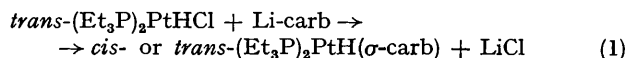


Monohydrido-complexes of Platinum(II) Containing Metal–Carbon σ -Bonded Dicarba-*closo*-dodecaborane(12) Ligands

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Summary Platinum(II) hydrido-carborane-complexes of the type *cis*- or *trans*-(Et₃P)₂PtH(σ -carb) containing a metal-carbon σ -bond have been prepared and their hydrido-chemical shifts, coupling constants, and stretching frequencies have been determined.



In the course of our research on transition-metal complexes incorporating *o*- and *m*-carborane [1,2- and 1,7-dicarba-*closo*-dodecaborane(12), respectively] bonded through metal-carbon σ -bonds,¹ we have prepared and characterized platinum(II) hydrido-complexes of the type *cis*- and *trans*-(Et₃P)₂PtH(σ -carb), where carb = 2-R-1,2-B₁₀C₂H₁₀⁻ and 7-R-1,7-B₁₀C₂H₁₀⁻ (R = H, Me, and Ph), which appear to be the first examples of this kind of complex. They were prepared according to equation (1) by the following procedure. Excess of 1-lithium-carborane² in Et₂O was

treated under N₂ at 25° with a solution in Et₂O of *trans*-(Et₃P)₂PtHCl.³ The mixture was stirred for 30 min and the solvent was removed *in vacuo*. The crude products were washed with MeOH and recrystallized from CH₂Cl₂-MeOH giving 60–80% yields of pure, air-stable crystalline compounds (I)–(VII). Satisfactory analytical and molecular weight data were obtained for all the complexes. ¹H N.m.r. data for the hydrido-ligand together with Pt–H stretching frequencies are in the Table.

The ¹H n.m.r. data suggest a *cis*-configuration for complexes (I)–(IV) (dd structure) and a *trans*-configuration for complexes (V)–(VII) (triplet structure). The τ (PtH) values for the *trans*-complexes (V)–(VII) are comparable

TABLE

Hydrido-chemical shifts, coupling constants, and stretching frequency for the complexes (Et₃P)₂PtH(σ -carb).

	σ -carb	<i>cis</i> or <i>trans</i>	τ (PtH) ^a	<i>J</i> (PtH)/Hz	<i>J</i> (PH)/Hz	ν (PtH) ^d /cm ⁻¹
(I)	1,2-B ₁₀ C ₂ H ₁₁ ⁻	<i>cis</i>	16.38 ^b	968	{ 186 22.2	2110
(II)	1,7-B ₁₀ C ₂ H ₁₁ ⁻	<i>cis</i>	15.78	952	{ 194 23.3	2130
(III)	7-Me-1,7-B ₁₀ C ₂ H ₁₀ ⁻	<i>cis</i>	15.66	953	{ 194 22.8	2130
(IV)	7-Ph-1,7-B ₁₀ C ₂ H ₁₀ ⁻	<i>cis</i>	15.94 ^c	950	{ 195 22.1	2128
(V)	2-Me-1,2-B ₁₀ C ₂ H ₁₀ ⁻	<i>trans</i>	24.04	680	19.9	2133
(VI)	2-Ph-1,2-B ₁₀ C ₂ H ₁₀ ⁻	<i>trans</i>	24.71	691	20.5	2130
(VII)	7-Ph-1,7-B ₁₀ C ₂ H ₁₀ ⁻	<i>trans</i>	23.92	664	20.1	2118 ^e

^a Measured in C₆H₆, except where stated, at 30°, Me₄Si as internal standard. ^b In CH₂Cl₂. ^c In CDCl₃. ^d In CCl₄. ^e In C₆H₆.

with those of the corresponding *trans*-hydridohalogeno-complexes,⁴ whereas $J(\text{PtH})$ values in our case are generally smaller. A similar $J(\text{PtH})$ was found recently⁵ for the σ -cyclohexenyl hydrido-complex *trans*-(Ph_3P)₂PtH($\sigma\text{-C}_6\text{H}_9$), [$\nu(\text{PtH})(\text{CH}_2\text{Cl}_2)$ 1925 cm^{-1} , $\tau(\text{PtH})$ (CDCl_3) 15.46, $J(\text{PtH})$ 608 Hz]. It is noteworthy that the hydrido-carborane-

complexes obtained exhibit either *cis*- or *trans*-configuration, whereas all previously reported⁶ monohydrido-derivatives of platinum(II) containing two monodentate neutral ligands are exclusively *trans*.

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