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1,2- AND 1,7-DICARBA-*closo*-DODECARBORANE(12)PLATINUM(II) COMPLEXES FORMED THROUGH METAL—CARBON σ BONDS: *cis*- AND *trans*-MONOHYDRIDO DERIVATIVES

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Summary

New neutral platinum(II) monohydridocarborane complexes of general formula *cis*- and *trans*-$L_2PtH(\sigma\text{-carb})$, where L = $(C_2H_5)_3P$, $(C_6H_5)_3P$, $(C_6H_5)_2(CH_3)P$, $(C_6H_5)(CH_3)_2P$ and carb = 2-R-1,2- or 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = H, CH_3, C_6H_5), have been prepared. The configurations of the complexes obtained have been assigned by ^1H NMR spectroscopy. The *cis*-monohydridocarborane complexes here reported are the first examples of neutral *cis*-monohydrido derivatives of platinum(II) containing platinum—carbon σ bonds. ^1H NMR chemical shifts and coupling constants of the prepared complexes are also reported, and used in a tentative evaluation of the *trans*-influence of the carborane ligands.

Introduction

In a recent communication [1] we described the synthesis and characterization of *cis*- and/or *trans*-bis(triethylphosphine)monohydridocarboraneplatinum(II) complexes. These complexes containing the carborane ligands 2-R-1,2-$B_{10}C_2H_{10}^-$ or 7-R-1, 7-$B_{10}C_2H_{10}^-$ (R = H, CH_3, C_6H_5) bonded through metal—carbon σ bonds were prepared in high yield by a simple method.

It is noteworthy that the hydridocarborane complexes thus obtained exhibit either *cis*- or *trans*-configuration whereas the few previously reported monohydrido complexes of platinum(II) containing a platinum—carbon σ bond are exclusively *trans* [2]. We now report the details of the preparation of several uncharged hydridotriethyl-, -triphenyl-,-diphenylmethyl- or -dimethylphenyl-phosphine complexes of platinum(II) containing 1,2- or 1,7-dicarba-*closo*-dodecabo-

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rane(12) derivatives as anionic ligands. The obtained complexes have been fully characterized by proton NMR and infrared spectroscopy.

Results and discussion

Monohydridocarboraneplatinum(II) complexes of the general formula $L_2PtH(\sigma\text{-carb})$, where $L = (C_2H_5)_3P$, $(C_6H_5)_3P$, $(C_6H_5)_2(CH_3)P$, $(C_6H_5)(CH_3)_2P$ and carb $= B_{10}C_2H_{10}R^-$, have been prepared by treating a diethyl ether solution or suspension of *trans*-$L_2Pt(H)Cl$ with an excess of 1-Li-2-R-1,2- or 1-Li-7-R-1,7-$B_{10}C_2H_{10}$ (R = H, CH_3, C_6H_5) at room temperature (eq. 1).

$$trans\text{-}L_2Pt(H)Cl + Li\text{-carb} \rightarrow cis\text{- or } trans\text{-}L_2Pt(H)(\sigma\text{-carb}) + LiCl \qquad (1)$$

The hydridocarborane complexes obtained are listed in Table 1 with pertinent analytical data. These complexes are white crystalline compounds, monomeric in solution, they are diamagnetic and behave as non-electrolytes at 25°C in CH_2Cl_2 solution. The configurations of the obtained products were determined from the proton NMR data for the hydrido ligand as shown in Table 2.

The ^1H (hydride) resonances of complexes I—IV and VII—XIII exhibit a 1 : 1 doublet of doublets structure in agreement with a *cis*-configuration. On the other hand, a *trans*-configuration was assigned to the complexes V and VI for which the ^1H (hydride) NMR spectra show a 1 : 2 : 1 triplet structure owing to magnetic equivalence of the two phosphorous nuclei in mutual *trans* position. All of these signals are flanked by satellites due to coupling with the platinum-195 isotope.

