Direct Oxidative Addition–Reductive Elimination Reactions Between *trans*-[MCl(CO)L_2] and [MCl_3(CO)L_2] or *trans*-[$PtCl_4(PEt_3)_2$] (M = Rh or Ir, L = tertiary phosphine)

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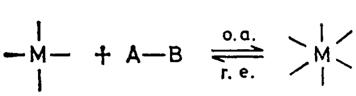
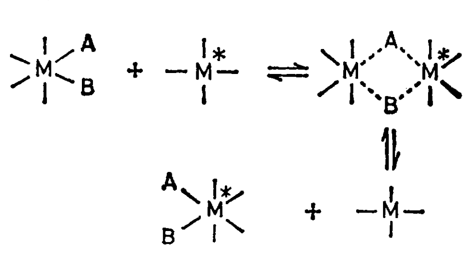
Complexes of the type *trans*-[MCl(CO)L_2] and [MCl_3(CO)L_2], M = Rh or Ir, L = PMe_2Ph or PEt_2Ph, have been shown to react with each other, presumably by a double chloro-bridged intermediate, and undergo rapid oxidative addition–reductive elimination; phosphine exchange is much slower. Similar results were obtained when *trans*-[$PtCl_4(PEt_3)_2$] was treated with *trans*-[MCl(CO)$(PEt_3)_2$], M = Rh or Ir, for which rapid and complete conversion into *trans*-[$PtCl_2(PEt_3)_2$] and [MCl_3(CO)$(PEt_3)_2$] occurred. Phosphorus-31 n.m.r. data are given.

OXIDATIVE addition (o.a.) and the reverse, reductive elimination (r.e.), are very important in co-ordination/organometallic chemistry and catalysis.[1-9] In the most commonly occurring form these reactions may be represented as in (1) (M = metal in a complex, A–B = molecule). It seemed possible that in some cases complexes of the types shown in equation (1) could react with one another *directly*, *i.e.* that they might undergo rapid, mutual oxidative addition–reductive elimination *viz.* (2). This type of interaction does not seem to have been considered before although it could be important in causing disproportionation, isomerization, and other complications in kinetic and preparative studies.



(1)

We chose first to study complexes of the type *trans*-[MCl(CO)$(PR_3)_2$] (M = Rh or Ir) and their corresponding trichlorides. Complexes of these and related types have been studied very extensively [1-5,7,8] and it is known that the iridium(I) complexes have a greater tendency to undergo oxidative addition than the rhodium(I) complexes. We find that a solution (in C_6H_6–C_6D_6) of *trans*-[IrCl(CO)$(PMe_2Ph)_2$] and [$RhCl_3$(CO)$(PMe_2Ph)_2$] [configuration (1)], initially 0.05 mol dm^{-3} in each complex, converts to an equimolar mixture of *trans*-[RhCl(CO)$(PMe_2Ph)_2$] and [$IrCl_3$(CO)$(PMe_2Ph)_2$] in less than 5 min at 22 °C, as shown by ^{31}P-{^1H} n.m.r. spectroscopy (see Figure 1). The conversion was also followed at low temperature in deuteriotoluene. Conversion is very slow at or below −30 °C ($t_{\frac{1}{2}}$ ~ hours) whilst at −22 °C conversion proceeds smoothly. No intermediate could be detected and there was no induction period *i.e.* free radicals do not seem to be involved. An equimolar mixture of *trans*-[IrCl(CO)$(PEt_2Ph)_2$] and [$RhCl_3$(CO)$(PEt_2Ph)_2$] reacted similarly but more slowly than with the PMe_2Ph complexes. It is known that *trans*-[IrCl(CO)$(PMe_2Ph)_2$] has a greater tendency to be protonated by benzoic acid than *trans*-[IrCl(CO)$(PEt_2Ph)_2$],[10] and we now find that a mixture of *trans*-[IrCl(CO)$(PMe_2Ph)_2$] and [$IrCl_3$(CO)$(PEt_2Ph)_2$] [configuration (1)] in C_6H_6–C_6D_6, initially 0.05 mol dm^{-3} in each complex, shows after 15 min at 22 °C that conversion to *trans*-[IrCl(CO)$(PEt_2Ph)_2$] and [$IrCl_3$(CO)$(PMe_2Ph)_2$] is almost complete with only a trace of species containing mixed phosphines and a few percent of the starting complexes. Over several hours the concentrations of mixed species *trans*-[IrCl(CO)$(PMe_2Ph)$$(PEt_2Ph)$] and [$IrCl_3(CO)(PMe_2Ph)(PEt_2Ph)$] gradually build up; ^{31}P n.m.r. data are in the Table. As might be expected phosphine exchange with rhodium(I) species is faster than with iridium(I). Thus a C_6H_6–C_6D_6 solution of *trans*-[RhCl(CO)$(PMe_2Ph)_2$] and [$RhCl_3$(CO)$(PEt_2Ph)_2$], initially 0.05 mol dm^{-3} in each, shows after 20 min that the major species are [$RhCl_3$(CO)$(PMe_2Ph)_2$] and *trans*-[RhCl(CO)$(PEt_2Ph)_2$] but that the species with mixed phosphines are also produced in considerable amounts, see Figure 2 and the Table. Phosphine exchange does not occur between the rhodium(III) species. Thus a benzene solution of a mixture of



