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CYCLOPALLADATED *o*-CARBORANES. PALLADIUM TRANSFER FROM CYCLOPALLADATED N,N-DIMETHYLBENZYLAMINES, 1C-DIPHENYLPHOSPHINO-*o*-CARBORANE AND η^3-ALLYLS IN CARBOXYLIC ACID SOLVENTS*

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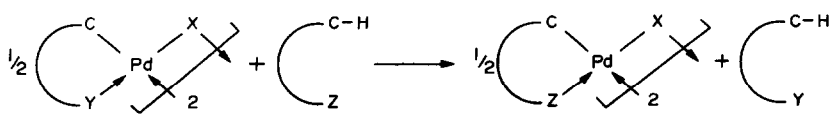
Abstract—1-Diphenylphosphinomethyl-*o*-carborane, *o*-$HCB_{10}H_{10}CCH_2PPh_2$ (DPMC), reacts with Na_2PdCl_4 (methanol) or $PdCl_2(PhCN)_2$ (benzene) to give the "bis-adduct" *trans*-[$PdCl_2$(DPMC)$_2$], which on thermolysis in *n*-propanol transforms into the five-membered Pd—P—C—C—B palladacycle, di-μ-chlorobis[(1-diphenylphosphinomethyl-*o*-carboranyl-B,P)palladium(II)] (**IIa**), as a mixture of B(3) and B(4) metallated isomers according to ^{1}H and ^{31}P NMR. If the internal palladation is performed in the presence of LiBr or NaI, the corresponding bromo- or iodo-bridged dimers are obtained. Complex **IIa** can also be prepared via ligand exchange in carboxylic acid solvents. In particular, palladium(II) migrates from cyclopalladated chloro-bridged N,N-dimethylbenzylamine or 1C-diphenylphosphino-*o*-carborane, i.e. from complexes with C,N-five- and B,P-four-membered palladacycles, respectively, to 1-diphenylphosphinomethyl-*o*-carborane yielding **IIa**. Migration of palladium(II) is also observed from the compounds with great stability towards acetic acid, namely the [$PdCl(\eta^3$-allyl)]$_2$ dimers. No such processes except with this particular ligand were found in the case of palladium(II) allyls and other entering ligands (azobenzene, 2-phenylpyridine, α-methylstyrene). The exchange processes described clearly show that complex **IIa** is characterized by a remarkable thermodynamic stability in acetic acid which accounts for the course of many exchange reactions.

The σ-bond metathesis for C—H and related bonds in transition metal complexes is an intriguing problem.[1] In general, there are three key mechanisms of such metathetical transformations. The first, involving reductive C—H bond elimination, followed by oxidative addition, is typical, for example, of rhodium(I/III),[2] iridium(I/III),[3] and platinum(0/II)[4] couples; the second observed for scandium(III)[1] and thorium(IV)[5] complexes occurs via a concerted four-centred mechanism; finally, the third, realized in palladium(II) complexes,[6] is induced by the acid cleavage of the metal–carbon bond followed by subsequent metallation of the incoming ligand. The latter pathways were previously exemplified by the ligand exchange reactions of type (1), involving the starting cyclopalladated chloro- or acetato-bridged dimer and incoming ligand.[6]



(1)

In the present paper we report on several related reactions which involve not only the C—H bond metathesis but that of B—H and η^3-allyl bonds

* The key compounds used in this study are shown in Fig. 1.

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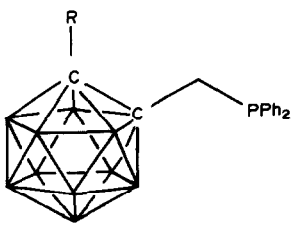
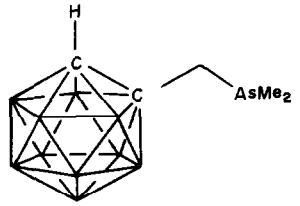
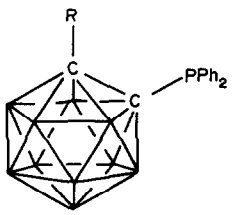