The stereochemical course of substitution reaction 1 appears to depend both on the coordinated phosphines and on the entering carborane ligand. Thus, in the case of bis(triethylphosphine) derivatives reaction 1 occurs with retention of configuration yielding only *trans*-complexes (V and VI), when the entering carborane ligands are those having the highest steric hindrance, i.e. the C(2)-substituted derivatives of 1,2-carborane. On the other hand, complexes having *cis*-configuration are the only products isolated, independent of the type of carborane entering ligand, when the substitution reaction involves platinum(II) complexes containing triphenyl-, diphenylmethyl- or dimethylphenyl-phosphines as neutral ligands. Spectroscopic analyses of the crude reaction products exclude the formation of detectable amounts of *trans*-species along with the isolated *cis*-species. Furthermore, the identity between the IR spectra of the crude products and those of the recrystallized pure compounds rules out the possibility that the purification caused isomerization. Moreover, attempts to isomerize the *cis*-complexes to the corresponding *trans*-isomers failed, and only decomposition was observed.

It should be noted that the usual rule for the platinum(II) complexes is that the substitution reaction takes place with retention of configuration [3]. In addition, all previously reported neutral monohydrido derivatives of platinum(II) of the type L_2PtHX (X = halides, pseudohalides, σ-C_6H_9, σ-C≡CPh; L = monodentate ligand) are exclusively *trans* [4]. However, in the case of the substitution reaction 1 change of configuration with formation of *cis*-derivatives seems to be the rule rather than the exception. Either a dissociative process or a mechanism involving a trigonal bipyramid intermediate having the entering and leaving

TABLE 1

ANALYTICAL AND IR DATA OF THE MONOHYDRIDOCARBORANEPLATINUM(II) COMPLEXES, $L_2PtH(\sigma\text{-carb})$

Complex	-carb	L	Config-uration	M.p. (°C)	Analysis (found (calcd.)) (%)		$\nu(Pt—H)$ (cm^{-1}) [a]	
					C	H	Nujol	Solution
I	$2\text{-H-1,2-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*cis*	116—117	28.97 (29.21)	7.51 (7.35)	2060s; 2080(sh)	2116s [b]
II	$7\text{-H-1,7-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*cis*	113	29.22 (29.21)	7.64 (7.35)	2130s	2130s [c]
III	$7\text{-}CH_3\text{-1,7-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*cis*	100	30.73 (30.55)	7.35 (7.52)	2120s; 2080(sh)	2130s [b]
IV	$7\text{-}C_6H_5\text{-1,7-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*cis*	126—128	37.31 (36.86)	7.10 (7.11)	2123s	2128s [b]; (2125s [c])
V	$2\text{-}CH_3\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*trans*	129—130	30.36 (30.55)	7.94 (7.52)	2160s	2133s [b]
VI	$2\text{-}C_6H_5\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_2H_5)_3P$	*trans*	143	37.05 (36.86)	7.39 (7.11)	2130s	2130s [b]
VII	$2\text{-}C_6H_5\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_6H_5)_3P$	*cis*	169	55.99 (56.22)	5.00 (4.93)	2123s	2127s; 2170(sh) [d]
VIII	$7\text{-}C_6H_5\text{-1,7-}B_{10}C_2H_{10}^-$	$(C_6H_5)_3P$	*cis*	135	55.69 (56.22)	4.91 (4.93)	2106s	nm
IX	$2\text{-H-1,2-}B_{10}C_2H_{10}^-$	$(C_6H_5)_2(CH_3)P$	*cis*	128—129	45.53 (45.46)	5.67 (5.17)	2090s	nm
X	$2\text{-}CH_3\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_6H_5)_2(CH_3)P$	*cis*	121—122	45.85 (46.21)	5.46 (5.35)	2114s	2127s [c]
XI	$2\text{-}C_6H_5\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_6H_5)_2(CH_3)P$	*cis*	133—134	49.70 (50.05)	5.11 (5.19)	2190s	2126s; 2154(sh) [e]
XII	$7\text{-}C_6H_5\text{-1,7-}B_{10}C_2H_{10}^-$	$(C_6H_5)_2(CH_3)P$	*cis*	135—136	49.37 (50.05)	5.27 (5.19)	2103s	2116s [e]
XIII	$2\text{-}C_6H_5\text{-1,2-}B_{10}C_2H_{10}^-$	$(C_6H_5)(CH_3)_2P$	*cis*	95—96	41.64 (41.67)	5.86 (5.53)	2152s	2132s [d]

[a] s, strong; (sh), shoulder; nm, not measured. [b] In CCl_4. [c] In C_6H_6. [d] In CH_2Cl_2. [e] In $CHCl_3$.

