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THREE- AND FOUR-COORDINATE RHODIUM(I)—CARBORANE COMPLEXES CONTAINING METAL—CARBON σ BONDS

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In earlier papers [1—6] we have reported the preparation and characterization of several transition metal complexes containing 2-R-1,2- and 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = H, CH_3, C_6H_5) ligands bonded through metal—carbon σ bonds. The high steric requirements of the polyhedral carboranes and the considerable electron-withdrawing power of the carborane carbon atoms make their use as anionic ligands particularly suitable for obtaining transition metal complexes having unusual stoichiometry and reactivity. In a preliminary paper [3] we reported the preparation and characterization of some neutral rhodium(I) complexes incorporating 2-R-1,2-$B_{10}C_2H_{10}^-$ and 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = CH_3, C_6H_5) ligands that can be regarded as the first examples of formally three-coordinate species of rhodium(I).

We wish to report here the list of the rhodium(I)—carborane complexes previously prepared together with two new compounds, and a collection of results regarding their exchange reactions with phosphorus ligands.

EXPERIMENTAL

The solvents were of reagent-grade quality and were dried and degassed before use. $(Ph_3P)_2Rh(\sigma\text{-carb})$ complexes were prepared by a previously reported method [3]. All reactions were carried out under an argon atmosphere. Infrared spectra were obtained as Nujol mulls with a Perkin—Elmer Model 457 spectrometer. ^1H NMR spectra were recorded with a Bruker HFX-90 spectrometer. Conductivity measurements (25°C, 10^{-3} *M* in CH_2Cl_2 solutions) were obtained with an LKB bridge.

Exchange reaction between $(PPh_3)_2Rh(\sigma\text{-carb})$ and $R_nR'_{3-n}P$

General procedure.

A diethyl ether suspension of $(PPh_3)_2Rh(\sigma\text{-carb})$ was treated under an argon atmosphere at —15°C with a four-fold excess of the appropriate triphosphine. An orange precipitate was soon formed. After stirring for 1 h the precipitate was separated by filtration in an argon atmosphere and washed with dry methanol. Further purification was performed by recrystallization from CH_2Cl_2—CH_3OH. The yields of pure products (see Table 2) were 60—70%.

1-[(Me₂PhP)₃Rh(H)]-2-C₆H₄-1,2-(σ-B₁₀C₂H₁₀), XI

$1\text{-}[(Me_2PhP)_3\underline{Rh(H)]\text{-}2\text{-}C}_6H_4\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, *XI*

0.6 g (4.32 mmole) of Me_2PhP was added under argon, at 0°C to 1.0 g (1.18 mmole) of $1\text{-}[(Ph_3P)_2Rh]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-carb})$ suspended in 15 ml of diethyl ether. From the dark-red solution so formed, a pale-yellow woolly solid was separated in the course of a few minutes. After stirring for 1 h, the solid was filtered and washed with *n*-hexane. The crude product was purified by recrystallization from 1,2-dichloroethane-methanol. The yield of pure product, white crystals, was 0.5 g (60%), m.p. 133—134°C.

$1\text{-}[((PhO)_3P)_3Rh]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, *XII*

A suspension of 0.3 g (0.38 mmole) of $1\text{-}[(Ph_3P)_2Rh]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ in 5 ml of diethyl ether was treated under argon at room temperature with 1.93 mmole of $(PhO)_3P$. A yellow-green solution was immediately formed. Successively, in the course of 1 h a yellow woolly solid was separated which was then dissolved by addition of CH_2Cl_2. A yellow precipitate was obtained by addition of methanol. The solid was separated by filtration under argon, washed with dry diethyl ether and further purified by recrystallization from CH_2Cl_2—CH_3OH. The yield was 66% of pure yellow crystals, m.p. 121—124°C.

RESULTS AND DISCUSSION

The rhodium(I)—carborane complexes which we have so far prepared are reported in Table 1.

