Contribution from the Istituto di Chimica Generale ed Inorganica, Bari, Italy

The Interaction of a Cyclo-octa-1,5-diene-iridium Complex with Molecular Hydrogen

M. Gargano, P. Giannoccaro, and M. Rossi

Received October 9, 1972

The reaction of the olefin-complex $IrCl(C_8H_{12})PPh_3$ (C_8H_{12} = cyclo-octa-1,5-diene) with hydrogen produces a new hydrido-complex whose chemical and spectroscopic properties are reported. An interesting hydrogen-deuterium exchange-reaction is also discussed.

Introduction

Following our studies on π-complexes containing the olefin *cis,cis*-cyclo-octa-1,5-diene[1-4] we have studied the reactivity of the square planar-complexes of formula $MCl(C_8H_{12})PPh_3$ (M = Rh and Ir) toward molecular hydrogen. The Ir-complex readily produces the compound $Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2$, whose analytical and structural characterization are reported in this note, whereas the reaction of the less reactive Rh-complex will be discussed in a forthcoming paper.

Experimental Section

All the solvents were of reagent-grade quality. The solutions of the compounds were manipulated under an atmosphere of nitrogen. Samples for m.p. determination were contained in evacuated tubes. Infrared spectra were measured on nujol mulls in a Perkin-Elmer mod. 337 spectrometer and n.m.r. spectra in a Varian HA 100 using $CDCl_3$ as solvent and TMS as an internal reference. G.l.c. determinations were carried out using a Hewlett-Packard 5750 instrument.

Dihydridodi-μ-chloro-π-cyclo-octa-1,5-dienebis(triphenylphosphine)diiridium. $Ir_2H_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$ Hydrogen was bubbled at atmospheric pressure into a solution of $IrCl(C_8H_{12})P(C_6H_5)_3$ (0.3 g, 0.5 mmol) in toluene (4 ml) at 80°C, for about 10 minutes. The resulting solution, cooled under nitrogen atmosphere at −10°C, produced yellow crystals of the solvate-complex $Ir_2H_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2 . C_7H_8$ (0.25 g, 0.21 mmol, Yield 84%), d.p. 202°C. *Anal.* Calcd for $C_{51}H_{52}Cl_2P_2Ir_2$: C, 51.8; H, 4.4; P, 5.2; Cl, 6.0. Found: C, 51.5; H, 4.2; P, 5.3; Cl, 6.1%.

Recrystallization of the product from dichloromethane and pentane gave yellow crystals of the solvent-free complex. D.p. 195°C. *Anal.* Calcd for $C_{44}H_{44}Cl_2P_2Ir_2$: C, 48.5; H, 4.1; Cl, 6.5; P, 5.7. Found: C, 49.0; H, 4.3; Cl, 6.5; P, 5.8%.

Cyclo-octene and a small quantity of cyclo-octane were identified in the mother liquor by g.l.c. using a 20% DEGS on chromosorb P column (5 m × 2 mm) at 110°C.

Reaction with Deuterium. This reaction was similarly carried out as in the case of H_2, bubbling deuterium into a solution of $IrCl(C_8H_{12})P(C_6H_5)_3$ (0.3 g) in toluene (4 ml) at 80°C for 10 minutes. The i.r. spectrum of the product showed the presence of Ir-D bands at 1600 and 1570 cm^{-1} and Ir-H bands at 2230 and 2210 cm^{-1}. An isotopic exchange in the C_8H_{12} ligand was observed by means of the n.m.r. spectrum (see Table I).

Dideuteridodi-μ-chloro-π-cyclo-octa-1,5-dienebis(triphenylphosphine)diiridium. $Ir_2D_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$. Deuterium was bubbled into a solution of $Ir_2H_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$ (0.2 g) in toluene (2 ml) at 70°C for 4 minutes. In the crystallized product the exchange of the hydridic hydrogen with deuterium was observed by means of the i.r. spectrum, which showed the presence of ν(Ir-D) very strong and ν(Ir-H) very weak. The isotopic exchange in the C_8H_{12} ligand was not observed in this case.

