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Preliminary communication

ADDITION OF DIMETHYLPHENYLPHOSPHINE AT BRIDGING VINYL, ACETYLENE AND PHENYLACETYLIDE LIGANDS IN TRIOSMIUM CLUSTERS*

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Summary

PMe_2Ph readily adds at carbon in the compounds $HOs_3(CH{=}CH_2)(CO)_{10}$, $HOs_3(C{\equiv}CPh)(CO)_{10}$ and $Os_3(CH{\equiv}CH)(CO)_{10}$ to give zwitterionic 1:1 adducts; the addition to the vinyl compound is reversible and further reaction leads to $Os_3(CO)_{10}(PMe_2Ph)_2$ with ethylene displacement.

Nucleophilic addition at alkenes coordinated to transition metals, especially in cationic complexes, is well-known, but attack by neutral nucleophiles at neutral complexes is rare. We have now found a facile, but in one case reversible, addition of PMe_2Ph at carbon in alkene— and alkyne—triosmium complexes to give zwitterions having phosphonium centres and metal-based negative charges.

Typically, a solution of $HOs_3(CH{=}CH_2)(CO)_{10}$ (I) [1, 2, 3], in hexane reacts rapidly and quantitatively with one equivalent of PMe_2Ph at about 20 °C to give a yellow crystalline precipitate of $HOs_3(CHCH_2PMe_2Ph)(CO)_{10}$ (II). The carbonyl absorption spectrum (around 2000 cm^{-1}) of II is of similar pattern to that of I but shifted by about 30 cm^{-1} to lower wavenumbers, indicating that I and II have similar structures but with greater negative charge at the metal atoms of II. The ^1H NMR spectrum is totally consistent with the structure shown for II, notably H^a gives a 12-line multiplet at δ 5.39 ppm showing coupling to $C\underline{H}_2$, $Os\underline{H}$ and $^{31}\underline{P}$. In contrast, pyridine adds to osmium rather than carbon with ethylene displacement to give the 2-pyridyl compound $HOs_3(NC_5H_4)(CO)_{10}$ (III) which we originally prepared at > 110 °C by the direct reaction of pyridine with $Os_3(CO)_{12}$ [4]. This does not, of course, preclude an initial attack at carbon to give a pyridinium compound since in other cases [5] nucleophilic attack at carbon eventually leads to ligand displacement. Indeed similar behaviour is found in our

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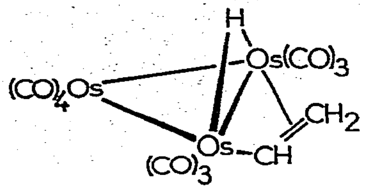
TABLE 1

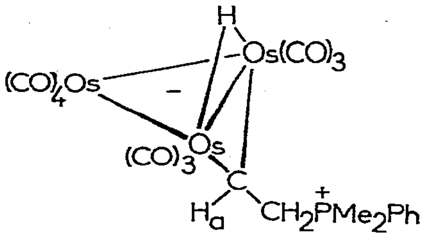
^{1}H NMR DATA (100 MHz AT 27 °C IN $CDCl_3$) AND INFRARED DATA (IN CYCLOHEXANE) FOR ZWITTERIONS

Compound	δ^a	Assignment	J (Hz)		ν(CO) (cm^{-1})			
$HOs_3(CHCH_2PMe_2Ph)(CO)_{10}$^{b}	7.0	Ph	J(ac)	3.3	2083m	2030vs	2022s	2002(sh)
(II)	5.39	$C\underline{H}^a$	J(ab)	7.3	2000s	1985(sh)	1981s	1972(sh)
	2.82	$C\underline{H}_2^b$	J(a^{31}P)	16.7	1954m	1946m	1927w	
	1.06	$(C\underline{H}_3)_2^d$	J(d^{31}P)	13.0				
	−15.97	$Os\underline{H}^c$	J(b^{31}P)	11.0				
			J(c^{31}P)	1.7				
$HOs_3(C_2HPMe_2Ph)(CO)_{10}$	7.74	Ph	J(a^{31}P)	40.7	2090m	2044vs	2037s	2007vs
(VI, R = H)	6.60	$C\underline{H}^a$	J(ab)	1.3	1992s	1983m	1975m	1966m
	2.08	$C\underline{H}_3^c$	J(c^{31}P)	13.5	1947w			
	1.95	$C\underline{H}_3^c$	J(b^{31}P)	2.5				
	−16.04	$Os\underline{H}^b$						
$HOs_3(C_2PhPMe_2Ph)(CO)_{10}$	7.84	Ph	J(b^{31}P)	3.2	2089m	2046vs	2037s	2008vs
(VI, R = Ph)	7.34	Ph	J(c^{31}P)	12.3	1990(sh)	1986s	1979m	1973m
	2.49	$C\underline{H}_3^c$		12.5	1967s	1949m		
	1.76	$C\underline{H}_3^c$						
	−16.35	$Os\underline{H}^b$						

[a] Downfield from TMS (ppm). [b] In toluene-d_8.



