

[PtCl(C₆H₄CH₂O)(PhCH₂O)PN(Ph)P(OCH₂Ph)₂], the first example of an *ortho*-metallated platinum(II) complex of a P–N–P ligand[†]

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The reaction of PhN{P(OCH₂Ph)₂}₂ with Pt(COD)Cl₂ at room temperature gives the *ortho*-metallated complex, **2** via intra C–H activation and the elimination of HCl, as well as the expected *cis* chelated complex **1**.

Keywords: *ortho*-metallated platinum complex

The use of platinum metal complexes containing bis(phosphine) ligands in organic synthesis is well documented.^{1,2} To date, several platinum metal derivatives anchored with one or more bis(phosphine) ligands have been synthesised^{3–7} and are well characterised, including a number of complexes showing *ortho*-metallation through intra-C–H activation. While exploring the transition metal organometallic chemistry of phosphorus based bis(phosphine) ligands, we have found that the reaction of phenylaminobis(dibenzoyloxyphosphine) with Pt(cod)Cl₂ gives an interesting *ortho*-metallated Pt(II) derivative **2** along with the expected *cis*-chelated complex, [PtCl₂{η²-((OCH₂P)₂NPh)] (**1**). We presume that the initially formed *cis*-chelated complex undergoes intra-molecular rearrangement to eliminate one of the chlorine atom as HCl followed by the *ortho*-metallation. Although this type of intra molecular CH activation is well known with carbon bridged bis(phosphines), it is new to the analogous nitrogen bridged bis(phosphines).

The complexes **1** and **2** have been identified by their ³¹P NMR data and by elemental analysis. The ³¹P NMR spectrum of complex **1** exhibits a singlet at δ 89.7 with a large ¹J_{PtP} coupling of 4667 Hz characteristic of mutually *cis*-oriented phosphorus centres. The *ortho*-metallated product exhibits two doublets in its ³¹P NMR spectrum at δ 50.7 and δ 48.7 with a ²J_{PtP} value of 42.7 Hz. Further both the doublets are associated with very large ¹J_{PtP} couplings of 5381 and 5363 Hz respectively, clearly indicating the mutual *cis*-disposition of the two phosphorus centres.⁸

In summary we have reported the first example of an *ortho*-metallated platinum(II) complex involving a P–N–P based ligand. The P–N–P based ligands show remarkable thermal

stability compared to P–C–P based ligands and show more flexibility compared to P–O–P based ligands and are easy to prepare with desired substituents on both phosphorus and nitrogen centres.⁶ The above features should make these class of ligands more suited in homogeneous catalysis for a variety of organic transformations. The utilisation of these ligands in stabilising transition metal organometallic fragments and in catalytic studies are under active investigation in our laboratory.

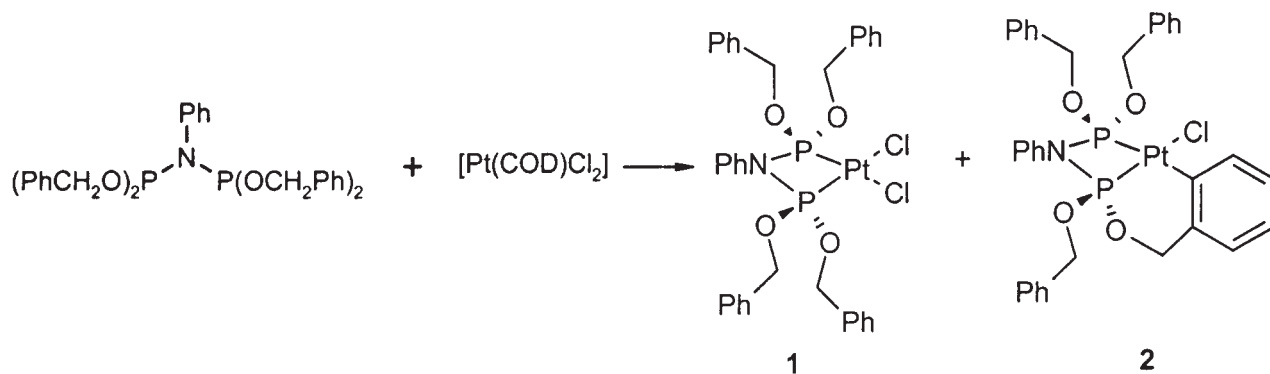
Experimental

A solution of PhN{P(OCH₂Ph)₂}₂ (0.3 mmol, 0.2 g) in CH₂Cl₂ (15 ml) was added dropwise to a solution of [Pt(COD)Cl₂] (0.3 mmol, 0.11 g) also in CH₂Cl₂ (10 ml) with stirring at 25°C; the stirring was continued for 3 h before the solution was concentrated to 8 ml, diluted with 3 ml hexane, and cooled to 0°C to give the following crystalline products in good yield. Compounds **1** and **2** were separated by fractional crystallization in a 1:2 mixture of CH₂Cl₂ and *n*-hexanes.

1, Yield: 65%, m.p. 210°C(d). Found: C, 48.10; H, 3.85; N, 1.59%. C₃₄H₃₃Cl₂NO₄P₂Pt requires C, 48.17; H, 3.89; N, 1.59% ¹H NMR (CDCl₃): δ(phenyl) 7.16–7.40(m, 25H), δ(CH₂), 4.22(d, 8H) (³J_{PH} = 2Hz). **2**, Yield: 22%, m.p. 182°C (d). Found: C, 50.28; H, 3.93; N, 1.65%. C₃₄H₃₂ClNO₄P₂Pt requires C, 50.34; H, 3.96; N, 1.73%. ¹H NMR (CDCl₃): δ(phenyl) 7.16–7.40(m, 24H), δ(CH₂) 4.14(d, 8H) (³J_{PH} = 2Hz).

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Scheme 1

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

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