TABLE 2

PROTON NMR [a] DATA OF THE MONOHYDRIDOCARBORANEPLATINUM(II) COMPLEXES

Complex	Configuration	solvent [b]	Hydrido resonances			Phosphine—ethyl resonances	
			τ	J(Pt—H)	J(P—H)	τ	
I	*cis*	C	16.40 dd	980	186 22.2	9.05 cm 8.20 cm	
II	*cis*	B	15.78 dd	952	194 23.3	9.03 cm 8.45 cm	
III	*cis*	B	15.66 dd	953	194 22.8	9.16 cm 8.56 cm	
IV	*cis*	B	15.74 dd	951	194 21.8	8.95 cm 8.22 cm	
V	*trans*	B	24.04 t	680	19.9	9.19 [d] 8.37 cm	
VI	*trans*	B	24.71 t	691	20.5	9.26 [d] 8.37 cm	
VII	*cis*	C	17.40 dd	—	191 18.6	—	
		D	17.32 dd[c]	977	192 19.2		
VIII	*cis*	C	16.59 dd	1015	196 19.9	—	
						Phosphine—methyl proton resonances	
						τ	^2J(P—CH$_3$)
IX	*cis*	C	16.14 dd	1039	193 22.5	8.67 d 8.20 dd	9.0 7.9
X	*cis*	C	16.59 dd	981	195 20.8	8.75 d 8.02 dd	9.1 7.8
XI	*cis*	C	16.73 dd	968	194.4 19.3	8.94 d 8.04 dd	9.1 7.9
XII	*cis*	DCE	15.75 dd	1026	202 22.4	8.73 d 8.13 dd	9.1 7.6
XIII	*cis*	D	16.79 dd	978	198 21.5	8.74 d 8.58 dd	9.8 8.0

[a] Measured at ca. 27°C and 90 MHz. τ values (±0.02) in ppm relative to internal TMS (τ 10.00). J(Pt—H) ±0.5 Hz unless show to be approximate: J(H—H) ±0.1 Hz. d, doublet; dd, doublet of doublets; t, triplet; cm, complex multiplet; s, singlet; br s, broad singlet. [b] Solvents: C = dichloromethane; B = benzene, DCE = 1.2 dichloroethane; D = deuterochloroform. [c] Measured with Bruker WP-60FT NMR spectrometer at 60 MHz. [d] Five-line structure (J = 7.7 ± 0.4 Hz) due to coupling with the CH$_2$ protons and with the *trans* ^{31}P nuclei equivalenty. [e] Broad singlet with ^{195}Pt satellites (^3J = ca. 25 Hz).

group in the apical position would account for steric change [5]. However, since these substitution reactions take place heterogeneously in diethyl ether and information on the role of the solvent is not available, it is not clear whether the observed configurations are the result of kinetic or thermodynamic control, and speculation on the reaction mechanism is unjustified. We think that steric factors play an important role in determining the course of reaction 1 in that the carborane entering ligand is a large group and *cis*-configuration would lead to a less crowded environment of the metal atom. In accordance with this a *cis*-con-

Assignment	Other resonances τ	Other resonances Assignment
CH_3 protons	6.06 s	carborane CH proton
CH_2 protons		
CH_3 protons	7.2 br s	carborane CH proton
CH_2 protons		
CH_3 protons	8.36 s	carborane CH_3 protons
CH_2 protons		
CH_3 protons	2.55 cm	carborane C_6H_5 protons
CH_2 protons	3.13 cm	
CH_3 protons	7.95 s	carborane CH_3 protons
CH_2 protons		
CH_3 protons		
CH_2 protons		
—		
—		

^3J(Pt—CH_3)	^4J(H—H)	Assignment	τ	Assignment
31.7	—	PCH_3 *trans* to carborane	6.5 br s [e]	carborane CH proton
~17	1.2	PCH_3 *trans* to hydride		
30.2	—	PCH_3 *trans* to carborane	7.92 s	carborane CH_3 protons
~16	1.1	PCH_3 *trans* to hydride		
31.4	—	PCH_3 *trans* to carborane		
~15	1.1	PCH_3 *trans* to hydride		
30.0	—	PCH_3 *trans* to carborane		
~16	1.2	PCH_3 *trans* to hydride		
40.4	—	PCH_3 *trans* to carborane		
~16	<1	PCH_3 *trans* to hydride		

figuration was also found to be peculiar to the previously reported platinum(II)-carbonare complexes [6,7].