R = H, 1C-diphenylphosphinomethyl-*o*-carborane (DPMC)

R = Me, 1C-diphenylphosphinomethyl-2C-methyl-*o*-carborane (DPMMC)



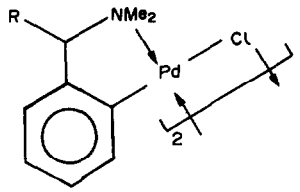
1C-dimethylarsinomethyl-*o*-carborane (DAMC)



R = H, 1C - diphenylphosphino - *o* - carborane (DPC)

R = Me, 1C - diphenylphosphino - 2C - methyl - *o*-carborane (DP2MC)

R = *i*-Pr, 1C-diphenylphosphino-2C-isopropyl-*o*-carborane (DPIC)

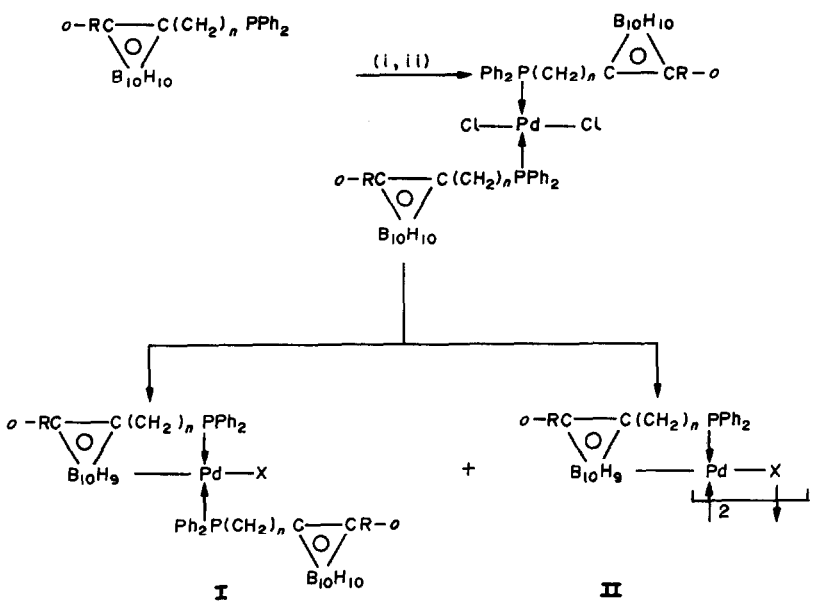


R = H, di-μ-chlorobis[(2-dimethylaminomethylphenyl-C^1,N)palladium(II)] ([PdCl(damp)]$_2$)

R = *S*-Me, di-μ-chlorobis[(*S*-2-dimethylaminoethylphenyl-C^1,N)palladium(II)] ([PdCl(*S*-daep)]$_2$)

R = *R*-Me, di-μ-chlorobis[(*R*-2-dimethylaminoethylphenyl-C^1,N)palladium(II)] ([PdCl(*R*-daep)]$_2$)

Fig. 1. The compounds used in the present study.



	R	*n*	X
a	H	1	Cl
b	Me	1	Cl
c	H	0	Cl
d	Me	0	Cl
e	*i*-Pr	0	Cl
f	H	1	Br
g	H	1	I
h	Me	0	Br

Scheme 1. (i)—Na_2PdCl_4–MeOH; (ii)—$PdCl_2(PhCN)_2$–C_6H_6.

as well and lead to cyclopalladated *o*-carboranes.[7] Some of the results presented here have been previously communicated.[8]