Reaction of $Ir_2H_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$ with $P(C_6H_5)_3$. A mixture of the complex (260 mg, 0.24 mmol) and triphenylphosphine (130 mg, 0.49 mmol), in toluene (4 ml) was stirred under nitrogen until complete dissolution. By addition of a portion of pentane, white crystals of the known $IrH_2Cl\{P(C_6H_5)_3\}_3$[6,7] (220 mg, 0.19 mmol slowly precipitated. *Anal.* Calcd for $C_{54}H_{47}ClP_3Ir$: Cl, 3.5; P, 9.1. Found: Cl, 3.5; P, 8.9%.

By adding a second portion of pentane orange needles of the already known $IrCl(C_8H_{12})P(C_6H_5)_3$[5] (100 mg, 0.16 mmol) were obtained. *Anal.* Calcd for $C_{26}H_{27}ClPIr$: Cl, 5.9; P, 5.2. Found: Cl, 6.0; P, 5.3%.

Reaction of $Ir_2H_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$ with $P(C_6D_5)_3$. This reaction was carried out as above except that $P(C_6D_5)_3$ was used instead of $P(C_6H_5)_3$. By careful crystallization almost pure $IrH_2Cl\{P(C_6H_5)_3\}_2P(C_6D_5)_3$ and $IrCl(C_8H_{12})P(C_6D_5)_3$ were obtained. The amount

---

(1) S. Otsuka and M. Rossi, *J. Chem. Soc. (A)*, 2630 (1968).
(2) S. Otsuka and M. Rossi, *ibidem*, 497 (1969).
(3) M. Rossi and A. Sacco, *Chem. Comm.*, 471 (1969).
(4) M. Lavecchia M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, *4*, 29 (1970).
(5) G. Winkhaus and H. Singer, *Chem. Ber.*, 99, 3610 (1966).
(6) L. Vaska, *J. Am. Chem. Soc.*, *83*, 756 (1961).
(7) M. Angoletta and A. Araneo, *Gazz. Chim. Ital.*, 93, 1343 (1963).

of the hydrogenated triphenylphosphine in the complexes was determined by recording the i.r. band at 1100 cm^{-1} present in the co-ordinated $P(C_6H_5)_3$ and absent in the co-ordinated $P(C_6D_5)_3$. Dichloromethane solutions of the complexes ($\sim 2 \times 10^{-2}M$) in a 0.5 mm NaCl cell were examined using standard solutions of pure $IrH_2Cl\{P(C_6H_5)_3\}_3$ and of $IrCl(C_8H_{12})P(C_6H_5)_3$. The results of these analysis were $P(C_6H_5)_3/Ir = 2.1$ in $IrH_2Cl\{P(C_6H_5)_3\}_2P(C_6D_5)_3$ and $P(C_6H_5)_3/Ir = 0.1$ in $IrCl(C_8H_{12})P(C_6D_5)_3$.

Reaction of $Ir_2D_2Cl_2(C_8H_{12})\{P(C_6H_5)_3\}_2$ *with olefins.* A sample of the deuterated complex (0.2 g), dissolved in dichloromethane (3 ml) was treated with an excess of cyclo-octene (0.5 ml) at room temperature for 20 minutes. By addition of pentane yellow crystals separated. The analysis and the chemical properties of this compound were similar to those of the starting complex. However, its i.r. spectrum showed the disappearance of the original Ir-D bands at 1600 and 1570 cm^{-1}, whereas new Ir-H bands appeared at 2230 and 2210 cm^{-1}. The same result was obtained using 1-pentene instead of cyclo-octene; in this case the isomerization of the olefin to give *cis*- and *trans*-2-pentene was observed by g.l.c. using a 20% Benzyl Cyanide-Silver Nitrate (2: 1) on Chromosorb P column (3 m × 2 mm) at 20°C.