Unlike the *trans*-complexes V and VI which are indefinitely stable as solids and in solution, the bis(triethylphosphine) derivatives having the *cis*-configuration (I—IV) slowly decompose in solution yielding uncharacterized products. Similar decomposition is also exhibited in solution by the *cis*-complexes (IX—XIII) containing diphenylmethyl- or dimethylphenyl-phosphines as ligands, whereas the triphenylphosphine *cis*-derivatives (VII and VIII) appear to be stable. Thus, the stability of the *cis*-complexes is dependent on the type of the coordinated phosphine, and we have found that the stability decreases as the ligands are changed in the order: $PPh_3 \gg PEt_3 \sim PPh_2Me > PPhMe_2$.

The IR spectra of the obtained hydridocarborane complexes (Table 2) exhibit, in addition to the absorption bands due to the phosphine ligands, strong absorption bands in the region 2540—2620 cm^{-1} which are assigned to the B—H stretching of the dicarba-*closo*-dodecaborane(12) ligands and strong bands between 2110 and 2133 cm^{-1} attributable to the Pt—H stretching mode. In some cases the ν(Pt—H) bands appear accompanied by a shoulder on the high- or low-frequency side. In particular, the spectra of the complexes I and III in Nujol show a shoulder which is absent from the solution spectra but, in the case of complexes VII and XI the shoulder is exhibited only in solution. Since the presence of mixtures of isomers in solution is ruled out by ^1H NMR spectroscopy the observed shoulders are possibly due, in the solid state, to the presence of different crystallographic forms of the same isomer or, in solution, to a type of solvent interaction; such shoulders on the ν(Pt—H) bands are frequently found with monohydrido complexes of platinum(II) [8].

The ^1H NMR chemical shifts (hydride) and coupling constant values (J(Pt—H)) found (Table 2) for the complexes having *cis*-configurations are in agreement with those reported for hydrido complexes of platinum(II) in which the hydride is *trans* to a phosphine ligand [9]. Furthermore the *trans*-complexes (V and VI) show ^1H(hydride) resonances centered at ca. τ 24 ppm (in benzene solution) suggesting an unexpected relatively low *trans*-influence of the carborane group. In fact, by comparison with the values reported for the *trans*-$[(C_2H_5)_3P]_2PtH(X)$ compounds, where X = halogenide or pseudohalogenide, the *trans*-influence of the carborane group seems to be of the same order of magnitude as that of a bromide or thiocyanate ligand [10] and this is also consistent with the ν(Pt—H) values found (Table 1). On the other hand, the J(Pt—H) values of these *trans*-monohydridocarborane complexes appear to be very low and are typical of *trans*-hydrido complexes containing groups having a high *trans*-influence (e.g.: J(Pt—H) 608 Hz for *trans*-$((C_6H_5)_3P)_2PtH(\sigma\text{-}C_6H_9)$ [11] and J(Pt—H) 778 Hz for *trans*-$((C_2H_5)_3P)_2PtH(CN)$ [10]). We believe that this lack of correlation observed between chemical shifts and coupling constants is possibly due to constraints introduced by the bulky carborane ligand bonded to the platinum which must cause significant distortion from the *trans*-square planar configuration [7]. Other information on the carborane *trans*-influence can also be obtained from the ^3J(Pt—P—CH_3) values relative to the phosphine-methyl protons *trans* to carborane in IX—XII which result to be of the order of 31 Hz (Table 2). These relatively large coupling constant values confirm that the *trans*-influence of the carborane ligands is notably lower than that exhibited by σ-C bonded "organic groups". In fact, it is well-known that ^3J(Pt—P—CH_3) *trans* to all the σ-bonded organic groups are low, indicating a high *trans*-influence [12] (e.g., ^3J(Pt—P—CH_3) is 18.5 Hz for $[Pt(CH_3)(PMe_2Ph)_3]^+$ [13] and 14.4 Hz for *cis*$(Ph_2MeP)_2Pt(CH_3)Cl$ [14]). Moreover, this suggestion also appears to be in accordance with the hydride chemical shift data for the *trans*-complexes V and VI discussed above. It is also interesting to compare the chemical shifts of the phosphine-methyl protons *trans* to carborane with those of the phosphine *trans* to hydride. In particular, it is observed that the τ(P—CH_3) values relative to the phosphine *trans* to the carborane increase with increasing steric hindrance of the carborane itself, whereas those relative to the phosphine *trans* to the hydride ligand show the opposite trend. Furthermore, the difference between τ(P—CH$_3$) *trans* to carborane and τ(P—CH$_3$) *trans* to hydride in the series *cis*-(PPh$_2$Me)$_2$PtH(σ-carb) (IX—XII) appears to decrease with decreasing steric hindrance of the carborane ligand. Thus, the largest difference between these τ(P—CH$_3$) values is observed in the case of the C(2)-phenyl-substituted carborane derivative ($\Delta\tau$ = 0.90 ppm, complex XI) and the smallest is exhibited by the complex containing unsubstituted carborane ($\Delta\tau$ = 0.47 ppm, complex IX). This observed behaviour may be interpreted in terms of steric effects. In fact, since the bulky carborane ligands must cause some restriction to the rotation of the coordinated phosphines which would be likely larger in the case of C(2)-substituted carborane, some of the molecular configurations can be such that anisotropic effects from the ligands containing aromatic rings would give the observed variations in the chemical shifts [15].