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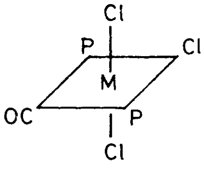

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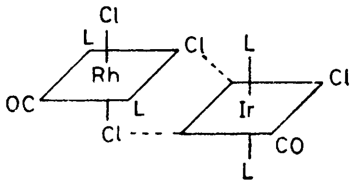

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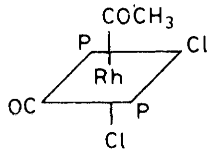

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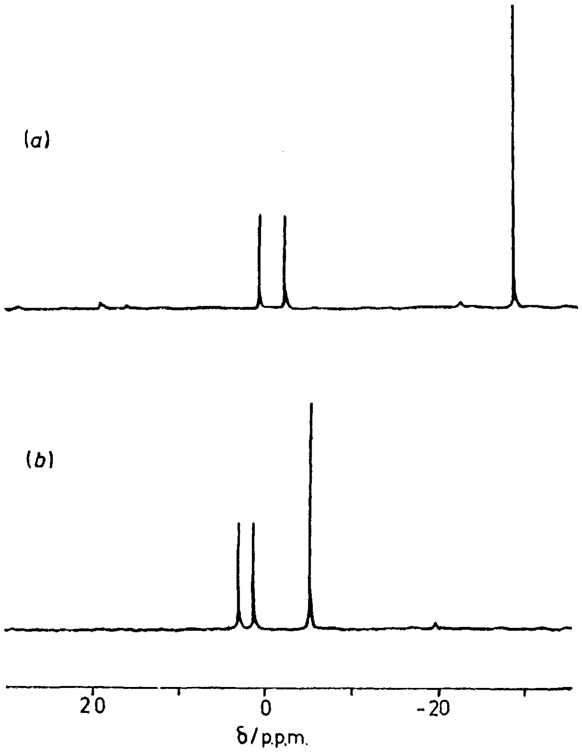


FIGURE 1 (*a*) $^{31}P-\{^1H\}$ n.m.r. spectrum of a benzene solution of *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ and $[IrCl_3(CO)(PMe_2Ph)_2]$ formed after 5 min from a $[RhCl_3(CO)(PMe_2Ph)_2]$–*trans*-$[IrCl(CO)(PMe_2Ph)_2]$ mixture, initially 0.05 mol dm^{-3} in each complex. (*b*) $^{31}P-\{^1H\}$ n.m.r. spectrum of a toluene solution of $[RhCl_3(CO)(PMe_2Ph)_2]$ and *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ at −50 °C showing that the complexes are unchanged

