Journal of Organometallic Chemistry, 84 (1975) 389—397

ISOMERISATION AND HYDROGENATION OF 1,5-CYCLOOCTADIENE CATALYSED BY $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$

M. GARGANO, P. GIANNOCCARO and M. ROSSI
Istituto di Chimica Generale ed Inorganica dell'Università, Via Amendola 173, 70126 Bari (Italy)

(Received August 6th, 1974)

Summary

The isomerisation of 1,5-cyclooctadiene catalysed by $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ under N_2 occurs through consecutive reactions $1,5\text{-}C_8H_{12} \rightleftharpoons 1,4\text{-}C_8H_{12} \rightarrow 1,3\text{-}C_8H_{12}$; the first reaction is reversible whereas the second is irreversible. Under H_2, a selective hydrogenation of the non-conjugated 1,5 and 1,4 isomers leads to cyclooctene. Mechanisms for the isomerization and hydrogenation are proposed.

Introduction

In our previous work the chelating diolefin *cis,cis*-1,5-cyclooctadiene was used to stabilize π-allyl complexes of cobalt [1,2] and rhodium [3] and hydrido complexes of iridium [3,4]. In particular, in the synthesis of $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$, we found an interesting hydrogen—deuterium scrambling between the cyclooctadiene hydrogens and molecular deuterium. For a better understanding of the interaction of the olefin ligand with the hydrido ligand we have examined the interaction of the free 1,5-cyclooctadiene with the iridium complex under varying experimental conditions.

Results and discussion

A benzene solution of $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ under nitrogen shows a catalytic activity toward the isomerisation of the free 1,5-cyclooctadiene. As shown in Fig. 1, both the 1,4- and the 1,3-cyclooctadienes are obtained as reaction products: the 1,4-isomer slightly predominates for low degrees of conversions but the 1,3 isomer becomes the major product after a few hours.

The rate of reaction slowly decreases during the isomerisation of the diene, and the fall off shows a dependence on the initial catalyst concentration and temperature. In fact, if a dilute solution of $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$

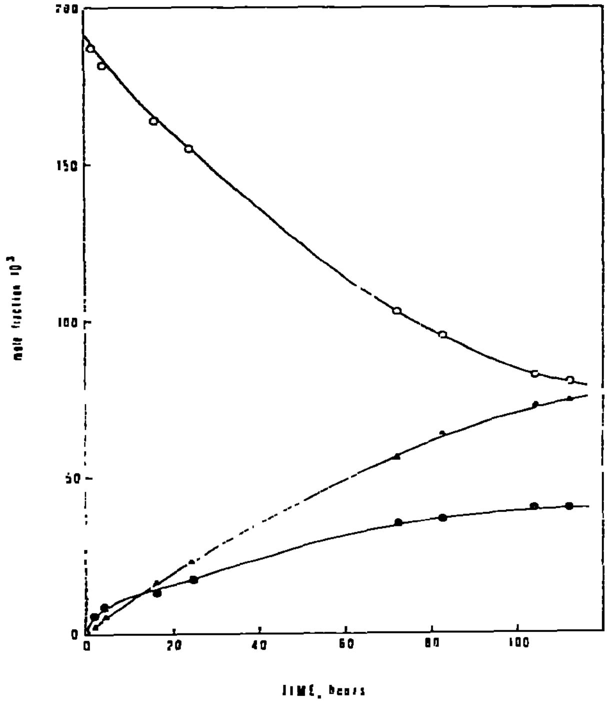


Fig. 1. Isomerisation of 1,5-cyclooctadiene (2.05 *M*) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (8.2×10^{-3} *M*) in benzene at 20° under N_2. o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; ▲, 1,3-cyclooctadiene.

(2.0×10^{-3} *M*) is used at high temperature (61°), the isomerisation reaction stops after a few hours leaving about 40% of the unreacted $1,5\text{-}C_8H_{12}$(Fig. 2). At a lower temperature (0°) and with a higher catalyst/diene ratio, the catalytic activity remains almost unchanged for a long time (Fig. 3).

