$Ru(CO)_2(PPh_3)_3$ and $Os(CO)_2(PPh_3)_3$. An Ethylene Complex of Ruthenium and a Dioxygen Complex of Osmium

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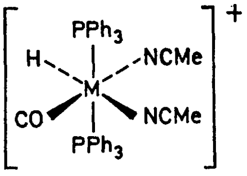
Summary The tris(phosphine) substituted carbonyls, $M(CO)_2(PPh_3)_3$ (M = Ru or Os) have been prepared by formal deprotonation of $[MH(CO)_2(PPh_3)_3]^+$ with methoxide ion; carbonyl groups are *trans* and a phosphine is easily lost leading to various derivatives including $Ru(C_2H_4)(CO)_2(PPh_3)_2$ and $Os(O_2)(CO)_2(PPh_3)_2$.

The known derivatives of $Ru(CO)_5$ and $Os(CO)_5$ are of the type $M(CO)_4L$[1] and $M(CO)_3L_2$, L = phosphine,[2] phosphite,[3] *etc.*, and in seeking greater reactivity through a higher degree of phosphine substitution, we have investigated possible routes to $M(CO)_2(PPh_3)_3$. Direct substitution is difficult and we have therefore devised the following approach. $\mathrm{MHCl(CO)(PPh_3)_3}$ reacts with $\mathrm{AgClO_4}$ in acetonitrile according to equation (1). The hydridobis(acetonitrile) cations have the geometry (see Table for ^{1}H n.m.r. data) shown in the Figure.

Physical data for ruthenium and osmium complexes[a]

	ν(CO) cm^{-1}
$\mathrm{[RuH(CO)(MeCN)_2(PPh_3)_2]^+}$ [b]	1960vs
$\mathrm{[RuH(CO)_2(PPh_3)_3]^+}$ [c]	1995vs
$\mathrm{Ru(CO)_2(PPh_3)_3}$	1905vs
$\mathrm{Os(CO)_2(PPh_3)_3}$	1895vs
$\mathrm{Ru(O_2)(CO)_2(PPh_3)_2}$ [d]	2005vs, 1945vs
$\mathrm{Os(O_2)(CO)_2(PPh_3)_2}$ [e]	1995vs, 1925vs
$\mathrm{Ru(C_2H_4)(CO)_2(PPh_3)_2}$	1955vs, 1900vs
$\mathrm{Ru(PhC{\equiv}CPh)(CO)_2(PPh_3)_2}$ [f]	1950vs, 1895vs

[a] Satisfactory elemental analyses have been obtained for all compounds reported. [b] ^{1}H N.m.r. τ 23·1 [triplet, J(P–H) 17·5 Hz], 8·2 and 8·6 (non-equivalent MeCN). [c] ^{1}H N.m.r. τ 16·4 [doublet of triplets $J(\mathrm{P{-}H})_{cis}$ 17, $J(\mathrm{P{-}H})_{trans}$ 121 Hz]. [d] $\nu(\mathrm{Ru{-}O_2})$ at 849 cm^{-1}. [e] $\nu(\mathrm{Os{-}O_2})$ at 820 cm^{-1}. [f] $\nu(\mathrm{C{\equiv}C})$ at 1776 cm^{-1}.



Figure

$$\mathrm{MHCl(CO)(PPh_3)_3 + AgClO_4 + 2MeCN \longrightarrow [MH(CO)(MeCN)_2(PPh_3)_2]ClO_4 + AgCl{\cdot}PPh_3} \qquad (1)$$

These are particularly versatile intermediates in that the two acetonitriles are of very different lability thus making accessible, by stepwise replacement reactions, a wide range of complexes including different isomeric forms by changing the order of ligand introduction. By reaction of these cations, first with CO in a fast reaction, and secondly with phosphine in a much slower reaction, the cations $\mathrm{[MH(CO)_2(PPh_3)_3]^+}$ result. The carbonyl groups are *trans* in these cations.

Attempted deprotonation with ethoxide ion results mainly in the formation of $\mathrm{MH_2(CO)(PPh_3)_3}$, indicating that reaction probably proceeds through $\mathrm{MH(OEt)(CO)(PPh_3)_3}$. This problem is avoided by use of methoxide ion or t-butoxide ion where the hydrogen-transfer reaction from the α-carbon atom is made more difficult, or prevented altogether, and the desired zerovalent complexes $\mathrm{M(CO)_2(PPh_3)_3}$ are formed as bright yellow crystals. The observation of a single ν(CO) (see Table) indicates an equatorial arrangement of phosphines and *trans* carbonyl groups.

$\mathrm{Ru(CO)_2(PPh_3)_3}$ probably dissociates in solution to $\mathrm{Ru(CO)_2(PPh_3)_2}$ since rapid addition of $\mathrm{H_2}$, $\mathrm{C_2H_4}$, $\mathrm{PhC{\equiv}CPh}$, and $\mathrm{O_2}$ occurs (see Table). $\mathrm{Ru(C_2H_4)(CO)_2(PPh_3)_2}$ is the first ethylene complex of ruthenium to be reported, other olefin complexes requiring strongly electron-withdrawing groups on the olefin[4] or the olefin as part of a chelating ligand.[5] $\mathrm{Os(CO)_2(PPh_3)_3}$ dissociates less readily and reaction with $\mathrm{O_2}$ is slow to yield $\mathrm{Os(O_2)(CO)_2(PPh_3)_2}$. Although dioxygen has previously been implicated in ligand oxidations at osmium centres *e.g.*, the oxidation of $\mathrm{OsCl(CO)(NO)(PPh_3)_2}$ to $\mathrm{Os(CO_3)Cl(NO)(PPh_3)_2}$,[6] no other dioxygen complex of osmium has been described.

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