RESULTS

Interaction of P-*donor* o-*carboranes with simple palladium salts*

The reaction between DPMC, as well as DPMMC, and Na_2PdCl_4 in methanol or $PdCl_2(PhCN)_2$ in benzene, both at 20°C, cleanly affords the simple bis-adducts *trans*-$[PdCl_2(DPMC)_2]$ or *trans*-$[PdCl_2(DPMMC)_2]$ (Scheme 1). The geometry of the former is supported by a single strong IR band at 350 cm^{-1}.[9] As expected, the ligand is coordinated through phosphorus and only one isomer is present as judged from the corresponding $^{31}P\{^1H\}$ NMR singlet resonance of the complexed ligand at δ 10.9. (The free ligand resonates at δ −16.3.) Thermolysis of *trans*-$[PdCl_2(DPMC)_2]$ in different solvents induces the B—H bond palladation to afford a mixture of monomeric and dimeric complexes **Ia** and **IIa**, the relative amounts of which depend on the nature of solvent (Scheme 1). In particular, one obtains a 1 : 1 mixture in toluene, while only the dimer is formed in isopropanol. When thermolysed in isopropanol in the presence of a 10-fold excess of NaBr or NaI, *trans*-$[PdCl_2(DPMC)_2]$ transforms into the corresponding bromo- and iodo-bridged dimers **IIf** and **IIg**, in good yields. Two peaks of bridging chlorides in the IR spectrum are seen at 287 and 248 cm^{-1} and of bromides at 216 and 200 cm^{-1} (cf. with ref. 10). As usual, halide bridges can be cleaved by pyridine or 4-methylpyridine to afford monomers **III**, which are sufficiently soluble in common solvents, and, thus, useful for NMR structural investigations. The corresponding data for **III**, as well as for **I** and **II**, are summarized in Table 1. The formation of the five-membered palladacycle with a Pd—P—C—C—B chain makes the methylene CH_2 protons diastereotopic, giving in the ^1H NMR spectrum two quartet doublets with ^2J(HP) and ^2J(HH). Two sets of signals in **I**–**III** suggests that the complexes are a mixture of B(3) and B(4) palladated carboranes as shown in Fig. 2. The ^{31}P NMR spectra of **III** confirm this, since again two resonances are observed. It should be pointed out that the latter signals are doubled in the parent dimers **II** (Table 1). The reason is that every linkage isomer [B(3) or B(4)] is probably a mixture of *ab–hg* and *ab–gh* (*trans* and *cis*) isomers (see Scheme 1).

Table 1. Parameters of the ^1H and ^{31}P NMR spectra of cyclopalladated *o*-carboranes

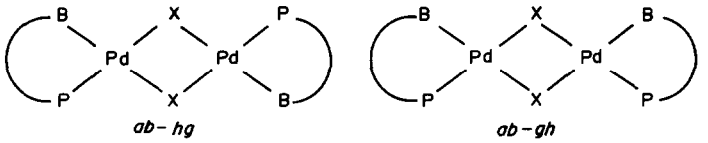
Compound (Isomer)		^1H[a]	^{31}P[b]
Ia	[B(3)]	3.40d(2H, PCH_2, ^2J(HP) 9.0), 3.50m(1H, PCH_2, ^2J(HH) 15.0; ^2J(HP) 12.0, ^4J(HP) 4.5), 4.03q(1H, PCH_2, ^2J(HH) 15.0, ^2J(HP) 7.0), 3.28s(1H, $C^{cb}H$), 5.75s(1H, $C^{cb}H$), 7.45m(10H, Ph), 7.78m(10H, Ph) ($CDCl_3$)	19.53d(^2J(PP) 398.0) 46.37d(^2J(PP) 398.0) ($CHCl_3$)
	[B(4)]		19.89d(^2J(PP) 398.0) 56.66d(^2J(PP) 398.0)
IIa	[B(3)] *ab–hg*[c]	3.99q(1H, PCH_2, ^2J(HH) 16.5, ^2J(HP) 6.0), 4.43q(1H, PCH_2, ^2J(HH) 16.5, ^2J(HP) 9.0), 5.24s(1H, $C^{cb}H$), 7.96m(10H, Ph)	54.55s, 55.15s [$(CH_3)_2CO$]
	ab–gh[c]	4.02q(1H, PCH_2, ^2J(HH) 16.5, ^2J(HP) 6.5), 4.49q(1H, PCH_2, ^2J(HH) 16.5, ^2J(HP) 9.0), 5.34s(1H, $C^{cb}H$), 7.96m(10H, Ph), [$(CD_3)_2CO$]	
	[B(4)]		59.67s, 60.07s [$(CH_3)_2CO$]
IIb	[B(3)]		54.61s, 54.82s [$(CH_3)_2CO$]
	[B(4)]		58.74[c] [$(CH_3)_2CO$]
IIc			4.7s ($CHCl_3$)
IId	[B(3)]		−2.3s, −2.7s ($CHCl_3$)
	[B(4)] *ab–hg*[c]	1.76s(3H, CH_3), 7.58m(10H, Ph)	11.8s, 12.0s ($CHCl_3$)
	[B(4)] *ab–gh*[c]	1.78s(3H, CH_3), 8.25m(10H, Ph) ($CDCl_3$)	