These complexes, of general formula $(Ph_3P)_2Rh(\sigma\text{-carb})$, were obtained by reacting a suspension of $(Ph_3P)_3RhCl$ in diethyl ether with an excess of the

TABLE 1

Rhodium—carborane complexes ($[(C_6H_5)_3P]_2Rh(\sigma\text{-carb})$)

Carb		Color	m.p. (°C) [a]	Ref.
I	$1,2\text{-}B_{10}C_2H_{\overline{11}}$	violet	183—185	[b]
II	$2\text{-Me-}1,2\text{-}B_{10}C_2H_{\overline{10}}$	burgundy red	188—190	3
III	$2\text{-Ph-}1,2\text{-}B_{10}C_2H_{\overline{10}}$	red-violet	178—181	3
IV	$1,7\text{-}B_{10}C_2H_{\overline{11}}$	orange	178—179	[b]
V	$7\text{-Me-}1,7\text{-}B_{10}C_2H_{\overline{10}}$	orange	182—184	3
VI	$7\text{-Ph-}1,7\text{-}B_{10}C_2H_{\overline{10}}$	orange	167—168	3

[a] All compounds melt with decomposition in a capillary tube sealed under vacuum.

[b] Analysis (%): calc. C = 59.22; H = 5.36. Found: (I) C = 59.03; H = 5.05; (IV) C = 57.78; H = 5.30.

appropriate lithium—carborane derivative (eqn. 1), and show an elemental analysis which is fully consistent with the formulation assigned in Table 1.

$$(Ph_3P)_3RhCl + Li\text{—}carb \xrightarrow{-Ph_3P} (Ph_3)_2Rh(\sigma\text{-}carb) + LiCl \qquad (1)$$

Li—carb = $1\text{-}Li\text{-}2\text{-}R\text{-}1,2\text{-}B_{10}C_2H_{10}$, $1\text{-}Li\text{-}7\text{-}R\text{-}1,7\text{-}B_{10}C_2H_{10}$

(R = H, CH_3, C_6H_5)

In the solid state these complexes are rather insensitive towards air and moisture, but are highly air-sensitive when placed in solution. They are diamagnetic as expected for d^8 complexes and non-electrolytes at 25°C in CH_2Cl_2. The IR spectra (Nujol mulls) of complexes I—VI show, in addition to the absorption bands due to the triphenylphosphine ligands, strong bands in the region 2540—2620 cm^{-1} attributed to the ν(B—H) absorptions of the dicarba-*closo*-dodecaborane(12) ligand. The complexes containing C(2)- or C(7)-substituted carborane ligands, complexes II, III, V and VI, do not exhibit carborane C—H stretching absorption around 3060 cm^{-1}, indicating that the ligands are bonded to the metal through the C(1)-carborane atom.

The 90 MHz ^1H NMR spectra are also in agreement with the reported formulations. Thus, the spectrum of the 1,2-methylcarboranecomplex(II) in CH_2Cl_2 (TMS as internal standard) exhibits a sharp singlet at τ = 8.0 of relative total intensity 3, which is assigned to the 2-methyl protons of the carborane ligand [7], and a multiplet centered at τ = 2.8, of relative total intensity 30, which has been assigned to the phenyl protons of the phosphine ligands. On the other hand, the NMR spectrum of complex I, which contains the unsubstituted $1,2\text{-}B_{10}C_2H_{\overline{11}}$ ligand, shows a broad singlet resonance at τ = 7.37, of relative total intensity 1, due to the carborane C—H proton.

G. Allegra et al. have lately carried out the structural analysis of $1\text{-}[(Ph_3P)_2Rh]\text{-}2\text{-}C_6H_5\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$, complex III [8]. The structural data confirm that the rhodium atom is surrounded by three ligands, i.e., two triphenylphosphine and one $2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{\overline{10}}$ ligands, and show that the metal and the donor atoms are in a substantially planar arrangement. However, in this case the coordination of carborane to rhodium(I) is supplied by a Rh—C σ bond and possibly also by a Rh—H—B bridge bond. Furthermore, from the structural information it appears that the presence of a large carborane ligand does not allow the coordination of more than two bulky triphenylphosphine ligands.