Results and Discussion

Preparation and properties. A hot toluene solution of $IrCl(C_8H_{12})PPh_3$[5] reacts with hydrogen at atmospheric pressure according to the following equation:

$$\underset{\text{I}}{2IrCl(C_8H_{12})PPh_3} + 2H_2 \rightarrow \underset{\text{II}}{Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2} + C_8H_{14} \qquad (1)$$

On cooling, the hydrido-complex II separates as bright yellow crystals containing one mole of toluene per mole of complex. Cyclo-octene, along with variable quantities of cyclo-octane depending upon the reaction time, is formed as reduction product of cyclo-octadiene. Recrystallization of the complex II from methylene chloride and pentane produces yellow plates of solvent-free compound, which is stable to oxygen both in the solid state and, for a few hours, in solution. The formula of the complex can be deduced in a straightforward manner from the elemental analysis and the following spectroscopic evidence and chemical properties:

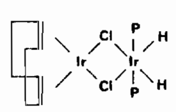
(i) the i.r. spectrum of the complex II shows two very strong bands at 2230 and 2210 cm^{-1} (nujol mull) which can be assigned to the Ir-H stretching vibrations; using D_2 instead of H_2 (see below) these bands are shifted to 1600 and 1570 cm^{-1}.

(ii) The n.m.r. spectrum shows an hydridic signal at τ 35.88 (triplet, $J_{P-H} = 16$ cps) and signals due to the protons of the co-ordinated olefin at τ 6.8, 8.1, 9.0 (see Table I). The spectrum remains almost unchanged in the temperature range of –60 to 50°C.

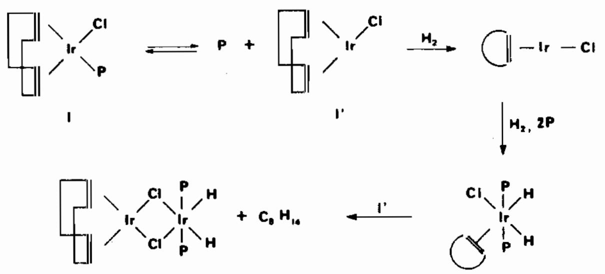
(iii) The complex II reacts with the stoichiometric amount of triphenylphosphine according to the following equation:

$$\underset{\text{II}}{Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2} + 2PPh_3 \rightarrow$$
$$\underset{\text{I}}{IrCl(C_8H_{12})PPh_3} + \underset{\text{III}}{IrH_2Cl(PPh_3)_3} \qquad (2)$$

Orange crystals of the known complex I[5] and white crystals of the already known complex III[6,7] are formed without evolution of hydrogen. These complexes have been quantitatively separated by using their different solubilities. Furthermore, useful indications on the structure of the complex can be obtained by reacting II with deuterated triphenylphosphine: almost pure $IrCl(C_8H_{12})P(C_6D_5)_3$ and $IrH_2Cl\{P(C_6H_5)_3\}_2P(C_6D_5)_3$ have been obtained. This result suggests for the complex II the formula



in which two chlorine atoms are bridging the (C_8H_{12})-Ir and $IrH_2(PPh_3)_2$ moieties. This formula is also in agreement with the triplet signal found for the hydridic protons in the n.m.r. spectrum. The mutual *cis* position of these hydrogen atoms is strongly suggested by the two very strong i.r. bands at 2230 and 2210 cm^{-1}. The values of these frequencies are similar to those found for hydrido-complexes having the hydrogen atoms in *trans* position to the chlorine atoms.[8] In the course of the reaction (1) a migration of the phosphine ligand from an iridium atom to the other occurs. This result may be reasonably explained assuming a reaction path (Scheme a) in which the first step is the dissociation of the complex $IrCl(C_8H_{12})$-PPh_3.



Scheme a.

Although this reversible dissociation is not easily obtained as in the case of the analogous complex $IrCl(C_8H_{12})AsPh_3$[9] it may occur at relatively high temperature (80°C) and could be assisted by the subsequent irreversible hydrogenation-reaction.

Hydrogen-Deuterium exchange. When the hot toluene (or benzene) solution of $IrCl(C_8H_{12})PPh_3$ reacts with deuterium instead of hydrogen, an interesting

---

[8] J. Chatt, R.S. Coffey, and B.L. Shaw, *J. Chem. Soc.*, 7391 (1965).
[9] K. Vrieze and P.W.N.M. van Leeuwen, *Progress in Inorg. Chem.*, Lippard Ed., *14*, 1 (1971) and reference therein.

