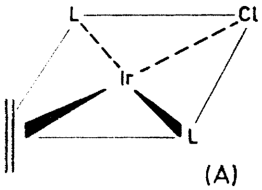
Hydrogenation and Isomerisation of Alkenes using $IrCl(PPh_3)_2$ and the Isolation of the Oxygen Adduct $IrCl(PPh_3)_2(O_2)(C_2H_4),C_6H_6$

By H. VAN GAAL, H. G. A. M. CUPPERS, and A. VAN DER ENT*

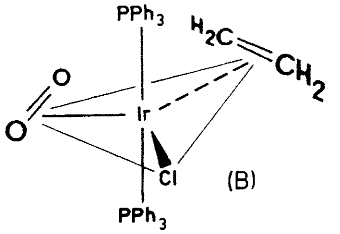
(*Unilever Research Laboratories, Vlaardingen/Duiven, Olivier van Noortlaan* 120, *Vlaardingen, The Netherlands*)

Summary $IrCl(PPh_3)_2$, prepared *in situ*, has been found to be a catalyst for the hydrogenation and isomerisation of alkenes; with molecular oxygen $IrCl(PPh_3)_2(C_2H_4)$ forms in benzene the five-co-ordinated adduct $IrCl(PPh_3)_2(O_2)$-$(C_2H_4),C_6H_6$.

IN contrast with the corresponding rhodium compound, chlorotris(triphenylphosphine)iridium(I), $IrCl(PPh_3)_3$, was recently reported to be inactive in the hydrogenation of alkenes.[1] This inactivity might be due to the stronger iridium–phosphine bond, which prevents the complex from becoming co-ordinatively unsaturated by the dissociation of a phosphine ligand. As was shown in hydrogenation experiments[2] using $RhCl(PPh_3)_n$ (n = 1,2,3), this dissociation is required to activate the substrate. We have tested the catalytic activity of benzene solutions of the iridium(I)–cyclo-octene complex, $[IrCl(C_8H_{14})_2]_2$, to which one or two equivalents triphenyl-phosphine or -arsine was added. It was found that the resulting systems were catalytically active for the hydrogenation and isomerisation of alkenes. The dependence of the initial rates of hydrogenation and isomerisation of hex-1-ene in benzene on the phosphine/iridium ratio is presented in the Figure. The maximum



(A)



(B)

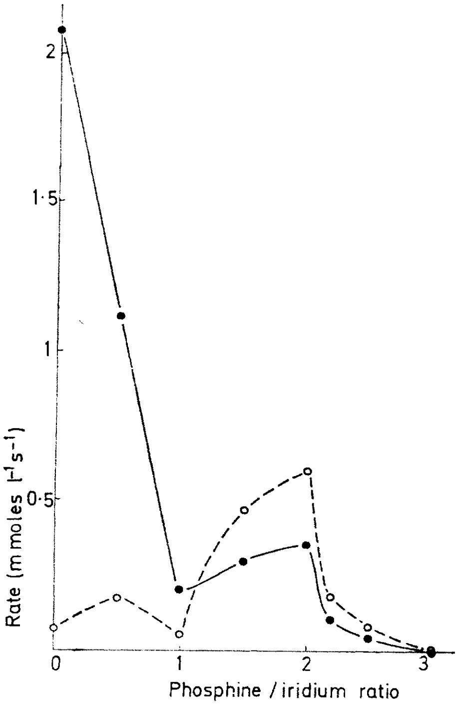


FIGURE. *Rates of hydrogenation* (○) *and isomerisation* (●) *of hex-*1*-ene* (0·27 *mole/l*) *in benzene using various mixtures of* $[IrCl(C_8H_{14})_2]_2$ ($0{\cdot}2310^{-3}$ *mole/l*) *and triphenylphosphine* (25°, 1 *atm.* H_2).