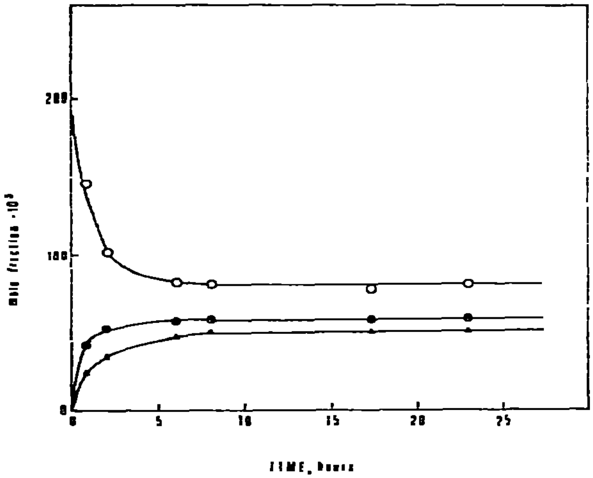


Fig. 2. Isomerisation of 1,5-cyclooctadiene (2.04 *M*) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (2.0×10^{-3} *M*) in benzene at 61° under N_2. o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; ▲, 1,3-cyclooctadiene.

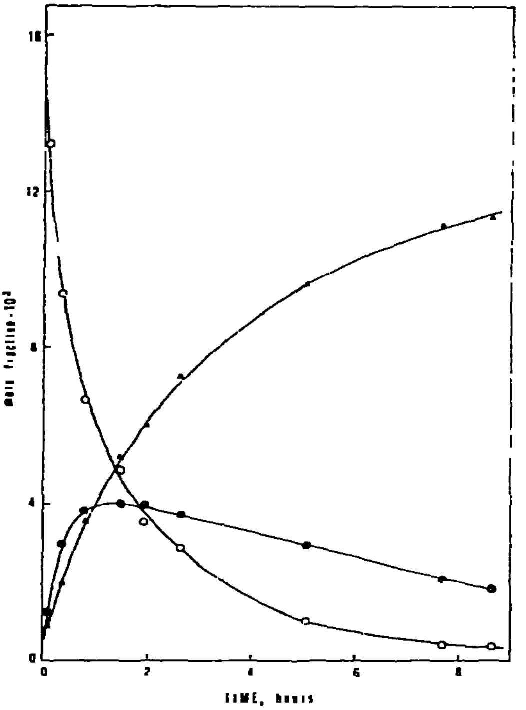


Fig. 3. Isomerisation of 1,5-cyclooctadiene (2.5×10^{-1} M) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (4.8×10^{-2} M) in dichloromethane at 0° under N_2. o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; ▲, 1,3-cyclooctadiene.

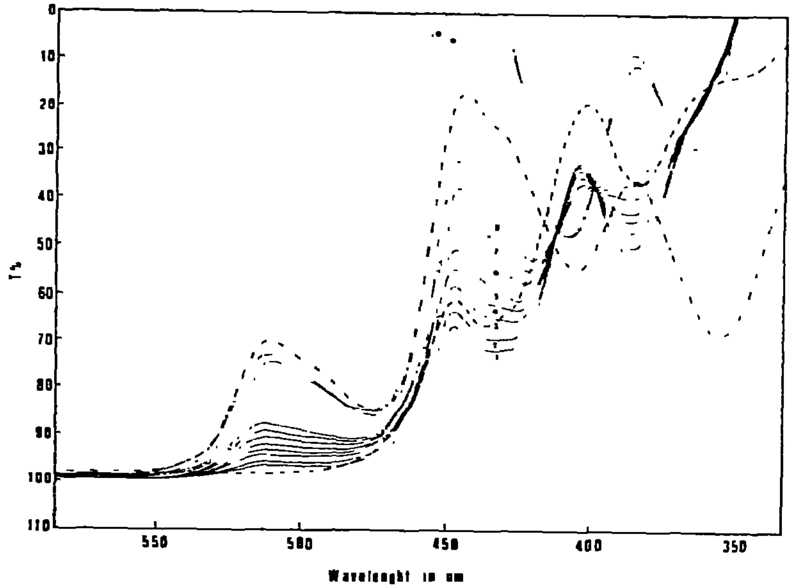


Fig. 4. Electronic spectra of the benzene solution containing $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (3.6×10^{-3} M) and $1,5\text{-}C_8H_{12}$ (2.0 M) at 20° at various times (as shown in Fig. 5). ———, reacting solution; — — —, $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (3.9×10^{-3} M) in benzene; — · — ·, $IrCl(1,5\text{-}C_8H_{12})PPh_3$ (1.7×10^{-3} M) in benzene.