continued overleaf

Table 1—*continued*

Compound (Isomer)		^1H[a]	^{31}P[b]
IIe	[B(4)]	0.47d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 1.15d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 2.06m(1H, CH$_3$C*H*, ^3J(HH) 7.0), 7.55m(10H, Ph) ($CDCl_3$)	
	ab–hg[c]		13.2s, 13.4s ($CHCl_3$)
	ab–gh[c]	0.51d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 1.15d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 2.06m(1H, CH$_3$C*H*, ^3J(HH) 7.0), 8.23m(10H, Ph) ($CDCl_3$)	
IIf	[B(3)]		56.34s, 57.16s
	[B(4)]		61.23[c] [$(CH_3)_2CO$]
IIg	[B(3)]		56.3s, 57.2s
	[B(4)]		61.2[c] [$(CH_3)_2CO$]
IIIa[d]	[B(3)]	3.29q(1H, PCH$_2$, ^2J(HH) 16.5, ^2J(HP) 7.8), 3.50q(1H, PCH$_2$, ^2J(HH) 16.5, ^2J(HP) 10.2), 3.65s(1H, C^{cb}H), 7.46m(6H, Ph), 7.84m(4H, Ph) ($CDCl_3$)	51.27s ($CHCl_3$)
	[B(4)]	3.30q(1H, PCH$_2$, ^2J(HH) 16.5, ^2J(HP) 7.8), 3.51q(1H, PCH$_2$, ^2J(HH) 16.5, ^2J(HP) 10.2), 4.03s(1H, C^{cb}H), 7.46m(6H, Ph), 7.84m(4H, Ph) ($CDCl_3$)	58.9s ($CHCl_3$)
IIIb	[B(3)]	2.23s(3H, CH$_3$), 3.07q(1H, PCH$_2$, ^2J(HH) 18.0, ^2J(HP) 6.0), 3.82q(1H, PCH$_2$, ^2J(HH) 18.0, ^2J(HP) 11.0), 7.40m(6H, Ph), 8.0m(4H, Ph) ($CDCl_3$)	53.0s ($CHCl_3$)
	[B(4)]	1.96s(3H, CH$_3$), 3.12q(1H, PCH$_2$, ^2J(HH) 15.0, ^2J(HP) 10.3), 3.36q(1H, PCH$_2$, ^2J(HH) 15.0, ^2J(HP) 9.0), 7.43m(6H, Ph), 7.92m(4H, Ph) ($CDCl_3$)	57.8s ($CHCl_3$)
IIId	[B(3)]	2.08s(3H, CH$_3$), 7.47m(6H, Ph), 8.35m(4H, Ph) ($CDCl_3$)	−1.4s ($CHCl_3$)
	[B(4)]	1.68s(3H, CH$_3$), 7.45m(6H, Ph), 8.30m(4H, Ph) ($CDCl_3$)	13.1s ($CHCl_3$)
IIIe	[B(4)]	0.45d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 1.13d(3H, C*H*$_3$CH, ^3J(HH) 7.0), 2.01m(1H, CH$_3$C*H*, ^3J(HH) 7.0), 7.53m(6H, Ph), 8.25m(4H, Ph) ($CDCl_3$)	14.8s ($CHCl_3$)
IIIf	[B(3)]		52.44s ($CHCl_3$)
	[B(4)]		59.76s ($CHCl_3$)
IIIg	[B(3)]		53.70s ($CHCl_3$)
	[B(4)]		61.17s ($CHCl_3$)
IIIh	[B(4)]		13.05s ($CHCl_3$)
IV	[B(3)]	1.50s(3H, CH$_3$As), 1.54s(3H, CH$_3$As), 2.66d(1H, CH$_2$As, ^2J(HH) 15.0), 2.99d(1H, CH$_2$As, ^2J(HH) 15.0), 3.46s(1H, C^{cb}H), 1.67s(3H, CH$_3$As), 1.73s(3H, CH$_3$As), 2.96d(1H, CH$_2$As, ^2J(HH) 14.0), 3.08d(1H, CH$_2$As, ^2J(HH) 14.0), 5.01s (1H, C^{cb}H) ($CDCl_3$)	—
	[B(4)]	1.43s(3H, CH$_3$As), 1.46s(3H, CH$_3$As), 2.57d(1H, CH$_2$As, ^2J(HH) 13.5), 2.84d(1H, CH$_2$As, ^2J(HH) 13.5), 3.78s(1H, C^{cb}H), 1.69s(3H, CH$_3$As), 1.70s(3H, CH$_3$As), 2.99[e](1H, CH$_2$As), 5.13s(1H, C^{cb}H) ($CDCl_3$)	—
V[f]	[B(3)]	1.69s(3H, CH$_3$As), 1.76s(3H, CH$_3$As), 2.68d(1H, CH$_2$As, ^2J(HH) 14.0), 2.95d(1H, CH$_2$As, ^2J(HH) 14.0), 3.56s(1H, C^{cb}H) ($CDCl_3$)	—
	[B(4)]	1.71s(3H, CH$_3$As), 1.72s(3H, CH$_3$As), 2.61d(1H, CH$_2$As, ^2J(HH) 14.0), 2.80d(1H, CH$_2$As, ^2J(HH) 14.0), 3.76s(1H, C^{cb}H) ($CDCl_3$)	—

