore, only two hydrogen atoms remain bonded to carbon and the AB (^1H n.m.r.) quartet shows that these are adjacent. The i.r. spectrum around 2 000 cm^{-1} is extremely similar to that of $[Os_3H_2(CO)_9(\mu_3\text{-}C_6H_4)]$ (4): data for (2) with those for (4) in parentheses (both in C_6H_{12}) 2 109 (2 109), 2 084 (2 082), 2 055 (2 056), 2 030 (2 035), 2 027 (2 025), 2 010 (2 010), 2 000 (2 000), and 1 982 (1 987, 1 984) cm^{-1}. Spectroscopic data for the *N*-methyl analogue (3) are quite similar to those for (2). These results (Table) are consistent with one of two structures, the one illustrated and an isomer identical except that the hydrogen atoms bridge the Os^1,Os^2 and Os^2,Os^3 pairs. The coalescence temperature for the exchange of osmium-bound carbon atoms of (4) is around −90 °C, so that even at −80 °C isomers of (2) may be in very rapid equilibrium by a hydride ligand migration between the Os^1–Os^3 and the Os^1–Os^2 edges. If this hydride migration is occurring it is very rapid but does not lead to exchange of the hydride ligands which we have observed at higher temperatures.

There are two pronounced differences between compounds (2) and (3). The hydride ^1H n.m.r. shifts have moved from δ −15.6 and −17.1 p.p.m. in (2) to δ −17.0 and −21.1 p.p.m. in (3), a much larger shift than would normally be expected for a simple substitution at a ligand of this sort. Secondly, the exchange between the hydride ligands is much slower in (2) (T_c = +17 °C) than in (3) (T_c = −65 °C). We have carried out a lineshape analysis of these signals to give kinetic data (see Experimental section). An interpretation of these observations is that the equilibrium position between the two possible isomers of (2) and (3) depends very much on the substitution at the nitrogen atom and that the chemical shifts are quite sensitive to the hydride positions. Exchange of the hydride ligands presumably requires an intermediate with the hydrides bridging the Os^1–Os^2 and Os^1–Os^3 pairs of metal atoms. The intermediate is more easily accessible when R = H so that exchange is faster. The differences in chemical shifts

Table. Hydrogen-1 n.m.r. data [a]

Compound	Solvent	Temp./ °C	δ/p.p.m.	Assignment	J/Hz
(2)	$CDCl_3$ [b]	27 [c]	7.43 (d) 6.65 (d)	H^a,H^b	4.2
			7.54 (s)	NH	
			−16.35 (s)	OsH	
(2)	$CDCl_3$ [b]	−40	−15.63 (d)	OsH	1.5
			−17.08 (d)	OsH	
(3)	$CDCl_3$	27	7.06 (d) 6.66 (d)	H^a,H^b	3.6
			3.60 (s)	NMe	
			−18.86 (s)	OsH	
(3)	$C_6D_5CD_3$ [d]	24	6.60 (d) 6.57 (d)	H^a,H^b	3.6
			3.10 (s)	NMe	
			−18.81 (s)	OsH	
(3)	$C_6D_5CD_3$ [d]	−80	6.69 (d) 6.47 (d)	H^a,H^b	3.6
			2.86 (s)	NMe	
			−17.0 (br)	OsH	
			−21.1 (br)		

[a] Recorded on 60 MHz unless stated otherwise; δ relative to $SiMe_4$ as standard. [b] At 100 MHz. [c] The broad hydride singlet at 27 °C becomes sharp at +70 °C. [d] At 200 MHz.

and rates of hydride exchange would thus both result from the favoured hydride positions depending upon R.

Experimental

Reaction of $[Os_3(CO)_{12}]$ *with Pyrrole.*—A solution of $[Os_3(CO)_{12}]$ (0.204 g) and pyrrole (4 cm^3) in decalin (50 cm^3) was heated under reflux for 4 h. The solvent was removed under vacuum and the residue separated by t.l.c. (SiO_2), eluting with light petroleum (b.p. 40—60 °C). Several minor bands were not characterised but there was one main yellow band which gave $[Os_3H_2(CO)_9(\mu_3\text{-}C_4H_2NH)]$ (2), as yellow crystals (0.108 g, 54%) (m.p. 163—165 °C) by dissolving the material in the minimum volume of chloroform and precipitating with pentane (Found: C, 17.6; H, 0.7; N, 1.4. $C_{13}H_5NO_9Os_3$ requires C, 17.55; H, 0.6; N, 1.55%). ν(CO) (cyclohexane) 2 109 (4), 2 084 (10), 2 055 (10), 2 030 (7), 2 027 (9), 2 010 (9), 2 000 (7), and 1 982 (5) cm^{-1} (relative intensities in parentheses); parent molecular ion observed (relative mass 895; ^{192}Os).

Reaction of $[Os_3(CO)_{12}]$ *with* N-*Methylpyrrole.*—A similar treatment of $[Os_3(CO)_{12}]$ (0.200 g) with *N*-methylpyrrole (3 cm^3) for 1.75 h gave two main yellow bands. The first gave $[Os_3H_2(CO)_9(\mu_3\text{-}C_4H_2NMe)]$ (3), as yellow crystals (0.092 g, 46%) (m.p. 165—168 °C) (Found: C, 18.75; H, 0.8; N, 1.35. $C_{14}H_7NO_9Os_3$ requires C, 18.6; H, 0.8; N, 1.55%). ν(CO) (cyclohexane) 2 110 (4), 2 080 (9), 2 054 (10), 2 031 (9), 2 026 (7), 2 004 (10), 1 993 (6), 1 983 (2), and 1 979 (5) cm^{-1}; parent molecular ion observed (relative mass 909; ^{192}Os). The other band gave yellow crystals (0.01 g) which were characterised, by comparing i.r. and ^1H n.m.r. spectra with those of authentic samples, as $[Os_3H(CO)_{10}(C_5H_4N)]$, previously prepared from $[Os_3(CO)_{12}]$ and pyridine.

Treatment of (2) *and* (3) *with* CO.—Bubbling CO through refluxing decalin solutions of (1) or (2) for 25 h gave no change in the i.r. spectra around 2 000 cm^{-1} and most of the material could be recovered unchanged.

Hydride Exchange.—The hydride exchange data for (2) were obtained from spectra recorded in the range −40 to 70 °C. Lineshape matching of these spectra with those calculated for the coalescence of two AX doublets (program DNMR3) gave the data k = 17.5 (253), 37.5 (263), 90 (273), 925 (303), and 1 730 (313) s^{-1} (temperature/K given in parentheses); $E_a = 51 \pm 6$ kJ mol^{-1} and $\log_{10}A = 11.8$. It was not possible to obtain limiting low-temperature spectra for (3); even at −90 °C fairly broad hydride singlets rather than doublets were destroyed. Spectra in the range −90 to −40 °C were used and lineshapes calculated for the coalescence of two singlets to give k = 30 (183), 98 (193), 1 880 (213), 7 250 (223), and 11 800 (233) s^{-1}; $E_a = 45 \pm 6$ kJ mol^{-1} and $\log_{10} A = 14.2$. These latter data are less reliable and it may be better just to consider the $\Delta G^\ddagger$ values from coalescence data: 57 ± 2 kJ mol^{-1} at 290 K for (2) and 39 ± 2 kJ mol^{-1} at 208 K for (3).

Acknowledgements

We thank the S.E.R.C. for a studentship (to C. C. Y.) and Johnson Matthey Ltd. for a generous loan of osmium.

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Received 10*th May* 1982; *Paper* 2/775