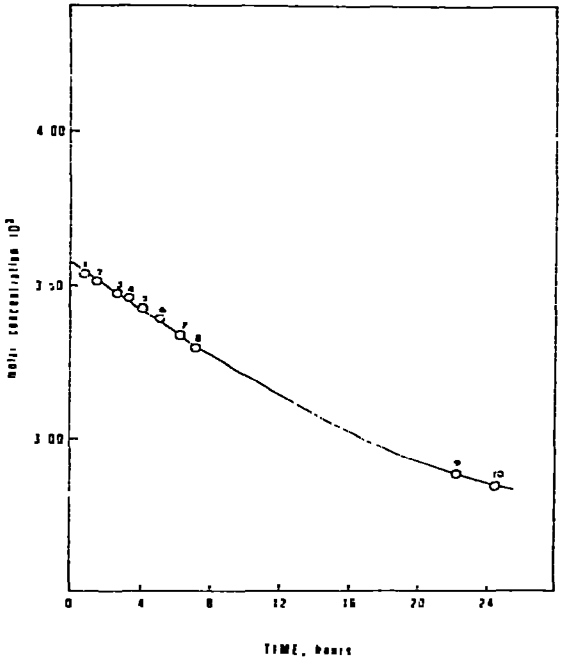


Fig. 5. Disappearance of $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ derived from the data reported in Fig. 4

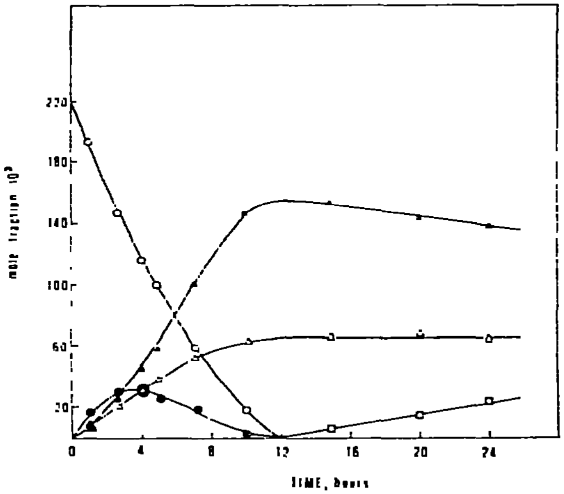
This fall in the catalytic activity has been attributed to the conversion of the active hydrido complex into an inert compound (reaction 1). This reaction is relatively slow at low temperature (0-20°), and can be followed by the change in the UV spectrum (Fig. 4 and 5), which shows the disappearance of $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (bands at 405 nm, ϵ 900; and at 447 nm, ϵ 270), and the concomitant appearance of $IrCl(1,5\text{-}C_8H_{12})PPh_3$ (bands at 386 nm, ϵ 1250; at 430 nm (sh); at 455 nm, ϵ 2130; and at 512 nm, ϵ 410).

$$Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2 + 2\ 1,5\text{-}C_8H_{12} \rightarrow 2\ IrCl(1,5\text{-}C_8H_{12})PPh_3 + C_8H_{14} \quad (1)$$

The catalyst $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ is consumed by reaction 1 but it can be reformed in situ when the reaction is carried out in the presence of hydrogen. Our previous results [4] show that $IrCl(1,5\text{-}C_8H_{12})PPh_3$ reacts with molecular hydrogen by reaction 2 to produce the original hydrido complex. The results for the catalysed reactions of 1,5-cyclooctadiene under hydrogen atmosphere at low (22°) and high temperature (68°), are shown in Figs. 6 and 7, respectively.

