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π-Cyclo-octa-1,5-diene Complexes of Rhodium and Iridium

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The reduction of $[RhCl(C_8H_{12})]_2$ *with sodium in THF, in the presence of cyclo-octa-1,5-diene and pyridine, produces a well characterized compound of formula* $Rh(C_8H_{13})(C_8H_{12})$. *This latter reacts with triphenylphosphine giving, under argon atmosphere,* $Rh(C_8H_{13})(PPh_3)_2$ *and, under hydrogen atmosphere,* $RhH(PPh_3)_4$. *The analogous reduction of* $[IrCl(C_8H_{12})]_2$ *gives a product rather difficult to characterize which, by reaction with triphenylphosphine gives place to* $IrH(C_8H_{12})(PPh_3)_2$ *under Ar, and to* $IrH_3(PPh_3)_2$ *under* H_2 *atmosphere.*

Introduction

Recently the synthesis and the reactions of π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt have been reported.[1,2,3] As an extension of our studies on low-valent metal complexes containing *cis, cis*-cyclo-octa-1,5-diene as ligand we report the preparation and the properties of some new rhodium and iridium complexes. The analytical and structural characterization derived by n.m.r. experiments are given for $Rh(C_8H_{13})(C_8H_{12})$. Although our attempts to prepare the analogous iridium derivative in the pure form failed, we found that the crude product of the reduction of $[Ir(C_8H_{12})Br]_2$ with sodium is a convenient material for the synthesis of a new hydrido complex of formula $IrH(C_8H_{12})(PPh_3)_2$.

Experimental Section

All compounds were prepared and manipulated in an atmosphere of argon. 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 H-100 instrument.

π-Cyclo-octenyl-π-cyclo-octa-1,5-dienerhodium. $Rh(C_8H_{13})(C_8H_{12})$. A mixture of $[RhCl(C_8H_{12})]_2$[4] (2.2 g, 4.5 mmol.), pyridine (2.8 g, 35 mmol.), cyclo-octa-1,5-diene (5 g, 46 mmol.) and sodium (0.3 g, 13 mmol.) in tetrahydrofuran (50 ml) was stirred at room temperature for 12 hr. After filtration the solvent was evaporated under reduced pressure and the resulting oil dissolved in n-pentane. On cooling to –80°C, yellow-orange needles separated, m.p. 60°C. The complex is soluble in all organic solvents. *Anal.* Calcd. for $C_{16}H_{25}Rh$: C, 60.0; H, 7.9. Found: C, 60.6; H, 8.0.

π-Cyclo-octenylbis(triphenylphosphine)rhodium. $Rh(C_8H_{13})(PPh_3)_2$. A solution of $Rh(C_8H_{13})(C_8H_{12})$ (0.3 g, 1 mmol.) in benzene (5 ml) was treated with triphenylphosphine (0.5 g, 2 mmol.). By adding n-pentane yellow-orange crystals separated. The ^1H n.m.r. spectrum of the compound is identical to that reported in the literature.[5] *Anal.* Calcd. for $C_{44}H_{43}P_2Rh$: C, 71.8; H, 5.8. Found: C, 70.2; H, 5.7.

Hydridotetrakis(triphenylphosphine)rhodium. $RhH(PPh_3)_4$. A solution of $Rh(C_8H_{13})(C_8H_{12})$ (0.3 g, 1 mmol.) in benzene (10 ml) was treated with triphenylphosphine (1 g, 4 mmol.) under hydrogen atmosphere. By adding n-pentane yellow crystals separated. The m.p. and the I.R. spectrum of the compound are identical to those reported in the literature.[6] *Anal.* Calcd. for $C_{72}H_{60}P_4Rh$: C, 75.0; H, 5.3. Found: C, 73.0; H, 5.3.

Reaction of $[Ir(C_8H_{12})Cl]_2$ *with cyclo-octa-1,5-diene, pyridine and sodium.* A mixture of $[Ir(C_8H_{12})Cl]_2$[7] (1.1 g, 1.6 mmol.), pyridine (1.3 g, 16.5 mmol.), cyclo-octa-1,5-diene (2 g, 18.5 mmol.) and sodium (0.1 g, 4 mmol.) in tetrahydrofuran (20 ml) was stirred at room temperature for several hours. After filtration, the solvent was evaporated under reduced pressure and the resulting oil was dissolved in benzene. By adding n-pentane a brown powder separated. The I.R. spectrum of the product showed the presence of pyridine and the elemental analysis were inconsistent with any formulation. Further crystallisation failed to give a pure compound.