hydrogenation rate at a ratio of 2 suggests the catalytically active species to be chlorobis(triphenylphosphine)iridium(I), $IrCl(PPh_3)_2$. At this optimum ratio, the system is about 10 times more active than the corresponding rhodium system. During the hydrogenation, the rate decreases because of isomerisation of hex-1-ene to *trans*- and *cis*-hex-2-enes, which are hydrogenated about 180 times more slowly. The remarkably high isomerisation activity of $[IrCl(C_8H_{14})_2]_2$—in contrast with the negligible activity of $[RhCl(C_8H_{14})_2]_n$—reflects the ability of $[IrCl(C_8H_{14})_2]_2$ to activate molecular hydrogen.

I.r. and n.m.r. data of some chloro-iridium–alkene complexes

Compound IrCl–L–R		I.r. as KBr pellet ν(C–F) (cm^{-1})	$\tau(C_2H_4)$ (in $CDCl_3$)	$\delta(C_2F_4)$ (in CH_2Cl_2, lock CF_3CO_2H ext.)
R	L			
(C_2H_4)	$(PPh_3)_2$		8·90 br	
$(C_2H_4)(O_2)$	$(PPh_3)_2$	880 ν(O=O)	6·67 br	
(C_2F_4)	$(PPh_3)_2$	1098, 1030, 817		22·7 t
(C_2F_4)	$(AsPh_3)_2$	1113, 1030, 803		20·5 s
(C_2F_4)	PPh_3	1096, 1027, 807		—

As part of an investigation of the mechanism of this catalysis, we studied the synthesis and properties of iridium(I)–phosphine and –arsine complexes. The isolation of $IrCl(PPh_3)_2C_2F_4$ from the iridium(I)–nitrogen compound, $IrCl(PPh_3)_2N_2$, by Stone and his co-workers[3] prompted us to report some of our results and especially a more general method to prepare iridium(I)–alkene addition products with the general formula $IrClL_n$alk (n = 1 or 2, L = triphenyl-phosphine, -arsine, or -stibine and alk = alkene). These compounds could be prepared by the addition of one or two equivalents of L to $[IrCl(C_2H_4)_2]_2$ (ref. 4) or to $[IrCl(C_2H_4)(C_2F_4)]_2$. (The latter can be isolated from a pentane suspension of the former after treatment with tetrafluoroethylene). I.r. and n.m.r. data of the most interesting compounds are given in the Table.

N.m.r. experiments show there is a fast exchange between free and co-ordinated ethylene in $IrCl(PPh_3)_2C_2H_4$. The position of the iridium–chlorine stretching vibration at 301 cm^{-1} suggests a square-planar structure (A) with chlorine *trans* to ethylene.

The corresponding C_2F_4 complex has the same structure, according to the triplet resonance in its ^{19}F n.m.r. spectrum (see Table). No exchange between free and co-ordinated C_2F_4 could be detected. The tendency of iridium(I) to form five-co-ordinated compounds is illustrated by the reaction of $IrCl(PPh_3)_2C_2H_4$ in benzene with molecular oxygen with the formation of the alkene–oxygen complex $IrCl(PPh_3)_2(O_2)(C_2H_4)$, C_6H_6. This compound is characterised by a sharp i.r. absorption band at 880 cm^{-1} due to co-ordinated oxygen and a broadened n.m.r. resonance at τ 6·67 due to co-ordinated ethylene. The tentative structure (B) is in agreement with the position of ν(Ir–Cl) at 303 cm^{-1}. This complex is the first known compound containing molecular oxygen and an alkene ligand co-ordinated to one metal atom and may be considered as a model compound for an intermediate in the homogeneous oxidation of alkenes by non-radical pathways.[5]

The substitution of ethylene by other ligands such as triphenylphosphine and pyridine results in the compounds $IrCl(PPh_3)_3(O_2)$ and $IrCl(PPh_3)_2(pyr)(O_2)$ with ν(O=O) at 849 and 843 cm^{-1}, respectively.

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