However, when complex III is reacted with carbon monoxide and benzonitrile, four-coordinated rhodium(I)—carborane complexes are obtained [3]. Successively, in order to investigate the importance of the size of the ligands on the coordination number of rhodium(I), we have carried out some exchange reactions between three-coordinate complexes and phosphorus ligands of lower bulkiness than the triphenylphosphine. These reactions were carried out under argon at −15—0°C (room temperature in the case of $(PhO)_3P$) in diethyl ether using a four-fold excess of the free ligand. The reaction products isolated are reported in Table 2.

TABLE 2

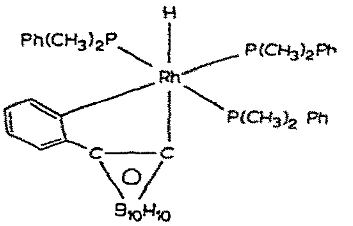
Products of the reactions between $[(C_6H_5)_3P]_2Rh(\sigma\text{-carb})$ and PR_3

Carb	PR_3	Product	m.p. (°C)[a]	Color	Analysis (%)
$1,2\text{-}B_{10}C_2H_{11}^-$	$MePh_2P$	$(MePh_2P)_2Rh(\sigma\text{-carb})$ (VII)	140—143	brick-red	Calcd.: C, 52.01; H, 5.76 Found: C, 52.88; H, 5.79
		$(MePh_2P)_3Rh(\sigma\text{-carb})$ (VIII)	147—149	orange	Calcd.: C, 58.15; H, 5.95 Found: C, 57.76; H, 6.27
$1,2\text{-}B_{10}C_2H_{11}^-$	Me_2PhP	$(Me_2PhP)_3Rh(\sigma\text{-carb})$ (IX)	136—139	orange	Calcd.: C, 47.27; H, 6.71 Found: C, 46.16; H, 6.97
$7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}^-$	Me_2PhP	$(Me_2PhP)_3Rh(\sigma\text{-carb})$ (X)	129—130	orange	Calcd.: C, 52.19; H, 6.57 Found: C, 51.74; H, 6.77
$2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}^-$	Me_2PhP	$1\text{-}[(Me_2PhP)_3\overline{Rh(H)]\text{-}2\text{-}C}_6H_4\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (XI)	133—134	white	Calcd.: C, 52.19; H, 6.57 Found: C, 51.31; H, 6.36
$2\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{10}^-$	$(PhO)_3P$	$[(PhO)_3P]_3Rh(\sigma\text{-carb})$ (XII)	121—124	yellow	Calcd.: C, 57.48; H, 4.91 Found: C, 57.19; H, 4.84

[a] All compounds melt with decomposition in a capillary tube sealed under vacuum.

Thus by reacting complex I with $MePh_2P$, followed by recrystallization from CH_2Cl_2/CH_3OH under argon of the red—orange crude product formed, only a three-coordinate brick-red complex (VII) is obtained. However, if the recrystallization is carried out in the presence of free $MePh_2P$, an orange product, VIII, is obtained which is a well-defined four-coordinate complex, stable in the solid state under inert atmosphere.

