Journal of
The Chemical Society,
Chemical Communications

NUMBER 11/1976 2 JUNE

Reaction of Transition-metal Complexes with Hydroperoxides: Oxidation of Carbonyl, Phosphine, and Carbon Ligands

By Ian J. Harvie and Francis J. McQuillin*
(*Department of Organic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne* NE1 7RU)

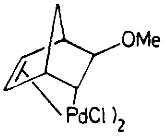
Summary [Rh(CO)Cl(PPh$_3$)$_2$], [Ir(CO)Cl(PPh$_3$)$_2$], and [{Rh(CO)$_2$Cl}$_2$] react with Bu^{t}O$_2$H to give CO$_2$ in what appears to be a stoicheiometric reaction; with *m*-ClC$_6$H$_4$CO$_3$H the carbon–metal bond in [MCl(CH$_2$Ph)(PPh$_3$)$_2$] (M = Pt or Pd) is cleaved to give *m*-ClC$_6$H$_4$CO$_2$CH$_2$Ph, and di-μ-chloro-bis{*endo*-η-2,3;η-5-(6-methoxybicyclo[2.2.1]hept-2-enepalladium(II)} yields a methoxytricyclo[2.2.1.0]-heptyl *m*-chlorobenzoate.

Transition-metal complexes may be expected to react with a hydroperoxide either (a) by electron transfer: $ML_n + RO_2H \rightarrow M^+L_n + RO\cdot + HO^-$; $M^+L_n + RO_2H \rightarrow ML_n + RO_2\cdot + H^+$; $RO\cdot + RO_2H \rightarrow ROH + RO_2\cdot$, or (b) by co-ordination at a vacant site, with the possibility of oxygen transfer to oxidisable ligands. Route (a) is implicated[1] in the catalytic decomposition of hydroperoxides by *e.g.* [Ir(CO)Cl(PPh$_3$)$_2$]. We now report what appear to be stoicheiometric processes of type (b).

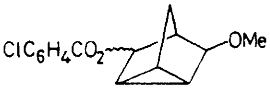
[Rh(CO)Cl(PPh$_3$)$_2$] in benzene under nitrogen consumed 1 equiv. of Bu^{t}O$_2$H to give CO$_2$ (0·95 equiv.), and [{RhCl(PPh$_3$)$_2$}$_2$], compared with authentic material, and with hydrogen yielding material showing a ^{1}H n.m.r. signal (τ 26·6, d of t, J 20 and 16 Hz) characteristic[2] of the dihydride. No Ph$_3$PO was detected, and it is of interest that the carbonyl is oxidised in preference to a phosphine ligand.

The carbonyl ligands in [{Rh(CO)$_2$Cl}$_2$] were found to be oxidised in the same manner; Bu^{t}O$_2$H (4 equiv.) gave CO$_2$ (4 equiv.), a little oxygen, and from the benzene solution a brown solid showing no ν_{CO}. This with CO in ethanol at 60 °C dissolved to give material (ν_{CO} 2100 and 2050 cm^{-1}) closely similar[3] to [{Rh(CO)$_2$Cl}$_2$].

The reaction of [Ir(CO)Cl(PPh$_3$)$_2$] proved to be more complex. Bu^{t}O$_2$H (2 equiv.) gave CO$_2$, Ph$_3$PO, and, from the benzene solution by chromatography, the known[1,4] yellow complex, [Ir(CO)Cl(PPh$_3$)$_2$(Bu^{t}O$_2$)$_2$], and a blue substance containing Ph$_3$P residues (i.r., n.m.r.), but showing no ν_{CO}, and giving C and H analyses suggesting an Ir : PPh$_3$: Cl ratio of 1 : 1 : 1.



