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INTRAMOLECULAR METALLATION OF *o*-CARBORANYLPHOSPHINE-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES

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Summary

Preparation of *trans*-[$P_2^{cb}MCl_2$]-type complexes (P^{cb} = *o*-$HCB_{10}H_{10}CCH_2PPh_2$ M = Pd, Pt), which readily undergo intramolecular metallation through the B–H bonds of the carborane cage to form exocyclic compounds involving a $\overline{P-C-C-B-M}$ bond system, is described. Both monomeric compounds, *trans*-[MCl(B-P)P^{cb}], and bridged complexes, such as [Pd_2Cl_2(B-P)$_2$], are formed, where (B-P) is intramolecular-metallated carborane phosphine. The bridging bond is readily cleaved under the action of various ligands (pyridine, PEt_3, etc.) to form monomeric compounds.

The cyclometallation reaction is a convenient method to synthesize carborane derivatives involving a B–M σ-bond (M = Mn [1], Re [2], Rh [3], Ir [3,4]). Intramolecular metallation of the transition metal complexes with P-donor ligands is widely used to form carbon–transition metal bonds [5]. We studied the possibility of employing this method in carborane chemistry for the activation of B–H bonds. 1-Diphenylphosphinomethyl-*o*-carborane (I), previously used by us to obtain cyclometallated carboranes with B–Rh and B–Ir bonds [3], was employed as a ligand. We found that the interaction of a Na_2PdCl_4 solution in methanol with phosphine I at 20°C results in the formation of a pale yellow complex, *trans*-[$P_2^{cb}PdCl_2$] (II), where P^{cb} = *o*-$HCB_{10}H_{10}CCH_2PPh_2$. Similarly, the platinum derivative, *trans*-[$P_2^{cb}PtCl_2$] (III), was obtained starting from a methanol solution of K_2PtCl_4-18-crown-6-ester complex (molar ratio 1 : 2). The compounds II and III may also be obtained under the action of $(PhCN)_2MCl_2$ (M = Pd, Pt) on I in

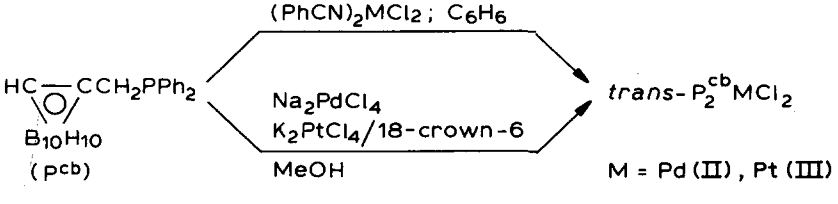


TABLE 1

ANALYTICAL AND MELTING POINT DATA

Compound	Empirical formula	Yield (%)	Colour	Analysis Found(calcd.)(%)				M.p. (°C)
				C	H	B	M	
II	$C_{30}H_{46}B_{20}Cl_2P_2Pd\cdot C_6H_6$	90–96	yellow	45.89 (45.99)	5.91 (5.57)	22.88 (22.99)	10.76 (11.32)	135–136 [b]
III	$C_{30}H_{46}B_{20}Cl_2P_2Pt$	95–99	pale yellow	38.03 (37.90)	4.75 (4.88)	23.20 (22.74)	20.37 (20.52)	183–185 [b]
IV	$C_{30}H_{45}B_{20}ClP_2Pd\cdot 0.5C_6H_6$	90–95 [a]	white	45.64 (45.83)	5.34 (5.59)	24.88 (25.00)	12.30 (12.30)	197–199 [c]
VI	$C_{30}H_{44}B_{20}Cl_2P_2Pd_2$		white	37.08 (37.28)	5.01 (4.59)	22.06 (22.37)	21.93 (22.02)	280–290 [d]
V	$C_{30}H_{45}B_{20}ClP_2Pt\cdot 0.5C_6H_6$	85–93	white	41.94 (41.57)	5.07 (5.07)	22.78 (22.68)	20.17 (20.46)	156–160 [d]
IX	$C_{65}H_{66}B_{11}P_3Pd$	80	white	66.96 (66.99)	5.66 (5.71)	10.04 (10.20)	10.10 (9.13)	182–184 [c]

[a] Combined yield of compounds IV and VI is presented (since their ratio depends on the conditions and mode of isolation used). [b] Decomposes with gas evolution. [c] Melts with decomposition. [d] Decomposes without melting.