$[RhCl_3(CO)(PMe_2Ph)_2]$ and $[RhCl_3(CO)(PEt_2Ph)_2]$ shows no change after 90 min at 22 °C. However, on adding *ca.* 5 mol per cent of *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ the mixed species $[RhCl_3(CO)(PMe_2Ph)(PEt_2Ph)]$ slowly appears, being *ca.* 10% of the total species after 90 min. Very shortly (*ca.* 5 min) after its addition no *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ was detected whereas *trans*-$[RhCl(CO)(PEt_2Ph)_2]$ had formed to the extent of a few percent.

^{31}P N.m.r. data for the rhodium and iridium complexes [a]

Complex	δ_P [b]	$^1J(RhP)$/Hz	$^2J(PP)$/Hz
$[RhCl(CO)L_2]$	−0.4	118	
$[RhCl(CO)Q_2]$	24.6	120	
$[RhCl(CO)LQ]$	−0.4	119	363
	25.2	120	
$[RhCl_3(CO)L_2]$	2.4	73	
$[RhCl_3(CO)Q_2]$	13.6	72	
$[RhCl_3(CO)LQ]$	2.9	72	533
	13.6	73	
$[IrCl(CO)L_2]$	−5.1		
$[IrCl(CO)Q_2]$	20.5		
$[IrCl(CO)LQ]$	−4.8		347
	20.0		
$[IrCl_3(CO)L_2]$	−28.4		
$[IrCl_3(CO)Q_2]$	−18.1		
$[IrCl_3(CO)LQ]$	−28.0		417
	−17.8		
$[RhCl(CO)Z_2]$	24.6	117	
$[RhCl_3(CO)Z_2]$	19.3	72	
$[IrCl(CO)Z_2]$	20.2		
$[IrCl_3(CO)Z_2]$	−13.0		

[a] Measured at *ca.* 22 °C in C_6H_6–C_6D_6; L = PMe_2Ph, Q = PEt_2Ph, Z = PEt_3. [b] In p.p.m. to high frequency of H_3PO_4.

We also investigated the reactions of the platinum(IV) complex *trans*-$[PtCl_4(PEt_3)_2]$ with *trans*-$[MCl(CO)(PEt_3)_2]$ (M = Rh or Ir), 0.05 mol dm^{-3} in each complex.

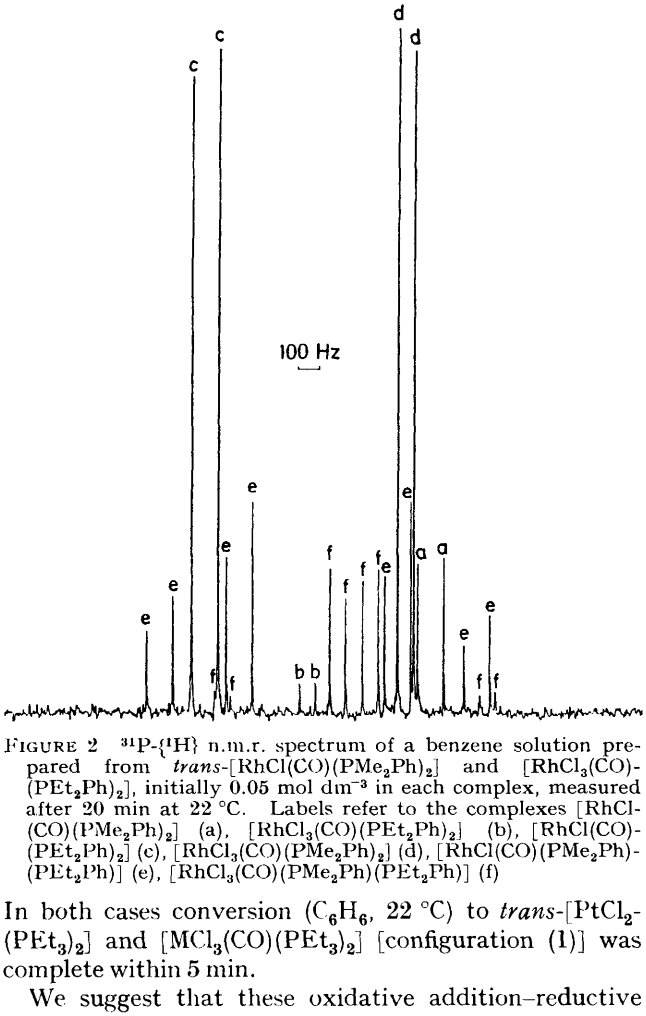
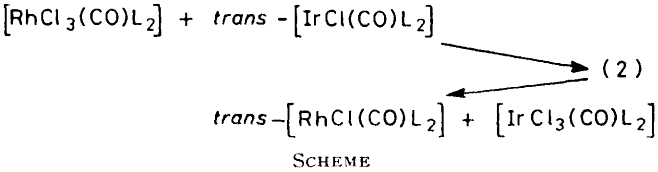