Hydridocyclo-octa-1,5-dienebis (triphenylphosphine) iridium $IrH(C_8H_{12})(PPh_3)_2$. A mixture of $[Ir(C_8H_{12})Br]_2$ (0.9 g, 1.2 mmol.), pyridine (0.7 g) cyclo-octa-1,5-diene (1.2 g) and sodium (0.8 g, 3.5 mmol.) in tetrahydrofuran (20 ml) was stirred for 20 hr at room temperature. After filtration and evaporation of the solvent, the resulting oil was dissolved in benzene

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(1) S. Otsuka and M. Rossi, *J. Chem. Soc.* (A), 2630 (1968).
(2) S. Otsuka and M. Rossi, *J. Chem. Soc.* (A), 497 (1969).
(3) M. Rossi and A. Sacco, *Chem. Comm.*, 471 (1969).
(4) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(5) C. A. Reilly and H. Thyret, *J. Am. Chem. Soc.*, *89*, 5144 (1967).
(6) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, *7*, 546 (1968).
(7) G. Winkhaus and H. Singer, *Chem. Ber.*, *99*, 3610 (1966).

(20 ml) and the solution treated with triphenylphosphine (0.6 g, 2.3 mmol.). By adding n-pentane white ivory crystals separated, m.p. 157-9°C. The complex is soluble in benzene and tetrahydrofuran but insoluble in n-pentane and ethanol. *Anal.* Calcd. for $C_{44}H_{43}P_2Ir$: C, 63.9; H, 5.2; P, 7.5. Found: C, 64.0; H, 5.2; P, 7.3.

Trihydridobis (triphenylphosphine) iridium. $IrH_3(PPh_3)_2$. A solution of $IrH(C_8H_{12})(PPh_3)_2$ (0.3 g) in benzene (5 ml) was stirred for 1 hr under hydrogen atmosphere at room temperature. White crystals slowly separated and the precipitation was completed by adding n-pentane. The m.p. and the I.R spectrum of the compound are identical to those reported in the literature.[8] *Anal.* Calcd. for $C_{36}H_{33}P_2Ir$: C, 59.9; H, 4.6. Found: C, 60.6; H, 5.0.

Results and Discussion

Treatment of $[RhCl(C_8H_{12})]_2$ in tetrahydrofuran with an equimolecular quantity of sodium in the presence of cyclo-octa-1,5-diene and pyridine gives a yellow solution from which the complex of formula $Rh(C_8H_{13})(C_8H_{12})$ was isolated as yellow crystals, very soluble in organic solvents. The ^1H n.m.r. spectrum of this compound strongly suggested a structure similar to that reported[9] for the analogous $Co(C_8H_{13})(C_8H_{12})$ complex. On the basis of this structure the correlation between n.m.r. resonances and hydrogen nuclei is reported in the Figure 1.

Moreover, spin decoupling experiments permit unambiguous assignment for certain nuclei along with spin coupling constants. Thus, the H_1 absorption is a triplet of doublets ($J_{1,2}$ 8 cps; J_{1-Rh} 2.5 cps) which collapses to a doublet (Figure 2) upon irradiation of H_2 nuclei at δ 3.9 p.p.m. This latter protons are also coupled with methylene hydrogens of the cyclo-octenyl group giving a multiplet (four peaks). The multiplet is transformed into a doublet (Figure 3) by irradiation at δ 1.88 p.p.m., where the absorption of the coupled methylene protons appear. The H_A and H_B nuclei are magnetically non equivalent owing to the anisotropy of the cyclo-octenyl ligand and their absorption bands are unresolved multiplets at δ 5.0 and 4.7 p.p.m. However, by irradiation of the coupled methylene protons of the cyclo-octadiene ligand at δ 1.96 and δ 2.35 p.p.m. a doublet of doublets appear

