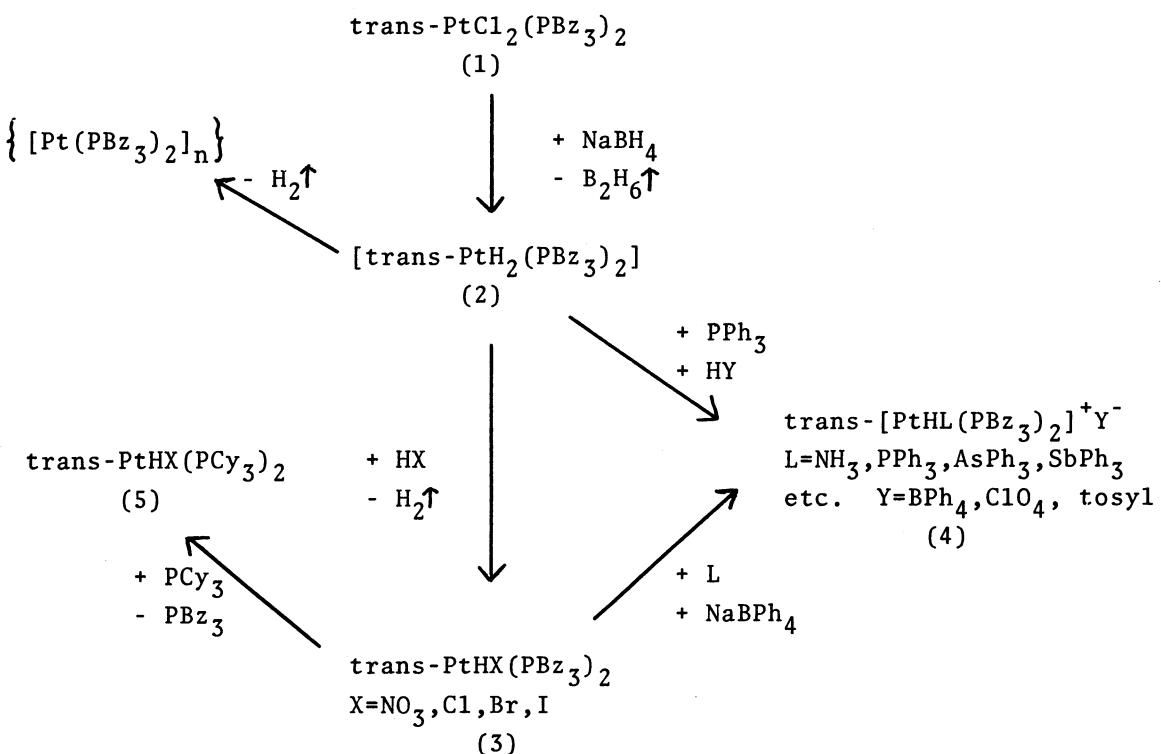


A NOVEL SYNTHETIC ROUTE TO MONOHYDRIDOPLATINUM(II)
COMPLEXES VIA A DIHYDRIDOPLATINUM(II) SPECIES

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A series of hydride complexes, $\text{PtHX}(\text{PBz}_3)_2$ or $[\text{PtHL}(\text{PBz}_3)_2]^{+Y^{-}}$ ($X=\text{NO}_3$, Cl, Br or I. $L=\text{NH}_3$, PPh_3 , AsPh_3 or SbPh_3 . $Y=\text{BPh}_4$, ClO_4 or tosyl.), has been prepared by a novel synthetic path via a dihydridoplatinum(II) species.

Usually square-planar-hydridoplatinum(II) complexes, $\text{PtHX}(\text{PR}_3)_2$, are prepared from the cis-isomers of bis(tertiary phosphine)dichloroplatinum(II), $\text{PtCl}_2(\text{PR}_3)_2$. It has long been believed that the trans-isomers are inappropriate for the synthesis of hydride complexes of platinum(II) because they merely give trace amounts of hydridoplatinum(II) complexes contaminated with starting trans-isomers.¹⁾ During the course of our studies on "the ligand mutual influence(LMI)"²⁾ in transition metal hydrides, we, however, have found that hydridoplatinum(II) complexes stabilized with tribenzylphosphines are quantitatively prepared from trans-isomers.



Trans-bis(tribenzylphosphine)dichloroplatinum(II) (1) was allowed to react with excess sodium tetrahydroborate in tetrahydrofuran-ethanol. After the mixture was freed of solvent in *vacuo*, the residue was extracted with benzene under argon atmosphere. The hydride complex (3) were isolated from benzene solution treated with aqueous inorganic acid(yield: ca. 90%). Cationic hydrides of platinum(II) (4) were quantitatively obtained from intermediate (2) or complexes (3). Tribenzylphosphines in (3) are displaced by other phosphines, the basicity of which is stronger than that of tribenzylphosphine. All the isolated complexes show satisfactory elemental analysis and spectroscopic data as listed in Table.

Compound		m.p. (°C)	ν_{Pt-H} (cm ⁻¹)	τ_H	$^1J_{H-Pt}$ (Hz)	$^2J_{H-P}$ (Hz)
$trans$ - $PtHX(PBz_3)_2$	X = Cl	162	2210	27.86	1290	12.0
	Br	181	2221	26.47	1345	11.0
	I	203	2192	23.62	1359	10.0
	NO_3	173	2283	34.39	1330	12.5
$trans$ - $PtHL(PBz_3)_2^+$	$L = NH_3$	146	2256	28.16	1042	13.5
			2123			
	PPh_3	192	2140	16.87	783	11.5
	BPh_4^-	171	2154	18.85	1009	11.0
	$AsPh_3$	167	2141	17.75	1173	9.0

In this way, tribenzylphosphine as a ligand brings about a novel synthetic route to hydridoplatinum(II) complexes. This is because a dihydrido-intermediate (2) with PBz_3 ($\nu_{Pt-H} = 1734$ cm⁻¹, $\tau_H = 12.40$, $^1J_{H-Pt} = 800.4$ Hz, $^2J_{H-P} = 19.0$ Hz) has relatively high thermal stability, compared with that of intermediate (2) with PEt_3 or PM_2Ph . The former intermediate in benzene decomposes slowly in ca. two days at ambient temperature with evolution of hydrogen gas, yielding the red solution of polymeric Pt(0) complex, while the latter has not yet been prepared owing to its instability.³⁾ But this argument does not imply that mono-hydridoplatinum(II) complex is necessarily prepared from *trans*-isomer if dihydrido-species is stable. In fact, by use of other phosphines such as PCy_3 or PPr_3^i which are known to give stable dihydridoplatinum(II) complexes,^{3),4)} we cannot directly obtain large amounts of platinum(II) hydrides from *trans*-isomer because starting material (1) are not enough soluble in any solvents to react smoothly with sodium tetrahydroborate.

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