$$2\ IrCl(1,5\text{-}C_8H_{12})PPh_3 + 2\ H_2 \rightarrow Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2 + C_8H_{14} \quad (2)$$

From the results it can be seen that molecular hydrogen is an effective cocatalyst for the isomerisation, since the catalytic activity of the solution is still present after a long time; however, under these conditions, an extensive concomitant hydrogenation reaction occurs both at low and high temperature. The data reported for the catalytic transformation of 1,5-cyclooctadiene, under an



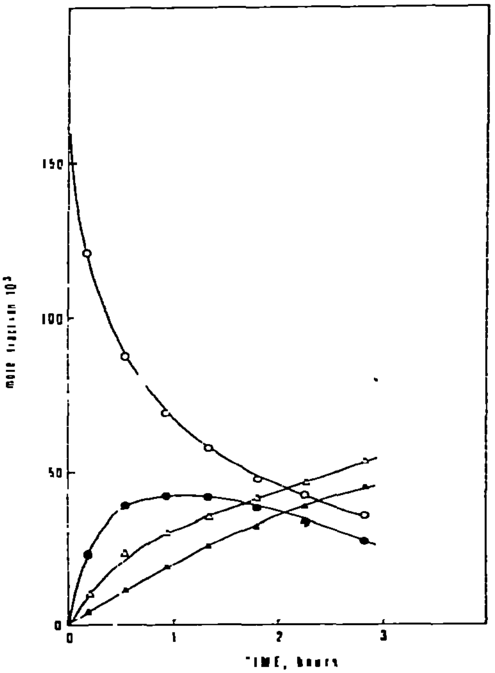


Fig. 6. Catalytic transformation of 1,5-cyclooctadiene (2.33 *M*) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (2.67 X 10^{-3}*M*) in benzene at 22° under hydrogen (1 atm). o, 1,5-cyclooctadiene, ●, 1,4-cyclooctadiene; Δ, = 1,3-cyclooctadiene; ▲, cyclooctene; □ , cyclooctane.

Fig. 7. Catalytic transformation of 1,5-cyclooctadiene (1.7 *M*) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ (2.7 X 10^{-3}*M*) in benzene at 68° under hydrogen (1 atm). o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; Δ, 1,3-cyclooctadiene; ▲, cyclooctene.

inert atmosphere or hydrogen, show that the pattern of the isomerisation process is very similar in both cases.

It is well known that several transition metal complexes catalyse the homogeneous isomerisation of the non-conjugated dienes to the conjugated isomers. In particular, the isomerisation of the 1,5-cyclooctadiene has been extensively studied by Tayim and Bailar using the $PtCl_2(PPh_3)_2$ /$SnCl_2$ catalyst [5]. They found that the isomerisation occurs through two consecutive first order reactions, as in eqn. 3. The kinetic data suggested that the conjugated and the non-conjugated dienes are similarly activated by the platinum complex. This behaviour has not been observed on our case, in which 1,3-cyclooctadiene is irreversibly produced. In fact, while the pure 1,4-cyclooctadiene does isomerise in the presence of the iridium complex to give both the 1,5 and the 1,3 isomers (Fig. 8), the 1,3-diene does not produce isomers under such conditions.

$$1,5\text{-}C_8H_{12} \rightleftharpoons 1,4\text{-}C_8H_{12} \rightleftharpoons 1,3\text{-}C_8H_{12} \qquad (3)$$

The difference in the interaction with the catalyst between the non-conjugated and conjugated diolefins is confirmed by their reaction with $Ir_2D_2Cl_2(1,5\text{-}C_8H_{12})$ $(PPh_3)_2$. An excess of 1,5 or of 1,4-cyclooctadiene rapidly leads to hydrogen exchange with the deuterido ligand to give $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$, while