Experimental

Reagent grade solvents were further purified by standard methods and were dried and degassed before use. *trans*-L$_2$PtHCl (L = (C$_2$H$_5$)$_3$P, (C$_6$H$_5$)$_3$P, (C$_6$H$_5$)$_2$(CH$_3$)P and (C$_6$H$_5$)(CH$_3$)$_2$P) were prepared by published methods [16,17,18]. The lithiocarborane derivatives were prepared by treating the carboranes with butyllithium [19]. All the substitution reactions were carried out under nitrogen. ^{1}H 90-MHz NMR spectra were recorded on a Bruker HFX-90 spectrometer. Infrared spectra were obtained with a Perkin—Elmer Model 457 spectrophotometer and calibrated against polystyrene film. Melting point were determined by a conventional hot-stage microscope and are uncorrected. Molecular weights were obtained with a Mechrolab Model 301 A osmometer.

cis-1-[(Et$_3$P)$_2$PtH]-2-H-1,2-(σ-B$_{10}$C$_2$H$_{10}$) (I)

A solution of 4.8 mmol of 1-Li-2-H-1,2-B$_{10}$C$_2$H$_{10}$ in 10 ml of diethyl ether was added to a solution of 0.7 g (1.5 mmol) of *trans*-(Et$_3$P)$_2$PtHCl in 10 ml of diethyl ether at room temperature. A white precipitate was immediately formed. After being stirred for 1 h, the mixture was evaporated under reduced pressure to give a white solid, which was then washed with methanol. The crude product was purified by recrystallization from tetrahydrofuran/methanol to give 0.63 g (yield 73%) of pure product, white crystals; m.p. 116—117°C. Mol.wt. found 570(in tetrahydrofuran); calcd. 576.

cis-1-[(Et$_3$P)$_2$PtH] 7-H-1,7-(σ-B$_{10}$C$_2$H$_{10}$) (II)

This was prepared as described for complex I by treating a solution of 5.0 mmol of 1-Li-7-H-1,7-B$_{10}$C$_2$H$_{10}$ in 10 ml of diethyl ether with a solution of 0.75 g (1.6 mmol) of *trans*-(Et$_3$P)$_2$PtHCl in 10 ml of diethyl ether. The yield of pure white crystals was 0.56 g (61%); m.p. 113°C. Mol.wt. found 585 (in tetrahydrofuran); calcd. 576.

cis-1-[(Et$_3$P)$_2$PtH]-7-CH$_3$-1,7-(σ-B$_{10}$C$_2$H$_{10}$) (III)

