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

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Summary $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$, $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$, and $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ react with $\text{Bu}^t\text{O}_2\text{H}$ to give CO_2 in what appears to be a stoichiometric reaction; with *m*- $\text{ClC}_6\text{H}_4\text{CO}_2\text{H}$ the carbon-metal bond in $[\text{MCl}(\text{CH}_2\text{Ph})(\text{PPh}_3)_2]$ ($\text{M} = \text{Pt}$ or Pd) is cleaved to give *m*- $\text{ClC}_6\text{H}_4\text{CO}_2\text{CH}_2\text{Ph}$, 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.

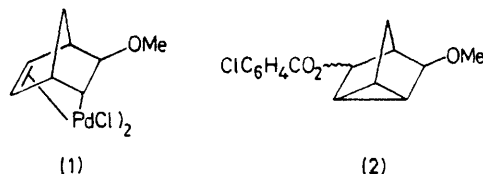
TRANSITION-METAL complexes may be expected to react with a hydroperoxide either (a) by electron transfer: $\text{ML}_n + \text{RO}_2\text{H} \rightarrow \text{M}^+\text{L}_n + \text{RO}\cdot + \text{HO}^-$; $\text{M}^+\text{L}_n + \text{RO}_2\text{H} \rightarrow \text{ML}_n + \text{RO}_2\cdot + \text{H}^+$; $\text{RO}\cdot + \text{RO}_2\text{H} \rightarrow \text{ROH} + \text{RO}_2\cdot$, or (b) by co-ordination at a vacant site, with the possibility of oxygen transfer to oxidisable ligands. Route (a) is implicated¹ in the catalytic decomposition of hydroperoxides by *e.g.* $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$. We now report what appear to be stoichiometric processes of type (b).

$[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in benzene under nitrogen consumed 1 equiv. of $\text{Bu}^t\text{O}_2\text{H}$ to give CO_2 (0.95 equiv.), and $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$, compared with authentic material, and with hydrogen yielding material showing a ^1H n.m.r. signal (τ 26.6, d of t, J 20 and 16 Hz) characteristic² of the dihydride. No Ph_3PO was detected, and it is of interest that the carbonyl is oxidised in preference to a phosphine ligand.

The carbonyl ligands in $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ were found to be oxidised in the same manner; $\text{Bu}^t\text{O}_2\text{H}$ (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 similar³ to $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$.

The reaction of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ proved to be more complex. $\text{Bu}^t\text{O}_2\text{H}$ (2 equiv.) gave CO_2 , Ph_3PO , and, from

the benzene solution by chromatography, the known^{1,4} yellow complex, $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\text{Bu}^t\text{O}_2)_2]$, and a blue substance containing Ph_3P 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.



Formation of the blue Ir-complex could be suppressed by carrying out the oxidation in dimethylformamide (DMF), by adding Et_3N 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 $\text{Bu}^t\text{O}_2\cdot$ radicals to $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$. We suggest that Et_3N , DMF, and CO may competitively exclude co-ordination of $\text{RO}_2\cdot$, but not the electron transfer process leading to $\text{RO}_2\cdot$ radicals.

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

The carbon-transition metal σ -bond was also shown to be oxidisable under similar conditions. The benzyl com-

plexes, $[\text{MCl}(\text{CH}_2\text{Ph})(\text{PPh}_3)_2]$ ($\text{M} = \text{Pt}$ or Pd), were found to react rapidly with $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ (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 ($M - \text{Cl}$), 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 ($\text{C}_5\text{H}_5\text{N}:\text{Pd} = 1$) and $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ (5 equiv.) gave, by chromatography of the product, material m/e 280, 278, 249, 247 ($M - \text{OMe}$), and 122 ($M - \text{ClC}_6\text{H}_4\text{CO}_2\text{H}$), 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]heptane⁵ 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 ($\text{R} = \text{Bu}^t$ or $m\text{-ClC}_6\text{H}_4\text{CO}$), co-ordination to the transition metal centre,⁷ lysis of the $\text{RO}-\text{OH}$ 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 $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ with $\text{Bu}^t\text{O}_2\text{H}$, but may become predominant with excess of hydroperoxide after oxidisable ligands have been removed.

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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.