On the other hand, when the exchange reaction is carried out using the smaller Me_2PhP entering ligand, only the orange complex, IX, is obtained. This complex is not stable in the presence of air; the analytical data together with the 90 MHz ^1H NMR spectrum in CH_2Cl_2, indicate that the rhodium is coordinated by four ligands, i.e. three phosphines and one $7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}^-$. The proton resonance spectrum exhibits a multiplet centered at $\tau = 2.6$ due to the phenylprotons of the phosphine ligands, a broad signal at $\tau = 8.58$ of relative intensity 2 and a 1:1 doublet centered at $\tau = 9.10$ [J(P—H) = 8.2 Hz], of relative intensity one. The latter doublet is due to the methyl protons resonance of the phosphine *trans* to carborane, whereas the broad signal at $\tau = 8.58$ could be a partially resolved doublet or triplets. Actually, the methyl resonance of two dimethylphenylphosphines in mutual *trans*-position usually gives a well defined 1:2:1 triplet due to the occurrence of "virtual" coupling with both phosphorus nuclei [9]. The broad structure observed in our case might be due to an accidental superimposition of two triplets of the methyl groups made inequivalent because of the distortion from the square planar structure caused by the bulky carboranyl ligand. An analogous four-coordinate complex, X, is formed by treating a suspension in diethyl ether of VI with Me_2PhP. Its ^1H NMR spectrum in CH_2Cl_2 exhibits a large multiplet at $\tau = 2.65$, due to the phosphine phenyl protons, a partially resolved 1:2:1 triplet at $\tau = 8.53$, of relative area 2 and a 1:1 doublet at $\tau = 9.17$ [J(P—H) = 8.4 Hz] of relative area 1. The triplet is attributed to the methyl proton resonance of the two phosphines in mutual *trans* position, whereas the doublet resonance is due to the methyl protons of the phosphine *trans* to carborane. On the other hand, complex III, which contains $2\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{10}^-$ as anionic ligand, behaves in a different way with respect to the other complexes. In fact, in this case exchange reaction with Me_2PhP yields a white stable crystalline product, XI, whose analytical and spectroscopic data allowed us to propose the structure reported in Fig. 1. The IR spectrum (Nujol) of such a compound shows, other than the $\nu_{(B-H)}$ absorption bands of the carborane ligand (2540—2620 cm^{-1}), a sharp strong band at 2090 cm^{-1} attributed to $\nu_{(Rh-H)}$. Moreover $\nu_{(C-C)}$ bands at 1552, 1567 and 1582 cm^{-1} are observed together with a strong band at 732 cm^{-1} which is in the range typical of the C—H out-of-plane deformations for *ortho*-disubstituted aromatics [10]. Its ^1H NMR spectrum (Fig. 2) shows two distinct 1:2:1 triplets at $\tau = 9.17$ [J(P—H) = 3.3 Hz] and at $\tau = 8.50$ [J(P—H) = 2.2 Hz], respectively, both of relative area 1, a well defined 1:1 doublet at $\tau = 8.93$ [J(P—H) = 7.3 Hz] and a complex multiplet centered at $\tau = 23$. The appearance of two distinct triplet resonances separated by 0.67 ppm arises from the absence of any plane of symmetry through the



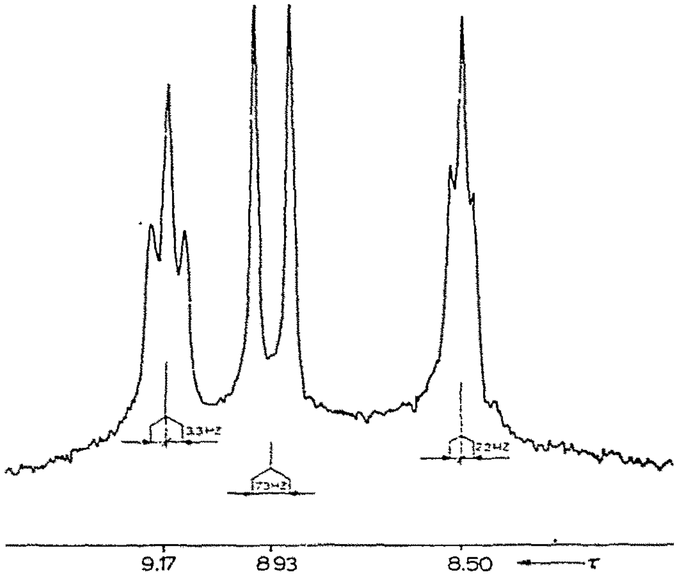
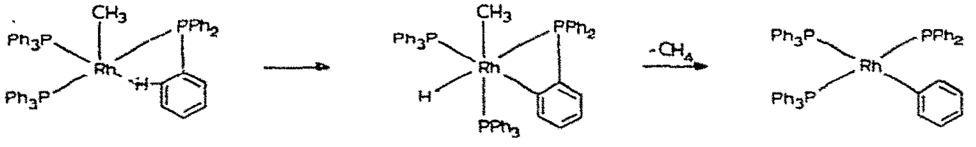


Fig. 1. Proposed structure of XI from analytical and spectroscopic data.