A solution of 4.7 mmol of 1-Li-7-CH$_3$-1,7-B$_{10}$C$_2$H$_{10}$ in 10 ml of diethyl ether was added to a solution of 1.0 g (2.1 mmol) of *trans*-$(Et_3P)_2PtHCl$ in 10 ml of diethyl ether at room temperature. The mixture was stirred for 30 min. The lithium chloride formed was filtered off and the solution evaporated to dryness under reduced pressure. The solid product was washed with methanol and recrystallized from CH_2Cl_2/CH_3OH to give 0.8 g (65%) of pure product, white crystals: m.p. 100°C. Mol.wt. found 617 (in C_6H_6); calcd. 590.

cis-$1\text{-}[(Et_3P)_2PtH]\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (IV)

This was prepared as described for complex I from $1\text{-Li-}7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}$ (3.2 mmol in 10 ml of diethyl ether) and *trans*-$(Et_3P)_2PtHCl$ (1.0 g, 2.1 mmol in 10 ml of diethyl ether). The yield of pure white crystals was 0.93 g (68%); m.p. 126—128°C. Mol.wt. found 655 (in C_6H_6); calcd. 652.

trans-$1\text{-}[(Et_3P)_2PtH]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (V) and *trans*-$1\text{-}[(Et_3P)_2PtH]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (VI)

These complexes were prepared as for I by treating 0.7 g (1.5 mmol) of *trans*-$(Et_3P)_2PtHCl$ in 10 ml of diethyl ether with a solution of 3.2 mmol of the appropriate lithium-carborane derivative in 10 ml of diethyl ether at room temperature. The crude products were recrystallized from tetrahydrofuran/methanol yielding 0.7 g (79%) of white crystals of V, m.p. 129-130°C, and 0.65 g (68%) of white crystals of VI, m.p. 143°C. Mol. wt. found 606 (in C_6H_6); calcd. for V 590. Mol.wt. found: 665 (in tetrahydrofuran); calcd. for VI 652.

cis-$1\text{-}[(Ph_3P)_2PtH]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (VII)

A solution of 2 mmol of $1\text{-Li-}2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}$ in 10 ml of diethyl ether was added to a suspension of 0.5 g (0.7 mmol) of *trans*-$(Ph_3P)_2PtHCl$ in 15 ml of diethyl ether. The mixture was stirred for 3 h at room temperature. The white solid was separated by filtration and washed with diethyl ether, and purified by recrystallization from CH_2Cl_2/CH_3OH to give 0.45 g (68%) of white crystals of pure VII; m.p. 169°C.

cis-$1\text{-}[(Ph_3P)_2PtH]\text{-}7\text{-}C_6H_5\text{-}1,7\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (VIII)

This complex was prepared as for complex VII in a yield of 75%; m.p. 135°C.

cis-$1\text{-}[(Ph_2MeP)_2PtH]\text{-}2(7)\text{-}R\text{-}1,2(7)\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (IX—XII)

A suspension of 0.7 g (1.1 mmol) of *trans*-$(Ph_2MeP)_2PtHCl$ in 10 ml of diethyl ether was treated with a solution of 2.3 mmol of the appropriate lithium-carborane derivative ($1\text{-Li-}2(7)\text{-R-}1,2(7)\text{-}B_{10}C_2H_{10}$) in 10 ml of diethyl ether at room temperature. The pale yellow solution was stirred for 30 min and then evaporated under reduced pressure to give a pale yellow solid. This was washed with methanol and purified by recrystallization from CH_2Cl_2/CH_3OH. The yields of pure white crystals of IX—XII were 60—70% based on the amount of platinum(II) reagent used.

cis-$1\text{-}[(PhMe_2P)_2PtH]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (XIII)

A solution of 1.2 mmol of $1\text{-Li-}2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}$ in 10 ml of diethyl ether was added to a suspension of 0.3 g (0.58 mmol) of *trans*-$(PhMe_2P)_2PtHCl$ in 10 ml of diethyl ether at 0°C. The yellow solution was stirred for 30 min at 0°C and then evaporated under reduced pressure to give a white solid, which was purified by recrystallization from $CHCl_3/CH_3OH$. The yield of pure XIII, white crystals, was 0.28 g (70%), m.p. 95—96°C.

Attempts to isomerize the cis-$L_2PtH(\sigma$-carb) complexes

The *cis*-complexes I—IV were kept between 25 and 40°C in benzene solution and in presence of catalytic amounts of free triethylphosphine. No *cis*→*trans* isomerization was observed and along with the starting hydrido complexes, uncharacterized decomposition products were obtained in all cases.

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