Table I.

Compound	τ-values and intensities[a]	ν_{M-H} and ν_{M-D}[b]
II	2-3(30), 6.8(3.9); 8.1(4.0); 9.0(3.9); 35.88[c]	2230(vs); 2210(vs)
IV[d]	2-3(30); 6.8(3.7); 8.1(1.6); 9.0(3.9); 35.82[c], 35.88[c]	2230(m); 2210(m) 1600(m); 1570(m)

[a] $CDCl_3$ solutions with TMS an internal reference; the numoer of protons is derived considering the aromatic hydrogens as standard. [b] Nujol mulls on NaCl-discs. [c] Not integrated. [d] Relative intensities of the n.m.r. signals and i.r. bands are reported as an example (see experimental procedure); different values are found using different experimental conditions (see text).

isotopic exchange takes place, as evidenced by the following observations:

(i) the reaction leads to products containing both hydrogen and deuterium bound to the metal; their relative amounts are function of the reaction time and temperature.

(ii) Some methylenic hydrogens in the co-ordinated cyclo-octadiene have been selectively substituted by deuterium atoms. These results are in agreement with the following equation:

$$\begin{aligned}&\underset{\text{I}}{2IrCl(C_8H_{12})PPh_3}+(x+y+z-2)D_2\rightarrow\\&\underset{\text{IV}}{Ir_2H_{2-x}D_xCl_2(C_8H_{12-y}D_y)(PPh_3)_2}\qquad(3)\\&+C_8H_{14-z}D_z+(x+y+z-4)HD\end{aligned}$$

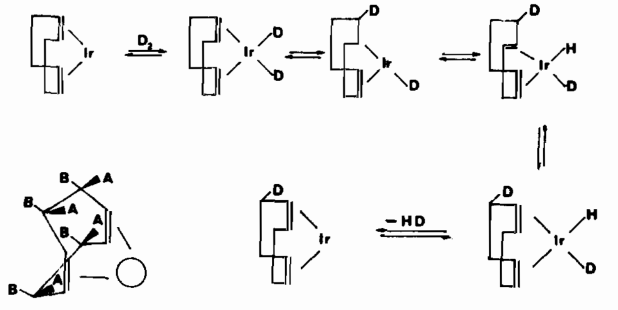
In fact, the partially deuterium-substituted crystals of IV show strong and sharp i.r. bands due to the Ir-D and to the Ir-H stretching vibrations (Table I), and a band at 2160 cm^{-1} due to the C-D stretching. In the ranges of temperature and time explored during our preparations (70-100°C; 1-60 min) the formation of Ir-H containing products was never suppressed: for short reaction times (1-5 min) the Ir-H species prevail over the Ir-D species, whereas the reverse occurs for longer reaction time. Furthermore, the appearance in the high field n.m.r. spectrum of two close but distinct triplets at τ 35.88 and τ 35.82 suggests the presence of IrH_2 and IrHD groups in the products IV.

The isotopic H-D substitution in the co-ordinated cyclo-octadiene is shown by the n.m.r. analysis (Table I).

The broad signals in the unsubstituted complex II, due to the olefinic protons (τ 6.8) and to the methylenic protons (τ 8.1 and τ 9.0) are strongly modified in the substituted products IV. The signals at τ 6.8 and τ 9.0 are here sharp (about singlets) with intensities of 4:4, whereas the signal at τ 8.1 is very weak, with intensity depending by the experimental conditions (time and temperature) used in the preparation. We have observed in fact a number of protons varying between 0.3 and 1.8.

The reaction of $IrCl(C_8H_{12})P(C_6D_5)_3$ and D_2 in C_6D_5 at 80° leads to hydrido- and deuterido-products analogous to those obtained in the reaction 3. This fact seems to rule out an isotopic exchange involving either the phosphine-ligand or the solvent.

The isotopic substitution in the C_8H_{12}-ligand may be explained with a *cis*-insertion, *cis*-elimination mechanism.



Scheme b.