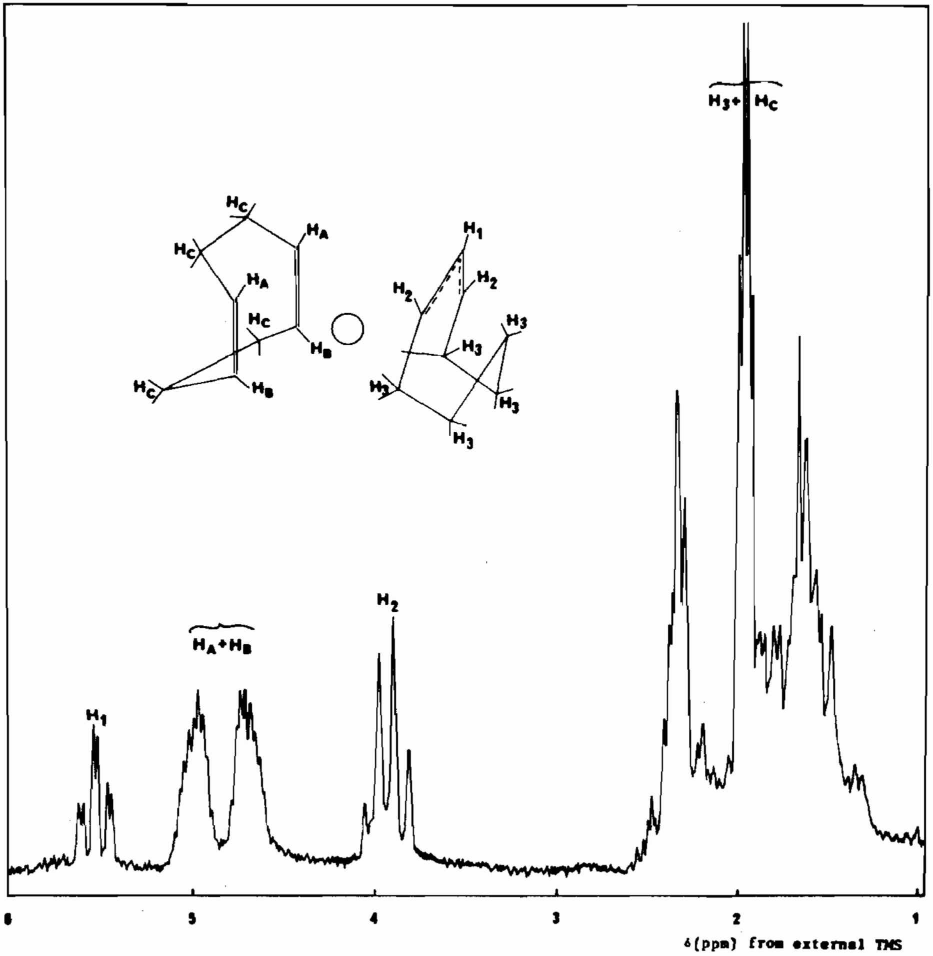

Figure 1.

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[8] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965).

[9] T. Watanabé, A. Takenaka, S. Koda, and S. Otsuka, *Acta Cryst.*, (A), *25*, S3, 163 (1969). S. Koda, A. Takenaka and T. Watanabè, *Chem. Comm.*, 1293 (1969).

for each absorbance (Figure 4a and 4b).

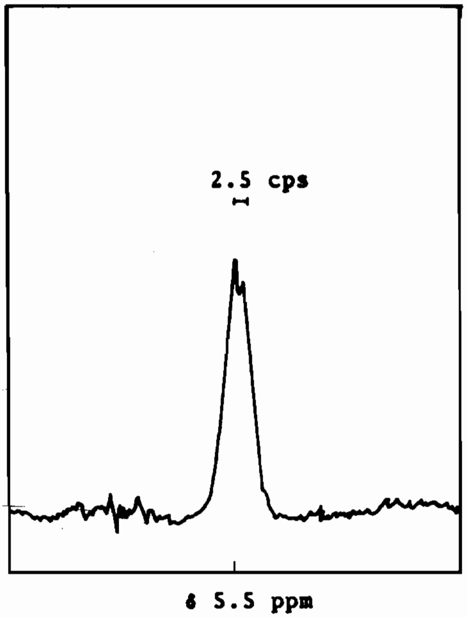

Figure 2.

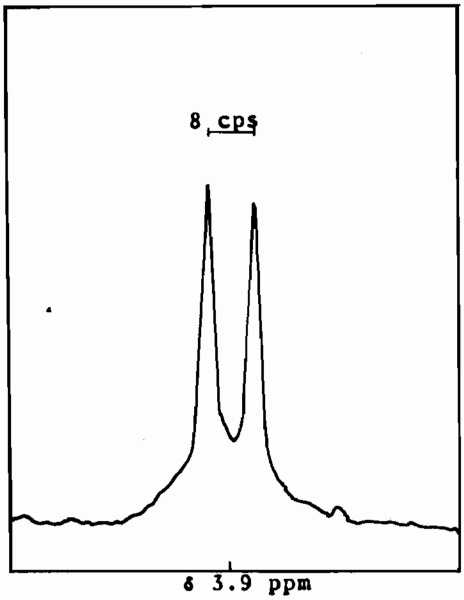

Figure 3.

