Diiodo-π-cyclopentadienyliridium and Its Derivatives

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Recently formation of dihalo-π-(pentamethylcyclopentadienyl)iridium from the reaction of iridium chloride hydrate with hexamethyl (Dewar benzene) was reported.[1] However, simple dihalo-π-cyclopentadienyliridium is not known as yet in spite of its ability to prepare complexes having a π-cyclopentadienyliridium group. We wish to report the preparation of diiodo-π-cyclopentadienyliridium and some derivatives thereof.

Cyclooctatetraene-π-cyclopentadienyliridium[2] [mp 114—116°C. IR(KBr): $\nu_{C=C}$ 1635 cm^{-1}. NMR(*p*-xylene): 4.27τ (singlet, –CH=CH–), 5.21τ (singlet, C_5H_5), 5.77τ (singlet, coordinated –CH=CH–).] was treated with equimolar amount of iodine in methylene chloride at room temperature to give insoluble brown crystals of diiodo-π-cyclopentadienyliridium (I) in almost quantitative yield. The infrared spectrum of I is very similar to that of the rhodium analogue.[4] A similar treatment of 1,5-cyclooctadiene-π-cyclopentadienyliridium did not give I but insoluble brown crystals having a combined composition of the reactant, $C_{13}H_{17}I_2Ir$, which was deduced on the basis of elemental analysis.

Similar to the rhodium analogue,[5] I reacted with triphenylphosphine in methylene chloride giving air-stable orange red crystals of diiodo-triphenylphosphine-π-cyclopentadienyliridium (II) [Yield 90%. Mp ~310°C (decomp). NMR($CDCl_3$): 2.2—2.7τ (C_6H_5), 4.57τ (doublet, J_{PH} 1.5 Hz, C_5H_5).]. Methyldiphenylphosphine and carbon monoxide also gave diiodo-methyldiphenylphosphine-π-cyclopentadienyliridium [Orange red crystals. Yield 82%. Mp 209—211°C. NMR($CDCl_3$): 2.1—2.7τ (C_6H_5), 4.57τ (doublet, J_{PH} 1.5 Hz, C_5H_5), 7.26τ (doublet, J_{PH} 11 Hz, CH_3).] and diiodocarbonyl-π-cyclopentadienyliridium [Red crystals. Yield 93%. Mp>180°C (decompn without melting). IR(KBr): ν_{CO} 2040 cm^{-1} (with a shoulder at 2020 cm^{-1}). NMR($CDCl_3$): 3.99τ (singlet, C_5H_5).] respectively.

The reaction of II with methylmagnesium iodide in tetrahydrofuran-benzene mixture gave air-stable orange red crystals of iodo-triphenylphosphine-π-cyclopentadienylmethyliridium [Yield 80%. Mp 233—236°C (decomp). NMR($CDCl_3$): 2.4—2.7τ (C_6H_5), 4.89τ (doublet, J_{PH} 1.5 Hz, C_5H_5), 8.37τ (doublet, J_{PH} 7 Hz, CH_3).]. The reaction of II with isopropylmagnesium bromide in the presence of carbon monoxide afforded triphenylphosphine-carbonyl-π-cyclopentadienyliridium[6] [Yellow crystals. Yield 18%. Mp 180—183°C. IR(Nujol): ν_{CO} 1925 cm^{-1}. NMR($CDCl_3$): 1.9—3.1τ (C_6H_5), 5.03τ (singlet, C_5H_5).] and in the presence of triphenylphosphine, ionic hydridoiridium complex of the formula, $[C_5H_5Ir(PPh_3)_2H]^+I^-$ [Colorless crystals. Yield 47%. Mp 194—198°C (decomp). IR(KBr): ν_{IrH} 2150 cm^{-1}. NMR($CDCl_3$): 2.4—3.0τ (C_6H_5), 4.60τ (singlet, C_5H_5), 24.4τ (triplet, J_{PH} 26 Hz, Ir–H).]. The last reaction differs from the cases of cobalt and rhodium analogues which gave bis(triphenylphosphine)-π-cyclopentadienyl-cobalt and -rhodium.[7]

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[1] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **91**, 5970 (1969).

[2] This compound was prepared by a procedure similar to that for the preparation of 1,5-cyclooctadiene-π-cyclopentadienyliridium.[3] Satisfactory results have been obtained for the analysis of all the compounds described in this communication.

[3] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1965**, 4997.

[4] R. J. Angelici and E. O. Fischer, *J. Amer. Chem. Soc.*, **85**, 3733 (1963).

[5] A. Kasahara, T. Izumi, and K. Tanaka, This Bulletin, **40**, 699 (1967).

[6] This compound was prepared in a higher yield from the reaction of Vaska's complex with sodium cyclopentadienide.[7]

[7] H. Yamazaki and N. Hagihara, "Symposium of Organometallic Compounds," Osaka, October 16, 1968; Preprints, p. 123.