

Phosphine-induced β -Aryloxy Elimination from Aryloxyethylplatinum(II) Complexes having Triphenylphosphine Ligands

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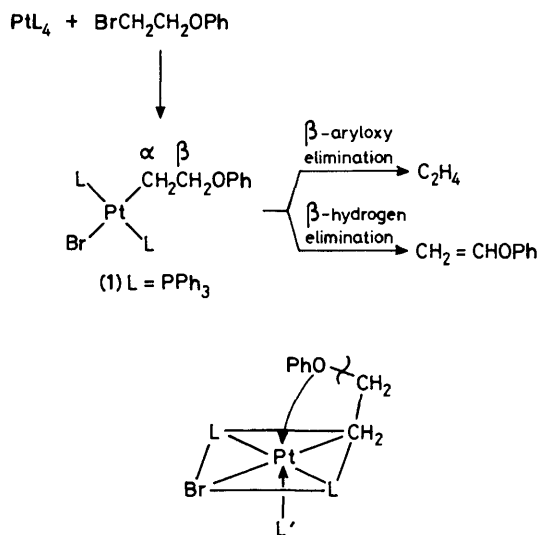
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Addition of phosphorus ligands such as triphenylphosphine and triethyl phosphite to $(\beta$ -aryloxyethyl)-(bromo)bis(triphenylphosphine)platinum(II) in solution accelerates β -aryloxy group elimination by platinum to liberate ethylene.

β -Hydrogen elimination from organotransition metal complexes constitutes one of the most important steps in various organic reactions promoted by transition metal complexes. Extensive investigations on the thermolysis of alkyl transition metal complexes have shed light on the mechanism for the β -hydrogen elimination process.¹ However, elimination of β -substituents other than hydrogen by the transition metal has not received much attention, although it has been postulated in a few transition metal-promoted reactions.² We report here the preparation of β -phenoxyethylplatinum(II) complexes having triphenylphosphine ligands, as well as a novel β -aryloxy group elimination reaction which is unusually accelerated by the addition of ligand.

Treatment of tetrakis(triphenylphosphine)platinum(0) with β -phenoxyethyl bromide in benzene at room temperature affords the *trans*-(β -phenoxyethyl)(bromo)bis(triphenylphosphine)platinum(II) complex (**1**), 66% yield, colourless needles from tetrahydrofuran-Et₂O, m.p. 193–196 °C (decomp.).[†] Similar complexes were obtained by treatment of the Pt⁰ complex with β -*p*-tolyl- (or *p*-methoxyphenyl)oxyethyl bromide, whereas ethylene was evolved during the preparation of β -(*p*-cyanophenoxy)ethylplatinum(II) and β -ethoxyethylplatinum(II) complexes.

Thermolysis of (**1**) in CH₂Ph₂ at 100 °C liberated ethylene and vinyl phenyl ether in *ca.* 1 : 2 ratio accompanied by a small amount of phenol. No coupling products were detected. The results are consistent with the competitive β -elimination of hydrogen and the phenoxy group from complex (**1**) to release phenyl vinyl ether and ethylene, respectively. *para*-Substituents on the phenoxy group such as Me and OMe have



little effect on the product ratio, whereas elimination of the β -(*p*-cyano)phenoxy group seems to take place readily (*vide supra*).

The rate of the reaction was followed by measuring the amount of ethylene evolved and found to be first order with respect to the concentration of (**1**). An unusual feature of this reaction is the acceleration effect of added phosphorus ligand on the β -aryloxy group elimination reaction. The ratio of ethylene to vinyl phenyl ether, *r*, increased with increasing amount of added triphenylphosphine ([PPh₃] = 0, 1.61, 4.84 mol/l: *r* = 0.5, 1.8, 5.7), and an increase in the rate of ethylene evolution was simultaneously observed. Addition of triethyl phosphite (10 equiv.) to (**1**) liberated ethylene almost quantitatively and only a trace of phenyl vinyl ether was detected.

[†] Satisfactory elemental analyses were obtained; $\nu(\text{C-O})$ 1240 cm⁻¹; ¹H n.m.r. (CDCl₃) δ 1.21 (m, with ¹⁹⁵Pt satellites, *J*_{PtH} 88 Hz, α -CH₂) and 3.05 (m, β -CH₂); ¹³C n.m.r. (CDCl₃) δ 9.8 (t, *J*_{CP} 5, *J*_{PtC} 675 Hz, α -CH₂) and 69.6 (s, β -CH₂), suggesting a *trans*-structure (ref. 3).

Strong π -accepting olefins such as maleic anhydride also accelerated the β -phenoxy group elimination.

The observation of the pronounced accelerating effect of the phosphorus ligands on the β -aryloxy group elimination from (**1**) is in sharp contrast to the retarding effect of tertiary phosphine ligands on the β -hydrogen elimination. While a dissociative mechanism for the β -hydrogen elimination has been proposed in the thermolysis of PtR_2L_2 ,¹ an associative mechanism involving a five-co-ordinate intermediate (**2**) \ddagger seems to be operative here. The electrophilicity of the Pt atom increases when a π -accepting ligand co-ordinates to (**1**), so that a facile abstraction of a more electronegative β -aryloxy group by Pt metal takes place. In the present example, tertiary phosphine and phosphite ligands seem to be acting as π -acceptor ligands similar to electronegative olefins such as maleic anhydride, rather than as σ -electron donors.⁴

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\ddagger It is possible that the intermediate has a cationic structure, $[\text{Pt}(\text{CH}_2\text{CH}_2\text{OPh})\text{L}_3]^+ \text{Br}^-$, which was not detected in the ^1H n.m.r. spectrum of (**1**) in the presence of PPh_3 .

References

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