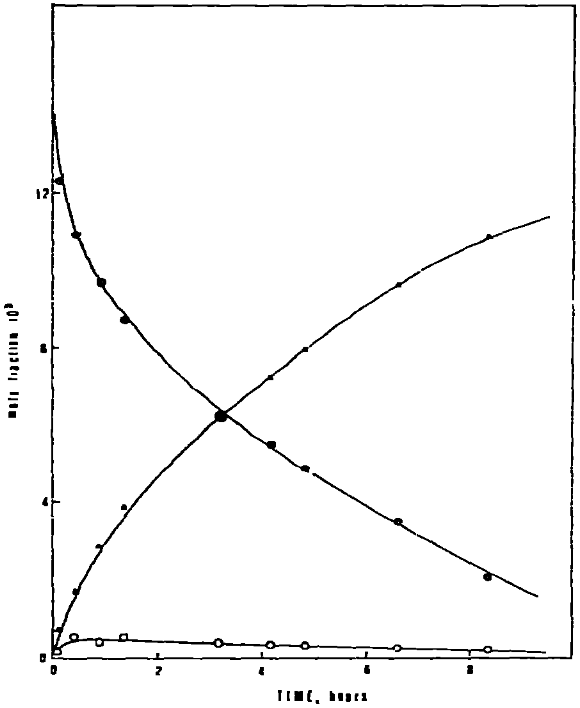


Fig. 8. Catalytic isomerisation of 1,4-cyclooctadiene ($2.3 \times 10^{-1} M$) with $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ ($4.8 \times 10^{-2} M$) in dichloromethane at 0° under N_2. o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; ▲, 1,3-cyclooctadiene.

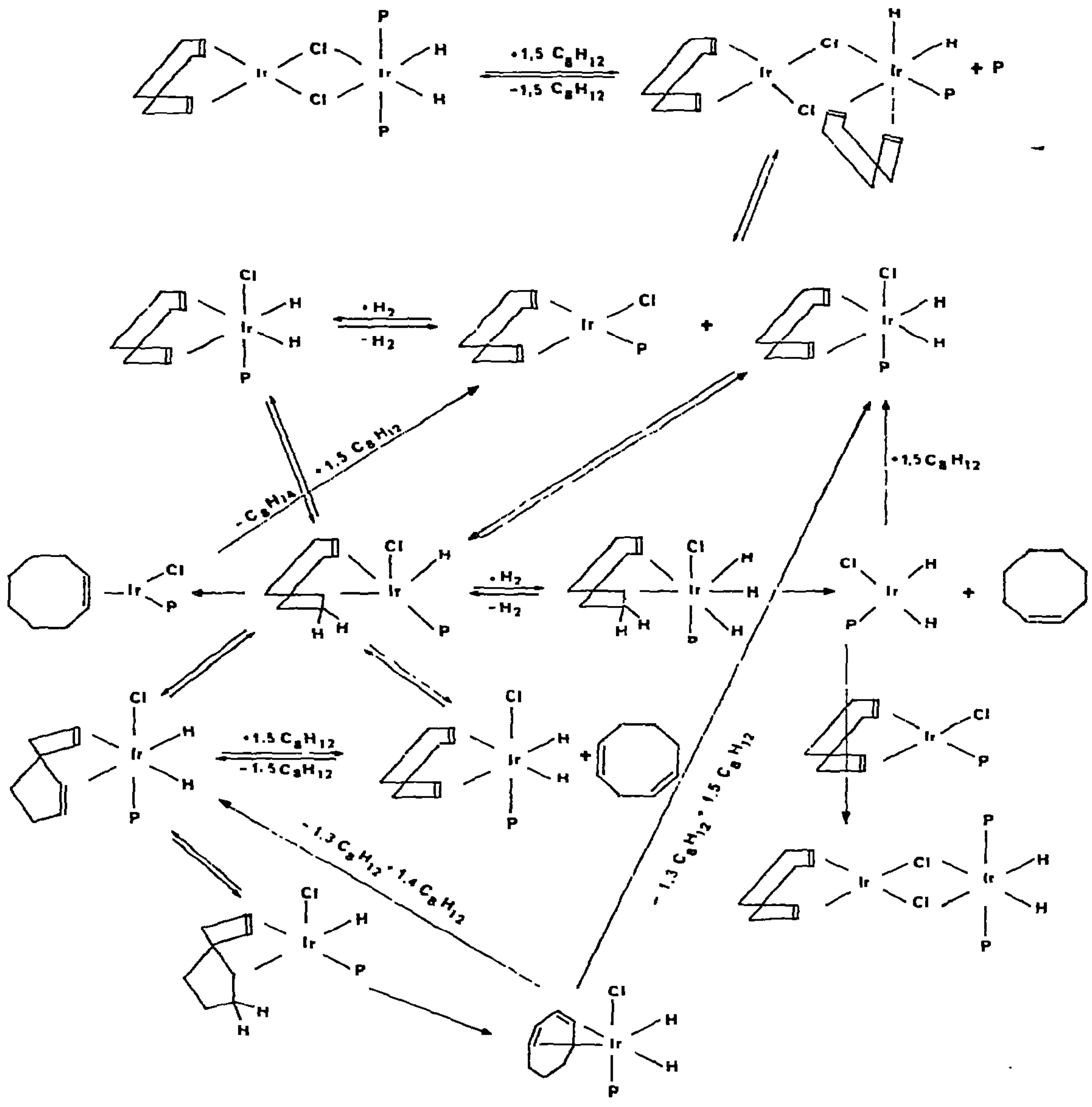
practically no isotopic exchange is observed when the 1,3-diene is used. When the transformation of 1,5-cyclooctadiene is carried out under hydrogen cyclooctene and cyclooctane are produced as hydrogenation products. From the data shown in Fig. 6 the following interesting features can be deduced: (i) the hydrogenation rate of the 1,5 and the 1,4 isomers is faster than that of the 1,3 isomer which is virtually not hydrogenated under these conditions, (ii) the hydrogenation of the cyclooctene to cyclooctane is slow and starts only after complete disappearence of the non-conjugated 1,5 and 1,4 isomers.