Fig. 2. ^1H (methyl) NMR pattern of 1-[(Me$_2$PhP)$_3$Rh(H)]-2-C$_6$H$_4$-1,2-(σ-B$_{10}$C$_2$H$_{10}$), XI. at 90 MHz.

two *trans*-phosphorus atoms and is indicative that the magnetic environments of the methyl groups on the same phosphorus atom are remarkably different [11]. The occurrence of the hydride resonance as a complex multiplet comes from the coupling of the hydride both with the three non-equivalent phosphorus nuclei and with the rhodium nucleus. Furthermore, the observed high chemical shift of this resonance is in agreement with an hydride *trans* to the carboranyl group [7].

W. Keim [12] reported that four-coordinate methyltris(triphenylphosphine)-rhodium(I) complex undergoes thermal decomposition with evolution of methane and formation of a new rhodium derivative. The author suggests the following reaction scheme (eqn. 2):

 (2)

According to this scheme insertion of rhodium into the hydrogen—carbon bond occurs in the *ortho*-position of a phenyl group of the phosphine with formation of an unstable hydridorhodium(III) intermediate which undergoes fast reductive elimination to yield the final product. The first step of the above mechanism likely operates also in the exchange reaction involving complex III. However, the resulting hydridocarborane—rhodium(III) complex is very stable and therefore elimination of carborane does not occur. In our opinion steric factors are very important in promoting the intramolecular oxidative addition occurring when complex III is reacted with Me_2PhP. In fact, in this case the first reaction product ought to be $(Me_2PhP)_3Rh(\sigma\text{-carb})$ in which the steric requirements of the carboranyl group may induce the internal metallation reaction by forcing the rhodium atom and the C(2)-carborane phenyl substituent close together above the molecular plane. Accordingly, molecular models suggest that the phenyl group present in the carboranyl ligand should be involved in the metallation rather than those of the phosphine ligands. This suggestion is also indirectly supported by the fact that analogous intramolecular reactions have never been observed for complexes containing other carborane derivatives. In particular, when the carborane ligand is the $7\text{-}C_6H_5\text{-}1,7\text{-}B_{10}C_2H_{10}^-$ isomer the carbon atoms of the C(7)-carborane phenyl substituent are too remote from the metal atom to allow any interaction.

We have also carried out the exchange reaction of complex II with triphenylphosphite, $P(OPh)_3$, which exercises a smaller strain energy than PPh_3 because of its smaller cone angle [13]. The exchange reaction is very fast. The yellow product formed, complex XII, is a four-coordinate rhodium(I) complex in which the coordination positions are filled by three triphenylphosphites and one $2\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{10}^-$. The results reported above strongly suggest that the steric requirements of the bulky carborane moieties are critical in allowing the coordination to rhodium(I) of only two PPh_3, but of three phosphorus ligands of lower bulkiness. In fact, when $(Ph_3P)_2Rh(\sigma\text{-carb})$ complexes are reacted with phosphines or phosphites of low steric hindrance Ph_3P is easily replaced and four-coordinate rhodium(I) complexes are formed.

This behaviour is in agreement with ligand competition experiments recently reported by C.A. Tolman et al. [13] who have found that the equilibrium constants, K_d, for ligand dissociation are strongly dependent on steric effects. Thus, a more extensive ligand dissociation appears to take place with ligands having higher steric requirements, this behaviour being primarily the consequence of an effect of the enthalpy of dissociation. In the case of the phosphorus ligands, an essentially strain-free minimum cone angle can be calculated by the method suggested by Tolman [13]. The cone angle appears to be 145° for Ph_3P, and 136°, 127° and 128° for $MePh_2P$, Me_2PhP and $(PhO)_3P$, respectively. These values also account for the extensive dissociation shown in solution by the four-coordinate complex VIII containing $MePh_2P$ in comparison with the stability of the corresponding complex IX coordinated by three smaller Me_2PhP ligands.

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