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Preparation and Reactions of Five-coordinate $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$ Complexes

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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, $[Rh(diene)L_2]^+$, 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, $Rh(diene)L_2Cl$, with subsequent loss of halide ion to form the four-coordinate cationic species. Evidence of the existence of these five-coordinate intermediates $Rh(diene)L_2Cl$ 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 $Rh(NBD)L_2Cl$ [11, 12]. We report here on the isolation of $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Cl$ and some related compounds.

Preparation and Properties of the $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$ Complexes

The addition of a triarylphosphine of low basicity such as $P(p\text{-}Cl\text{-}C_6H_4)_3$ to $[Rh(NBD)Cl]_2$ suspended in methanol results in the formation of an orange material. The suspension was filtered and the solid was identified as the neutral complex $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Cl$ from its analysis, molar conductivity and IR data (ν(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 $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Cl$ 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 $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Cl$ complex (29 mg) catalytically hydrogenate 1-heptene (300 mg) at a rate of 465 mol H_2(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 $P(p\text{-}Cl\text{-}C_6H_4)_3$ to yield $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Br$ and $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2I$. These compounds are also soluble in common organic solvents and were characterized by their elemental analyses, molar conductivities and spectroscopic properties.

$Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$ complexes exhibit (Table I) very low molecular weights relative to the expected values, suggesting strong dissociation of the five-coordinate complexes (eq. 1):

$$Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X \rightleftharpoons Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]X + P(p\text{-}Cl\text{-}C_6H_4)_3 \quad (1)$$

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

$$Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X \rightleftharpoons [Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2]^+X^- \quad (2)$$

could not be neglected in polar solvents, because addition of $NaPF_6$ to the suspension of $Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2Cl$ in methanol leads to the formation of the cationic complex $[Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2]^+PF_6^-\cdot$

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

Compound	$Rh(NBD)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$		$RhH_2[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$		$Rh(CO)[P(p\text{-}Cl\text{-}C_6H_4)_3]_2X$
	Molecular weights[a]		ν(RhH)[b]		ν(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

[a] Benzene. [b] cm^{-1} (KBr pellets).

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Reactions of the Rh(NBD)[P(p-Cl-C_6H_4)$_3$]$_2$X Complexes

The orange ethanol solutions of the Rh(NBD)-[P(p-Cl-C_6H_4)$_3$]$_2$X 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 RhH_2[P(p-Cl-C_6H_4)$_3$]$_2$X 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-C_6H_4)$_3$]$_2$X 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-C_6H_4)$_3$]$_2$X. 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-C_6H_4)$_3$ ligands are in progress.

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