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A Platinum Complex Bound to Iodinated Polystyrene by a Platinum-Carbon σ-Bond

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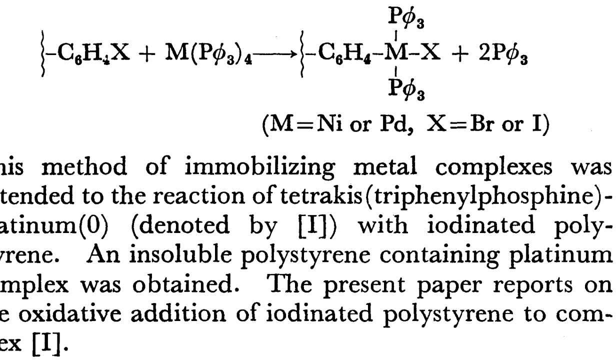
Synopsis. A platinum complex bound to iodinated polystyrene was prepared by the reaction of $Pt(P\phi_3)_4$ with iodinated polystyrene. The reaction of the synthesis was confirmed by means of direct oxidative addition of aryl iodide to $Pt(P\phi_3)_4$.

Recently much attention has been paid to the immobilizing of a soluble organotransition metal complex catalyst by fixing it on a polymer, not only from a practical point of view, but also for examining the effect of polymer ligand on the catalytic activity and selectivity. Polystyrene containing phosphorus, nitrogen or cyclopentadiene has been widely used to immobilize transition metal complexes such as $RhCl(CO)(P\phi_3)_2$ ($\phi=C_6H_5$)[1-3] and $TiCp_2Cl_2$ ($Cp=C_5H_5$)[4] through the coordination bond of metal-phosphine, metal-nitrogen or metal-cyclopentadiene.

In the preceding paper,[5] it was reported that treatment of a halogenated polystyrene with tetrakis(triphenylphosphine) nickel (0) or palladium(0) gave an insoluble nickel(II) or palladium(II) complex combined to polystyrene by metal-carbon σ-bond as follows:



$$\wr\text{-}C_6H_4X + M(P\phi_3)_4 \longrightarrow \wr\text{-}C_6H_4\text{-}\overset{P\phi_3}{\underset{P\phi_3}{M}}\text{-}X + 2P\phi_3$$

(M=Ni or Pd, X=Br or I)

This method of immobilizing metal complexes was extended to the reaction of tetrakis(triphenylphosphine)-platinum(0) (denoted by [I]) with iodinated polystyrene. An insoluble polystyrene containing platinum complex was obtained. The present paper reports on the oxidative addition of iodinated polystyrene to complex [I].

Platinum Complex Supported on Iodinated Polystyrene. To a benzene solution (150 ml) of iodinated polystyrene (3.0 g, average P.D. 1100, 96.4% iodination on *para*-position) prepared according to the method given in the literature[6] was added another benzene solution (100 ml) of [I] (5 g) under nitrogen atmosphere. The mixture was warmed up to 70—80 °C and kept for 5—6 hr with stirring, during which a precipitate was obtained. The precipitate was washed three times with benzene and twice with *n*-hexane, and then dried under vacuum. Pale yellow powder (3.6 g), insoluble in common solvents and stable in the air at ambient temperature, was obtained. The amount of platinum supported on iodinated polystyrene could be estimated to be about 4 atoms per ten phenyl rings by assuming that platinum was bound to the polymer as $\wr\text{-}C_6H_4\text{-}Pt(P\phi_3)_2I$. ^{31}P-FT-NMR[7] of the platinum-polystyrene complex suspended in methylene dichloride showed a fairly sharp absorption (26.7 ppm, $J_{Pt-P}=3066$ Hz) in a low field in reference to free triphenylphosphine. This indicates that the platinum-polystyrene complex has *trans*-square planar structure, since only one absorption and one large coupling constant of J_{Pt-P} were observed. It is to be noted that the local magnetic field around the platinum atom is well averaged out in the solvent, since NMR absorptions of solid materials are usually too broad to be detected due to local magnetic fields.

In order to clarify the synthesis reaction and to characterize the platinum-polystyrene complex, a direct oxidative addition of aryl iodide to complex [I] was attempted. The known method of preparing *trans*-bis(triphenylphosphine)σ-phenyl(halo) platinum(II) complexes is to utilize the thermal desulfurylation of $C_6H_5SO_2Pt(P\phi_3)_2X$,[8] which can be prepared from the oxidative addition of $C_6H_5SO_2X$ to complex [I]. The direct oxidative addition of phenyl halide to [I] has not been reported. This seems to be a difficult reaction, although $Pt(PEt_3)_4$ ($Et=C_2H_5$), which is regarded to have a more nucleophilic nature, is subjected to the oxidative addition of phenyl halide.[9] It was found, however, that σ-aryl platinum(II) complexes are readily synthesized only by warming the mixture of [I] and aryl iodide in benzene.

Oxidative Addition of Aryl Iodide to Complex [I]. A commercial iodobenzene (36 mmol) was added to a

TABLE 1. CHARACTERIZATION OF BIS(TRIPHENYLPHOSPHINE) σ-ARYL(IODO)PLATINUM(II)

Complex	Color	Found (%)			Calcd (%)			P-NMR (ppm[a)])	J_{Pt-P} (Hz)	Yield[b)] (%)
		C	H	I	C	H	I			
$C_6H_5Pt(P\phi_3)_2I$	White	55.1	3.95	13.5	54.6	3.79	13.8	27.2	3097	65
p-$C_6H_4CH_3Pt(P\phi_3)_2I$	White	55.9	3.98	13.1	55.1	3.94	13.6	26.9	3104	53
p-$C_6H_4NO_2Pt(P\phi_3)_2I$	Pale yellow	53.2	3.58 N(%): 1.29	12.7	52.1	3.51 N(%): 1.44	13.1	25.7	2971	71
p-$C_6H_4BrPt(P\phi_3)_2I$	White	51.1	3.51	20.2	50.3	3.39	20.7	26.4	3137	63
Pt Complex bound to polymer	Pale yellow	52.8	3.82	22.2				26.7	3065	

a) From free $P\phi_3$ in CH_2Cl_2. b) Based on the $Pt(P\phi_3)_4$ (mol) used.

benzene solution of [I] (4.5 g, 3.6 mmol) under nitrogen atmosphere. The solution was kept at 50—60 °C for 2—3 hr with stirring, during which a white crystal was deposited. The solution was decanted. The crystal was dissolved in hot benzene (200 ml), recrystallized by adding *n*-hexane, well washed with *n*-hexane, and then dried under vacuum. The same method was applied to *p*-tolyl, *p*-nitrophenyl, and *p*-bromophenyl iodide. There was practically no difference in the reactivity of these aryl iodides. No complex was obtained by the treatment with aryl bromide even at a higher temperature (80 °C), most of [I] being decomposed to metallic platinum. The results are summarized in Table 1. ^{31}P–FT–NMR of the complexes also shows that they all have the same *trans*-square planar structure as the platinum-polymer complex.

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