New Five-coordinate Iridium Complexes

Hiroshi YAMAZAKI, Masahiko TAKESADA and Nobue HAGIHARA

The Institute of Physical and Chemical Research, Yamato-machi, Saitama
The Institute of Scientific and Industrial Research, Osaka University, Yamada-Kami, Suita, Osaka

(Received November 6, 1968)

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-cyclooctadienerhodium 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-cyclooctadieneiridium 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 $C_{45}H_{45}P_2Ir$: C, 64.34; H, 5.40%. NMR (in C_6D_6): 2.3—3.2τ (C_6H_5), 6.1 and 7.0τ (=CH), 8.1τ (CH_2), 9.44τ (CH_3).). Methyl proton resonance appeared as a singelt and suggested the existence of the phosphine interchange process which could be schematically pictured as:

$$C_8H_{12}Ir(CH_3)P^1 + P^2 \rightleftarrows C_8H_{12}Ir(CH_3)P^1P^2$$
$$\rightleftarrows C_8H_{12}Ir(CH_3)P^2 + P^1$$

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 CH_2Cl_2) in which methyl protons showed triplet peaks of 1 : 2 : 1 ratio ($J_{PH}=10$ cps).

Vrieze and Volger[2] pointed out the presence of a five-coordinate short-lived intermediate (diolefin)-$MCl(L)_2$ (M = Rh, Ir and L = Group-V donor lignad) from the NMR studies of ligand exchange reaction of (diolefin)MCl(L), and they isolated $C_8H_{12}IrCl(PPh_3)_2$ 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 $C_{44}H_{43}P_2Ir$: C, 63.98; H, 5.25; P, 7.50%). IV was relatively more stable than III. The NMR spectrum (in $CDCl_3$) showed peaks at 2.5—3.0τ (C_6H_5), 6.2 and 6.5τ (=CH, Former peak is broader than the latter), and 8.4τ (CH_2). 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 phophine interchange proceed 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).