

Preparation and Reactions of Five-coordinate Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂X Complexes

LUIS A. ORO* and JOSE V. HERAS

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Spain

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It is well known that monodentate tertiary phosphine ligands, L, react with compounds of the type [Rh(diene)Cl]₂ to form the neutral derivatives Rh(diene)LCl [1–6]. When the reaction is carried out in polar media the cationic species, [Rh(diene)L₂]⁺, are formed and can be isolated by addition of a suitable anion [7–9]. It has been suggested [8] that the mechanism of chloride ion displacement by phosphine is most likely via the formation of a five-coordinate intermediate, Rh(diene)L₂Cl, with subsequent loss of halide ion to form the four-coordinate cationic species. Evidence of the existence of these five-coordinate intermediates Rh(diene)L₂Cl has been found by NMR measurements [5, 10].

Our intention at the outset was to use several tertiary phosphine ligands and to see if we could isolate some neutral five-coordinate intermediates of the type Rh(NBD)L₂Cl [11, 12]. We report here on the isolation of Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Cl and some related compounds.

Preparation and Properties of the Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂X Complexes

The addition of a triarylphosphine of low basicity such as P(*p*-Cl-C₆H₄)₃ to [Rh(NBD)Cl]₂ suspended in methanol results in the formation of an orange material. The suspension was filtered and the solid

*To whom correspondence should be sent at his present address: Department of Inorganic Chemistry, University of Zaragoza, Zaragoza (Spain).

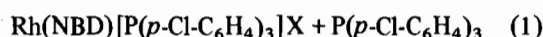
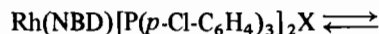
was identified as the neutral complex Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Cl from its analysis, molar conductivity and IR data ($\nu(\text{Rh-Cl})$: 282 cm⁻¹ (nujol)).

Attempts to isolate similar five-coordinate complexes using [Rh(COD)Cl]₂ have been unsuccessful. This observation could be in line with the higher π -acidity of NBD which enhances pentacoordination ability [5, 13].

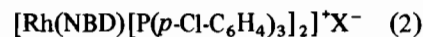
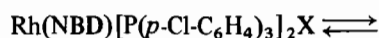
The bubbling of hydrogen at ordinary pressure through a solution of Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Cl leads to the formation of an orange solution which shows catalytic activity in the hydrogenation of cyclic and terminal olefines, e.g. 15 ml absolute ethanol solutions of the Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Cl complex (29 mg) catalytically hydrogenate 1-heptene (300 mg) at a rate of 465 mol H₂(mol Rh)⁻¹ h⁻¹.

Moreover [Rh(NBD)Br]₂ and [Rh(NBD)I]₂, prepared *in situ* by reaction of [Rh(NBD)Cl]₂ with NaBr and NaI, react with P(*p*-Cl-C₆H₄)₃ to yield Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Br and Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂I. These compounds are also soluble in common organic solvents and were characterized by their elemental analyses, molar conductivities and spectroscopic properties.

Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂X complexes exhibit (Table I) very low molecular weights relative to the expected values, suggesting strong dissociation of the five-coordinate complexes (eq. 1):



The measured conductivities show the complexes to be neutral, but the presence of some cationic species according to eq. 2



could not be neglected in polar solvents, because addition of NaPF₆ to the suspension of Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂Cl in methanol leads to the formation of the cationic complex [Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂]⁺PF₆⁻.

TABLE I. Relevant Properties of the Tri(*p*-chlorophenyl)phosphine Complexes.

Compound	Rh(NBD)[P(<i>p</i> -Cl-C ₆ H ₄) ₃] ₂ X		RhH ₂ [P(<i>p</i> -Cl-C ₆ H ₄) ₃] ₂ X		Rh(CO)[P(<i>p</i> -Cl-C ₆ H ₄) ₃] ₂ X
	Molecular weights ^a		$\nu(\text{RhH})^b$		$\nu(\text{CO})^b$
	Found	Calculated			
X = Cl	497	961	2040	2100	1990
X = Br	518	1006	2030	2140	1975
X = I	534	1053	2000	2115	1975

^aBenzene.

^bcm⁻¹ (KBr pellets).

Reactions of the Rh(NBD)[P(*p*-Cl-C₆H₄)₃]₂X Complexes

The orange ethanol solutions of the Rh(NBD)-[P(*p*-Cl-C₆H₄)₃]₂X complexes undergo immediate reaction when treated with molecular hydrogen, and from the resultant solutions reddish compounds can be isolated in good yield. The elemental analyses and spectral properties were consistent with RhH₂[P(*p*-Cl-C₆H₄)₃]₂X complexes. The IR spectrum (KBr pellets) of these complexes shows (Table I) two metal-hydride stretching frequencies [15, 16].

The bubbling of carbon monoxide at ordinary pressure through acetone solutions of Rh(NBD)-[P(*p*-Cl-C₆H₄)₃]₂X complexes produces the displacement of NBD and the elemental analyses and IR data agree with the formation of the monocarbonyl four-coordinate derivatives Rh(CO)[P(*p*-Cl-C₆H₄)₃]₂X. The compounds are yellow crystals, the IR spectra of which show a single band due to a CO stretching mode (Table I).

Further investigations on neutral and cationic complexes of rhodium with P(*p*-R-C₆H₄)₃ ligands are in progress.

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