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Direct Oxidative Addition-Reductive Elimination Reactions Between trans-[MCI(CO)L₂] and [MCI₃(CO)L₂] or trans-[PtCl₄(PEt₃)₂] (M = Rh or Ir, L = tertiary phosphine)

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Complexes of the type *trans*-[MCI(CO)L₂] and [MCI₃(CO)L₂], M = Rh or Ir, L = PMe₂Ph or PEt₂Ph, 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*-[PtCl₄(PEt₃)₂] was treated with *trans*-[MCI(CO)(PEt₃)₂], M = Rh or Ir, for which rapid and complete conversion into *trans*-[PtCl₂(PEt₃)₂] and [MCl₃(CO)(PEt₃)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

$$-\frac{I}{M} + A - B \xrightarrow{o.a.} M \xrightarrow{I} B$$
(1)

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.

We chose first to study complexes of the type trans-[MCl(CO)(PR₃)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 C₆H₆-C₆D₆) of trans-[IrCl(CO)(PMe₂Ph)₂] and [RhCl₃(CO)(PMe₂Ph)₂] [configuration (1)], initially 0.05 mol dm⁻³ in each complex, converts to an equimolar mixture of trans-[RhCl(CO)-(PMe₂Ph)₂] and [IrCl₃(CO)(PMe₂Ph)₂] in less than 5 min at 22 °C, as shown by ³¹P-{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 ($t_{\frac{1}{2}} \sim$ 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)(PEt₂Ph)₂] and [RhCl₃(CO)-(PEt₂Ph)₂] reacted similarly but more slowly than with the PMe₂Ph complexes. It is known that trans-[IrCl(CO)(PMe₂Ph)₂] has a greater tendency to be protonated by benzoic acid than trans-[IrCl(CO)(PMe₂Ph)₂], and we now find that a mixture of trans-[IrCl(CO)(PMe₂Ph)₂] and [IrCl₃(CO)(PEt₂Ph)₂] [configuration (1)] in C₆H₆-C₆D₆, initially 0.05 mol dm⁻³ in each complex, shows after 15 min at 22 °C that conversion to trans-[IrCl(CO)(PEt₂Ph)₂] and [IrCl₃(CO)(PEt₂Ph)₂] and [IrCl₃(CO)(PEt₂Ph)₂] [CON-



(PMe₂Ph)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_Ph)-(PEt₂Ph)] and [IrCl₃(CO)(PMe₂Ph)(PEt₂Ph)] gradually build up; ³¹P 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)(PMe₂Ph)₂] and [RhCl₃(CO)(PEt₂-Ph)2], initially 0.05 mol dm⁻³ in each, shows after 20 min that the major species are [RhCl₃(CO)(PMe₂Ph)₂] and trans-[RhCl(CO)(PEt,Ph),] 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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 $[RhCl(CO)(PEt_2Ph)_2]$ had formed to the extent of a few percent.

We also investigated the reactions of the platinum(IV) complex trans-[PtCl₄(PEt₃)₂] with trans-[MCl(CO)-(PEt₃)₂] (M = Rh or Ir), 0.05 mol dm⁻³ in each complex.



FIGURE 2 ³¹P-{¹H} n.m.r. spectrum of a benzene solution prepared from *trans*-[RhCl(CO)(PMe₂Ph)₂] and [RhCl₃(CO)-(PEt₂Ph)₂], initially 0.05 mol dm⁻³ in each complex, measured after 20 min at 22 °C. Labels refer to the complexes [RhCl-(CO)(PMe₂Ph)₂] (a), [RhCl₃(CO)(PEt₂Ph)₂] (b), [RhCl(CO)-(PEt₂Ph)₂] (c), [RhCl₃(CO)(PMe₂Ph)₂] (d), [RhCl(CO)(PMe₂Ph)-(PEt₂Ph)] (e), [RhCl₃(CO)(PMe₂Ph)(PEt₂Ph)] (f)

In both cases conversion $(C_6H_6, 22 \ ^\circ C)$ to *trans*-[PtCl₂-(PEt₃)₂] and [MCl₃(CO)(PEt₃)₂] [configuration (1)] was complete within 5 min.

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

$$[RhCl_{3}(CO)L_{2}] + trans - [IrCl(CO)L_{2}]$$

$$trans - [RhCl(CO)L_{2}] + [IrCl_{3}(CO)L_{2}]$$
Scheme

species (2) * (see Scheme). It would thus be an innersphere 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 ³¹P-{¹H</sup> n.m.r. spectra after bubbling argon through a benzene solution for several hours.



I⁻IGURE 1 (a) ³¹P-{¹H} n.m.r. spectrum of a benzene solution of trans-[RhCl(CO)(PMe₂Ph)₂] and [IrCl₃(CO)(PMe₂Ph)₂] formed after 5 min from a [RhCl₃(CO)(PMe₂Ph)₂]-trans-[IrCl(CO)-(PMe₂Ph)₂] mixture, initially 0.05 mol dm⁻³ in each complex. (b) ³¹P-{¹H} n.m.r. spectrum of a toluene solution of [RhCl₃(CO)(PMe₂Ph)₂] and trans-[IrCl(CO)(PMe₂Ph)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-

³¹P N.m.r. data for the rhodium and iridium complexes ^a

Complex	δr •	$^{1}J(RhP)/Hz$	$^{2}J(\text{PP})/\text{Hz}$
[RhCl(CO)L ₃]	-0.4	118	
RhCl(CO)Q	24.6	120	
[RhCl(CO)LO]	-0.4	119	363
	25.2	120	
$[RhCl_{a}(CO)L_{a}]$	2.4	73	
RhCl _a (CO)O 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		
[lrCl(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 $C_8H_6-C_8D_6$; $L = PMe_9Ph$, $Q = PEt_2Ph$, $Z = PEt_3$. ^b In p.p.m. to high frequency of H_3PO_4 .

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20 °C. After 18 h ca. 50% of the starting complexes had been converted into a complex mixture including [IrCl₃(CO)(PMe₂Ph)₂] of configuration (1). This slowness could reflect the instability of [Rh(COCH₃)(CO)-(PMe,Ph),].

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 ³¹P 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 ³¹P n.m.r. spectroscopy.

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