

New Five-coordinate Iridium Complexes

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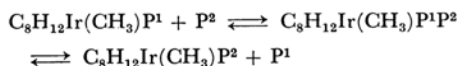
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Recently we have reported the preparation of methyl- and phenyl-(triphenylphosphine)-(1,5-cyclooctadiene)rhodium, and hydrido-tetrakis(triphenylphosphine)rhodium from the reactions of bis(1,5-cyclooctadiene)rhodium chloride (I) with methyl, phenyl and isopropyl Grignard reagents in the presence of triphenylphosphine, respectively.¹⁾ In the present communication, we wish to report the preparation of new five-coordinate methyl- and hydrido-iridium complexes resulting from an extended work to the iridium analogue of I.

Bis(1,5-cyclooctadiene)iridium chloride (II) and triphenylphosphine in benzene-ether mixture were treated with methylmagnesium iodide at an ice temperature. After hydrolysis, the organic layer was concentrated and subjected to chromatography on alumina with benzene as eluant. Concentration of the eluate, followed by the addition of hexane to the residue gave pale yellow crystals of methyl-bis(triphenylphosphine)-(1,5-cyclooctadiene)iridium (III) (Yield 17%, mp*¹ 146–147°C (with decomp). Found: C, 65.12; H, 5.45%. Calcd for C₄₅H₄₅P₂Ir: C, 64.34; H, 5.40%. NMR (in C₆D₆): 2.3–3.2τ (C₆H₅), 6.1 and 7.0τ (=CH), 8.1τ (CH₂), 9.44τ (CH₃). Methyl proton resonance appeared as a singlet and suggested the existence of the phosphine interchange process which could be schematically pictured as:



Phosphine interchange would be rapid enough at room temperature to cause disappearance of P–H

coupling. Evidence was obtained by the NMR spectrum at –60°C (in CH₂Cl₂) in which methyl protons showed triplet peaks of 1 : 2 : 1 ratio (*J*_{PH} = 10 cps).

Vrieze and Volger²⁾ pointed out the presence of a five-coordinate short-lived intermediate (diolefin)-MCl(L)₂ (M = Rh, Ir and L = Group-V donor ligand) from the NMR studies of ligand exchange reaction of (diolefin)MCl(L), and they isolated C₈H₁₂IrCl-(PPh₃)₂ when ethanol was used as solvent. It is interesting that the replacement of chlorine by methyl group made the five-coordinate iridium complex easy to isolate.

The reaction of II with isopropylmagnesium bromide in the presence of triphenylphosphine was carried out, in order to compare it with the case of rhodium in which cyclooctadiene was replaced by triphenylphosphine to give hydrido-tetrakis(triphenylphosphine)rhodium. According to a similar procedure, white needles of hydrido-bis(triphenylphosphine)-(1,5-cyclooctadiene)iridium (IV) were obtained in almost quantitative yield without loss of a cyclooctadiene ligand (mp*¹ 162–165°C (with decomp). Found: C, 64.22; H, 5.55; P, 7.33%. Calcd for C₄₄H₄₃P₂Ir: C, 63.98; H, 5.25; P, 7.50%). IV was relatively more stable than III. The NMR spectrum (in CDCl₃) showed peaks at 2.5–3.0τ (C₆H₅), 6.2 and 6.5τ (=CH), and 8.4τ (CH₂). Additional triplet of 1 : 2 : 1 ratio (*J*_{PH} = 22 cps) was found at 23.7τ which was assigned to hydrogen directly bonded to the iridium. It is obvious that the phosphine interchange proceeded more slowly in this complex than in III.

More detailed studies of this type of complexes are now in progress.

1) M. Takesada, H. Yamazaki and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 1121 (1968).

*¹ Measured in nitrogen filled capillary tube.

2) K. Vrieze and H. C. Volger, *J. Organometal Chem.*, **11**, 17 (1968).