(1)



(2)

Formation of the blue Ir-complex could be suppressed by carrying out the oxidation in dimethylformamide (DMF), by adding Et$_3$N to the benzene solvent, or by oxidation in benzene in a stream of CO. Conversely oxidation in benzene containing 2,4-di-t-butylphenol (2 equiv.) suppressed formation of the yellow peroxy complex, but not of the blue Ir-derivative. The latter clearly arises by ligand oxidation, and the peroxy complex probably by co-ordination of Bu^{t}O$_2\cdot$ radicals to [Ir(CO)Cl(PPh$_3$)$_2$]. We suggest that Et$_3$N, DMF, and CO may competitively exclude co-ordination of RO$_2$H, but not the electron transfer process leading to RO$_2\cdot$ radicals.

[RhCl(PPh$_3$)$_3$] with Bu^{t}O$_2$H (1 equiv.) gave, as expected, [{RhCl(PPh$_3$)$_2$}$_2$]. In this case oxidation *via* prior phosphine dissociation cannot be excluded. However, oxidation of the carbonyls noted above requires oxygen transfer from co-ordinated Bu^{t}O$_2$H.

The carbon–transition metal σ-bond was also shown to be oxidisable under similar conditions. The benzyl complexes, $[MCl(CH_2Ph)(PPh_3)_2]$ (M = Pt or Pd), were found to react rapidly with m-$ClC_6H_4CO_3H$ (2 equiv.) in benzene. Removal of solvent and chromatography (silica gel) of a light petroleum extract gave benzyl m-chlorobenzoate, τ 2—3 and 4·67, m/e 248, 246, and 211 (M — Cl), and a little benzyl alcohol; Ph_3PO was also isolated. Oxidation in the presence of 2,4-di-t-butylphenol gave the same result.

Similarly the Pd-complex (**1**) in CH_2Cl_2, treated successively with pyridine (C_5H_5N : Pd = 1) and m-$ClC_6H_4CO_3H$ (5 equiv.) gave, by chromatography of the product, material m/e 280, 278, 249, 247 (M — OMe), and 122 (M — $ClC_6H_4CO_2H$), τ 5·17, 6·53, 6·66, 8·83, 8·93, and 8·97. These data are consistent with a structure (**2**); *exo*-3-methoxytricyclo-[2.2.1.0]heptane[5] shows τ 6·73, 6·83, 8·76, 8·90, and 9·06. This result is reminiscent of the reaction of (**1**) with 1,2-bis-(diphenylphosphino)ethane followed by bromine.[6]

These results are consistent with reaction *via* RO_2H (R = Bu^t or m-ClC_6H_4CO), co-ordination to the transition metal centre,[7] lysis of the RO–OH bond, and transfer of oxygen from HO to carbonyl or phosphine, or of RO to a σ-bonded carbon ligand. It is of interest that alternative electron-transfer processes appear to be less important except in the reaction of $[Ir(CO)Cl(PPh_3)_2]$ with Bu^tO_2H, but may become predominant with excess of hydroperoxide after oxidisable ligands have been removed.

(*Received*, 1*st March* 1976; *Com.* 204.)

---

[1] B. L. Booth, R. N. Haszeldine, and G. R. H. Neuss, *J.C.S. Perkin I*, 1975, 209.
[2] C. A. Tolman, P. Z. Meakin, D. L. Lindner, and T. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 2762.
[3] R. Colton, F. H. Farthing, and J. E. Knapp, *Austral. J. Chem.*, 1970, **23**, 1351.
[4] B. L. Booth, R. N. Haszeldine, and G. R. H. Neuss, *J.C.S. Chem. Comm.*, 1972, 1074.
[5] Prepared by the method of S. J. Cristol, W. I. L. Seifert, D. W. Johnson, and T. B. Jurale, *J. Amer. Chem. Soc.*, 1962, **84**, 3918.
[6] D. R. Coulson, *J. Amer. Chem. Soc.*, 1969, **91**, 200.
[7] *Cf.* D. N. Jones and S. D. Knox, *J.C.S. Chem. Comm.*, 1975, 166.