π-Cyclo-octenyl-π-cyclo-octa-1,5-dienerhodium reacts with triphenylphosphine under argon producing the known[5] π-cyclo-octenylbis(triphenylphosphine) rhodium:

$$Rh(C_8H_{13})(C_8H_{12})+2PPh_3 \longrightarrow Rh(C_8H_{13})(PPh_3)_2+C_8H_{12}$$

whereas in the presence of hydrogen the already reported[6] hydridotetrakis(triphenylphosphine)rhodium is formed:

$$Rh(C_8H_{13})(C_8H_{12})+4PPh_3+2H_2 \longrightarrow RhH(PPh_3)_4+2C_8H_{14}$$

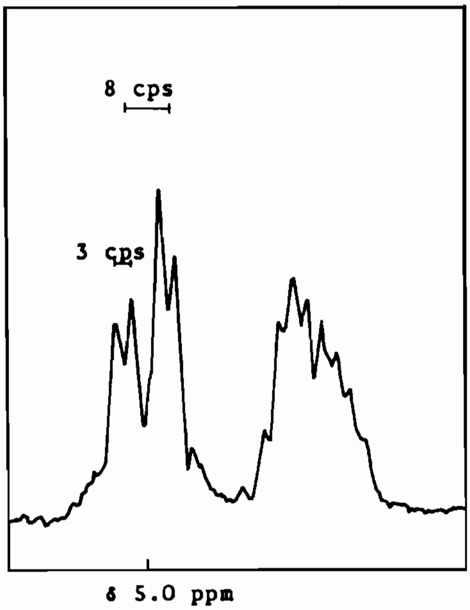

Figure 4a.

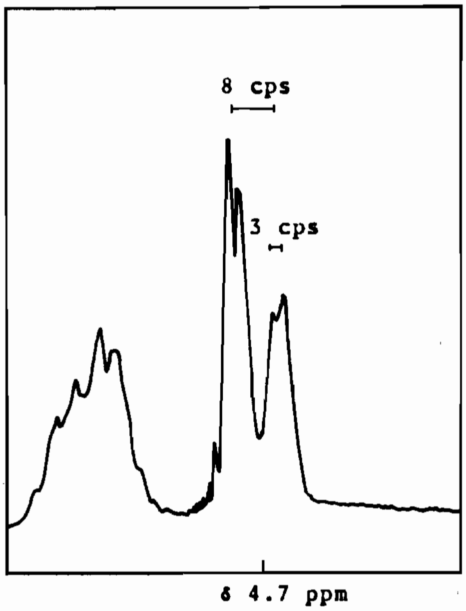

Figure 4b.

The reduction of $[IrX(C_8H_{12})]_2$ (X = Cl, Br) in tetrahydrofuran with sodium in the presence of cyclo-octa-1,5-diene and pyridine produces a brown solution. Our attempts to obtain a pure compound by repeated

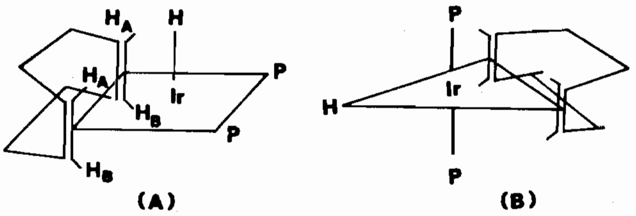

Figure 5.

crystallisation were unsuccessful. However, the crude product reacts with triphenylphosphine under Ar to give the complex of formula $IrH(C_8H_{12})(PPh_3)_2$ and under H_2 to give the already known[8] $IrH_3(PPh_3)_2$. The presence of a hydridic proton in $IrH(C_8H_{12})(PPh_3)_2$ is deduced from the I.R. spectrum, which shows a strong iridium-hydrogen stretching band at 2100 cm^{-1}, and from the high field peak in the n.m.r. spectrum.

The appearance of a triplet ($\delta = 13.3$ p.p.m. from the external TMS, $J_{H-P} = 24$ cps) suggests the equivalence of the phosphorus atoms; this result is interpretable by the structures shown in Figure 5. However, the less symmetrical structure (A) better agrees with the two observed resonances of H_A and H_B nuclei at δ 3.94 and δ 4.18 p.p.m.

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