TABLE 2

INFRARED AND ^{31}P NMR DATA

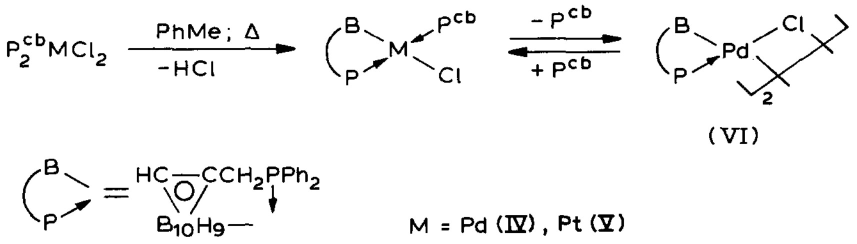
Compound	IR[a] ν(M–Cl) (cm^{-1})	^{31}P NMR[b]		
		δ_P[c] (ppm)	^2J(P–P) (Hz)	J(Pt–P) (Hz)
II	350	10.9[d]		
III	345	6.33[e]		2588
IV	279	(P^A)[h] = 46.37[f]	384.6	
		(P^B)[h] = 19.53		
V	274	(P^A)[h] = 46.96[f]	426.8	2930
		(P^B)[h] = 22.06		2899
VI		54.55; 55.15[d]		
VII, VIII[g]		48.82; 49.72[f]		

[a] Infrared spectra were recorded in Nujol on a Bruker JFS-113 Fourier spectrometer. [b] ^{31}P NMR spectra were run on a Bruker WP-200SY instrument, working frequency 81.026 MHz. [c] Positive values correspond to downfield shifts with respect to external standard (85% H_3PO_4). [d] Solution in acetone. [e] Solution in C_6D_6. [f] Solution in $CDCl_3$. [g] L = 4-methylpyridine. [h] The phosphorus atom notation is shown in Fig. 1.

benzene. In this case the compounds are isolated as the benzene solvates. The analytical and melting point data, as well as the yields of the new complexes, are listed in Table 1.

The complexes II and III were assigned the *trans* configuration on the basis of their far-infrared spectra (Table 2) in conformity with the data of Duddell and coworkers [6].

The palladium complex II, on heating in toluene, eliminates hydrogen chloride to form the exocyclic compound IV which dissociates readily in solution losing one molecule of phosphine I and yielding the less soluble dimeric chlorine-bridged complex VI. The platinum complex III under similar conditions yields just the monomeric derivative V.



(VI)

M = Pd (IV), Pt (V)

The compounds IV, V and VI contain a five-membered chelate metallocycle with a $\overline{\text{P–C–C–B–M}}$ bond system as shown in Fig. 1. The phosphorus atoms in IV and V are in *trans* position, as follows from the ^{31}P NMR data (Table 2) in accordance with Goodfellow's evidence [7]. Likewise, the low value for ν(M–Cl) agrees with the *trans* arrangement of the phosphorus atoms (Table 2) (similar to the corresponding ν(M–Cl) values for the aromatic derivatives with a C–M–Cl bond system [8]), suggesting that the chlorine atom in IV and V is in a *trans* position with respect to

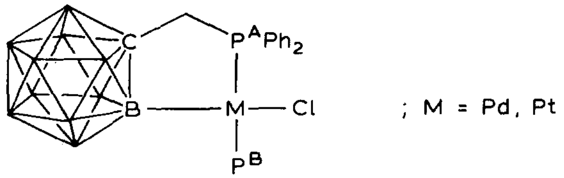
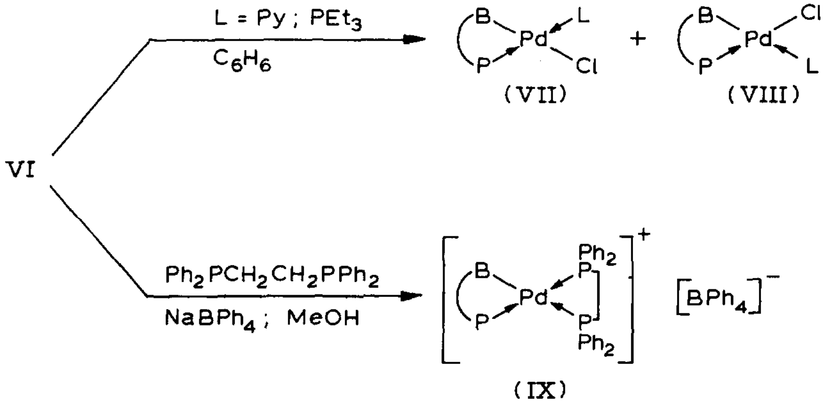


Fig. 1. Proposed structure of compounds IV and V.

the boron atom of the carborane cage. The ^{31}P NMR spectrum of compound VI contains two signals of similar chemical shifts (Table 2) with ratio 1 : 1, which may be attributed to the presence of two isomers - probably of *syn* and *anti* configurations.

The bridging bond in compound VI is readily cleaved under the action of donor ligands, such as pyridine, triethylphosphine, etc., to form monomeric compounds consisting of a mixture of two isomers VII and VIII. When treated with bidentate phosphines, such as $Ph_2PCH_2CH_2PPh_2$, the chlorine atom is displaced from the palladium coordination sphere, and the cationic complex IX is formed, which was characterized as its tetraphenylborate derivative.



It is to be noted in conclusion that 1-diphenylphosphino-*o*-carborane forms donor complexes with palladium and platinum as well, which, in analogy with complexes II and III, undergo intramolecular metallation to form four-membered exocyclic derivatives involving a B–M bond.

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