The selectivity observed in the iridium complex catalysed hydrogenation of the cyclooctadienes may be compared with that observed when other homogeneous catalysts are used. Thus, the $PtCl_2(PPh_3)_2/SnCl_2$ system [6], which requires more drastic conditions (temp. 100°, $P(H_2)$ 30 atm), is very effective for non-conjugated dienes and also shows a lower, though definite, rate of hydrogenation for the conjugated dienes. Furthermore, in this case, hydrogenation of the 1,3-diene is favoured over that of cyclooctene.

The Wilkinson's catalyst $RhCl(PPh_3)_3$ is less selective towards diene and monoene hydrogenation, since the rate observed for the 1,3-cyclooctadiene is comparable with that observed for the cyclooctene [7].

Scheme 1 presents the activation of 1,5-cyclooctadiene in the isomerisation and hydrogenation reactions.

The intermediate $IrH_2Cl(1,5\text{-}C_8H_{12})PPh_3$ can be produced by dissociation of one triphenylphosphine ligand. Under an inert atmosphere and at low temp-



erature this compound acts as the principal catalyst for the σ—π isomerisation of the 1,5 to the 1,4 and 1,3 isomers. This is probably because a structure having each olefinic double bond *cis* to only one hydrido ligand does not favour hydrogenation of the ligand. Under hydrogen, however, a multihydrido complex can be formed, and acts as a hydrogen donor to the diolefin, producing cyclooctene. The presence of the $IrH_2Cl(1,5\text{-}C_8H_{12})PPh_3$ intermediate is supported by two observations: (i) under nitrogen this complex can readily lose hydrogen to give the observed $IrCl(1,5\text{-}C_8H_{12})PPh_3$; (ii) with $IrCl(1,5\text{-}C_8H_{12})PPh_3$ under hydrogen at low temperature the catalytic transformation of the 1,5-cyclooctadiene occurs without an induction period (Fig. 9).