FIGURE 2 $^{31}P-\{^1H\}$ n.m.r. spectrum of a benzene solution prepared from *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ and $[RhCl_3(CO)(PEt_2Ph)_2]$, initially 0.05 mol dm^{-3} in each complex, measured after 20 min at 22 °C. Labels refer to the complexes $[RhCl(CO)(PMe_2Ph)_2]$ (a), $[RhCl_3(CO)(PEt_2Ph)_2]$ (b), $[RhCl(CO)(PEt_2Ph)_2]$ (c), $[RhCl_3(CO)(PMe_2Ph)_2]$ (d), $[RhCl(CO)(PMe_2Ph)(PEt_2Ph)]$ (e), $[RhCl_3(CO)(PMe_2Ph)(PEt_2Ph)]$ (f)

In both cases conversion (C_6H_6, 22 °C) to *trans*-$[PtCl_2(PEt_3)_2]$ and $[MCl_3(CO)(PEt_3)_2]$ [configuration (1)] was complete within 5 min.

We suggest that these oxidative addition–reductive elimination reactions go *via* a double chloro-bridged



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species (2) * (see Scheme). It would thus be an inner-sphere double electron-transfer process.

We find that the acetylrhodium(III) species $[RhCl_2(COCH_3)(CO)(PMe_2Ph)_2]$ of configuration (3) and *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ react only slowly in toluene at

* The iridium(III) and rhodium(III) species of configuration (1) show no tendency to lose dichlorine, for example they are stable in solvents which react with dichlorine. Neither these complexes nor *trans*-$[PtCl_4(PEt_3)_2]$ showed any trace of reduced species in their $^{31}P-\{^1H\}$ n.m.r. spectra after bubbling argon through a benzene solution for several hours.

20 °C. After 18 h *ca.* 50% of the starting complexes had been converted into a complex mixture including [$IrCl_3(CO)(PMe_2Ph)_2$] of configuration (**1**). This slowness could reflect the instability of [$Rh(COCH_3)(CO)(PMe_2Ph)_2$].

We would expect other potentially good bridging ligands *e.g.* Br, I, H, carboxylate, π-allyl *etc.* to be able to promote rapid, direct oxidative addition–reductive elimination between metal complexes. It is a factor which should be taken into account in preparative and mechanistic studies.

EXPERIMENTAL

The ^{31}P n.m.r. spectra were recorded with a JEOL FX100Q spectrometer using an internal deuterium lock and broad-band proton decoupling. Complexes were prepared by literature methods and their purity checked by ^1H and ^{31}P n.m.r. spectroscopy.

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