(I)



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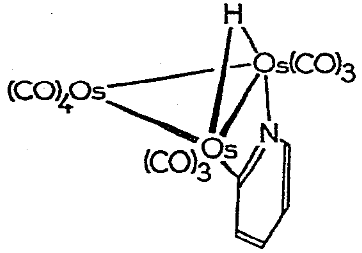

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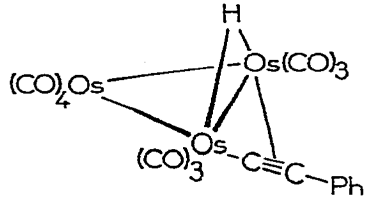


(V)

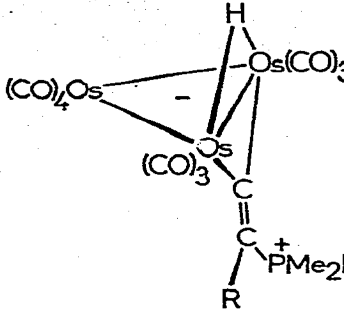
system since a solution of II in refluxing hexane for 2.5 h gives $Os_3(CO)_{10}(PMe_2Ph)_2$ [6] (IV), with recovery of an approximately equal amount of I. We propose reaction scheme 1.

$$\begin{tikzcd}
HOs_3(CH{=}CH_2)(CO)_{10}\ \text{(I)} \arrow[r, shift left, "+PMe_2Ph"] \arrow[d, "+2PMe_2Ph"] & HOs_3(CHCH_2PMe_2Ph)(CO)_{10}\ \text{(II)} \arrow[l, shift left, "-PMe_2Ph"] \\
Os_3(CO)_{10}(PMe_2Ph)_2 + C_2H_4\ \text{(IV)} &
\end{tikzcd}$$

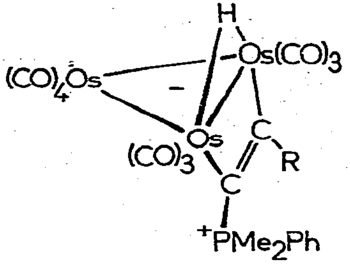
SCHEME 1

We have shown that II is formed reversibly from I since addition of MeI to a chloroform solution of II regenerates the vinyl compound; PMe_2Ph dissociating from II is quaternised by MeI forcing the equilibrium to the left. PMe_2Ph addition to $HOs_3(CPh{=}CHPh)(CO)_{10}$ [1] leads directly and rapidly at room temperature to IV, while a phosphonium species analogous to II is formed by PMe_2Ph addition to $HOs_3(CH{=}CHPh)(CO)_{10}$ [1] but this readily converts to IV at room temperature.

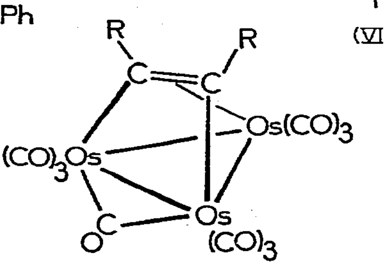
Most other alkene and alkyne complexes of Os_3 studied by us undergo similar additions at carbon at room temperature. The phenylacetylide $HOs_3(C{\equiv}CPh)(CO)_{10}$ (V) gives an adduct of structure VIa or VIb (R = Ph). Interestingly the acetylene analogue of V exists in the non-hydridic form $Os_3(CH{\equiv}CH)(CO)_{10}$ (VII, R = H) but this also reacts with PMe_2Ph to give the hydrido compound VIa or VIb (R = H). $Os_3(MeC{\equiv}CMe)(CO)_{10}$ (VII, R = Me) does not react with PMe_2Ph under the



(VIa)



(VIb)



(VII)

same conditions, either because of crowding or the lack of a readily transferable hydrogen atom. Triarylphosphite addition to $Fe_2(C{\equiv}CPh)(PPh_2)(CO)_6$ gives a complex [7] with ligand structure analogous to that in VIa while the mode of attachment as in VIb has been found in other related systems [8].

The compounds $HOs_3(MeCCHCH)(CO)_9$, $HOs_3(MeCCCH_2)(CO)_9$ (both derived from but-2-yne [1]), $HOs_3(EtPCH{=}CH_2)(CO)_9$ (derived from PEt_2Ph [9]), $Os_3(C_4H_4)(CO)_9$ [1] and $H_2Os_3(C{=}CH_2)(CO)_9$ all react in a related manner as evidenced from shifts of ν(CO) to lower frequencies on adding PMe_2Ph in excess to cyclohexane solutions. Equilibrium is rapidly reached in most cases but often a considerable excess of PMe_2Ph is required for complete conversion to the zwitterion.

These results indicate that nucleophilic attack at unsaturated hydrocarbon bridges in clusters will prove to be an important mode of reaction, whereas electrophilic attack (protonation) normally occurs at the metal atoms.

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