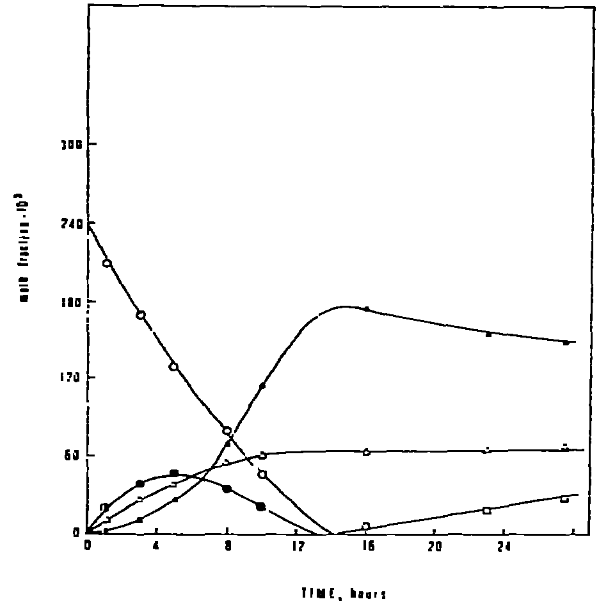


Fig. 9. Catalytic transformation of 1,5-cyclooctadiene (2.03 *M*) with IrCl(1,5-C_8H_{12})PPh_3 (6.55 × 10^{-3}*M*) in benzene at 22° under hydrogen (1 atm). o, 1,5-cyclooctadiene; ●, 1,4-cyclooctadiene; △, 1,3-cyclooctadiene; ▲, cyclooctene; □, cyclooctane.

The presence of a multihydrido complex under hydrogen is postulated because $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ is only a weak hydrogen donor towards the diolefins as clearly indicated by Figs. 4 and 5, which show that reaction 1 is very slow in absence of hydrogen. The multihydrido complex cannot be directly detected, however, in fact precipitation of the catalyst under hydrogen gives the pure $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ and the IR, NMR and electronic spectra of the catalyst solution under hydrogen atmosphere are not different from those observed under nitrogen atmosphere.

Experimental

All the solvents, which were reagent grade, were dried and distilled under nitrogen and the solutions were manipulated under nitrogen or hydrogen. UV spectra were recorded with Carl Zeiss DMR21 instrument.

The cyclooctadienes were distilled under nitrogen before use: the 1,5 and 1,3 isomers were supplied by Fluka and the 1,4 isomer was prepared by the bromination-reduction method [9].

The complexes $Ir_2H_2Cl_2(1,5\text{-}C_8H_{12})(PPh_3)_2$ [4] and $IrCl(1,5\text{-}C_8H_{12})PPh_3$ [8] were prepared by published methods. The products of the isomerisation and hydrogenation reactions were identified and quantitatively determined by GLC, with a Hewlett—Packard 5750 instrument, using 20% DEGS on Chromosorb P column (5 m × 2 mm) connected with a 15% Apiezon L on Chromosorb W column (2 m × 2 mm) at 110°; the samples of the reacting solutions were treated with acrylonitrile to quench the catalytic activity of the iridium complex and then analysed.

Acknowledgment

We thank Prof. A. Sacco for helpful discussions. This research was supported by Consiglio Nazionale delle Ricerche.

References

1 S. Otsuka and M. Rossi, J. Chem. Soc., A, (1968) 2630.
2 S. Otsuka and M. Rossi, J. Chem. Soc., A, (1969) 497.
3 M. Lavecchia, M. Rossi and A. Sacco, Inorg. Chim. Acta, 4 (1970) 29.
4 M. Gargano, P. Giannoccaro and M. Rossi, Inorg. Chim. Acta, 7 (1973) 409.
5 H.A. Tayim and J.C. Bailar, Jr., J. Amer. Chem. Soc., 89 (1967) 3420.
6 H.A. Tayim and J.C. Bailar, Jr., J. Amer. Chem. Soc., 89 (1967) 4330.
7 J.P. Candlin and A.R. Oldnam, Disc. Faraday Soc., 46 (1968) 60.
8 G. Winkhaus and H. Singer, Chem. Ber., 99 (1966) 3610.
9 S. Moon and C.R. Ganz, J. Org. Chem., 34 (1969) 465.