Thus, according to the σ-π interaction reported in the scheme B, some methylenic hydrogens do exchange with gaseous deuterium. The position of the hydrogens A is sterically more favoured than that of B with respect to a *cis*-elimination; it follows that four protons can be substituted in a preferential manner. This is strongly supported by the n.m.r. data which show the weakening of only one (τ 8.1) of the two signals due to the methylenic protons after reaction with deuterium.

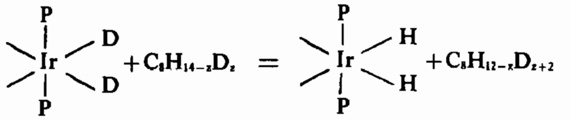
The exchange-reaction involves the reversible isomerization of 1,5-C_8H_{12} to 1,4-C_8H_{12}, whose equilibrium is displaced toward the much more strongly co-ordinated 1,5-C_8H_{12}. This stereospecific *cis*-addition, *cis*-elimination mechanism occurs also during the isomerization of mono-olefins as for example in the maleate-fumarate system catalyzed by $CoH(CO)_4$.[10] Furthermore, it is known that the isomerization of the free 1,5-C_8H_{12} to 1,3-C_8H_{12} via the 1,4-isomer is catalyzed by Rh- and Ir-complexes.[11] We also found that the complex II is able to promote this isomerization under mild conditions.[12]

The H-D exchange involves the $Ir(C_8H_{12})$ moiety present in some intermediate during the synthesis of $Ir_2D_2Cl_2(C_8H_{12})(PPh_3)_2$. Although we can not exclude a pre-equilibrium interaction between the starting complex and D_2, this is not supported by the experimental evidence. In fact, sample of the unreacted $IrCl(C_8H_{12})PPh_3$, recovered after short reaction time (1-2 min.) at 80° under D_2 atmosphere, do not show deuterium substitution appreciable by n.m.r. tecnique. Furthermore, the exchange is not observed in the reaction of pure $Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2$ with D_2 under mild conditions (70°C, few min.); it is observed only under more drastic conditions (120°C) when the decomposition of the product to Ir-metal is considerable.

---

(10) P. Taylor and M. Orchin, *J. Organomet. Chem.*, *26*, 389 (1971).
(11) J.K. Nicholson and B.L. Shaw, *Tet. Letters*, *39*, 3533 (1965).
(12) M. Gargano, P. Giannoccaro, and M. Rossi, work in progress.

Concomitantly to the C_8H_{12}-D_2 exchange reaction above discussed, other processes partecipate to the overall hydrogen-deuterium exchange observed in the reaction of $IrCl(C_8H_{12})PPh_3$ with D_2. These are the interaction of the hydrido-ligand with D_2:



(4)

(5)

The first equation explains the presence of Ir-H species in the reaction-products IV. The interaction of hydrido complexes with olefins to give exchange-complex $Ir_2D_2Cl_2(C_8H_{12})(PPh_3)_2$ is particularly effective in the exchange-reaction with cyclo-octene and with n-olefins even at room temperature. The reaction 5 take place both in the reaction of $IrCl(C_8H_{12})$-PPh_3 with D_2 and in the preparation of the pure deuterido-complex from $Ir_2H_2Cl_2(C_8H_{12})(PPh_3)_2$. In this latter case the isotopic substitution of the hydridic-hydrogens by gaseous deuterium is very slow at room temperature but it is completed in a few minutes at higher temperature (70°C) in presence of an excess of D_2.

The formation of products containing more Ir-H than Ir-D species after short reaction time in the reaction of $IrCl(C_8H_{12})PPh_3$ with D_2 suggests that the exchange of the deuterido-ligand with cyclo-octene (equation 4) is faster than the exchange of the hydrido-ligand with deuterium (equation 5).

Acknowledgment We thank Prof. A. Sacco for assistence, Mr. P. Bianco for analytical determinations and Mr. S. Cretì for n.m.r. spectra.

This research was supported by Consiglio Nazionale delle Ricerche.

(13) R.S. Coffey, *Tet. Letters, 43,* 3809 (1965).

(14) R.A. Shunn, *Inorg. Chem., 9,* 2567 (1970) and reference therein.