[a] Bruker WP-200SY (200 MHz).
[b] Bruker WP-200SY (81.01 MHz).
[c] Arbitrary assignment.
[d] L = d_5-py in all monomeric compounds, **III**.
[e] Unresolved signal.
[f] Recorded in the presence of d_5-py.



The nature of added metal halide has a remarkable effect on the rate of intramolecular metallation of *trans*-$[PdCl_2(DPMC)_2]$. The hot solution of the latter in *n*-propanol is yellow, and it becomes colourless when intramolecular palladation into **II** occurs. Thus, one can qualitatively estimate the relative rates in the presence of a 10-fold molar excess of MHal. At reflux, the fading occurs in a matter of 18–20, 10–15 and 5–7 min in the presence of LiCl, LiBr and NaI, respectively, the concentration of LiCl having negligible effect on the rate of internal metallation. Thus, the reactivity order Cl < Br < I suggests that this B—H bond palladation has a strong nucleophilic character. In accord with this is the relative amount of B(3) isomer formed (85%), which is independent of the nature of halide in the case of DPMC. In fact, the electron density is the lowest at B(3) of the *o*-carborane backbone,[11] and hence, the nucleophilic reagent would attack this position more readily. There is the same reactivity order in the case of DPMMC, but, contrary to DPMC, the relative amount of the B(4) isomer increases in the order Cl < Br < I (25, 35 and 70%, respectively), and this may reflect the steric effect of the methyl group at C(2), Fig. 2.

Direct palladation of DPC, DP2MC, and DPIC proceeds with such facility that the metallation occurs at 20°C giving four-membered palladacycles **Ic, IId** and **IIe**, respectively, in high yields (Table 2). Dimeric **IIc** is not formed under these conditions. The ratio of B(3) and B(4) isomers is the same as in the exchange reactions (see below). Only in the case of DP2MC is it strongly dependent on the solvent used. In particular, one obtains only the

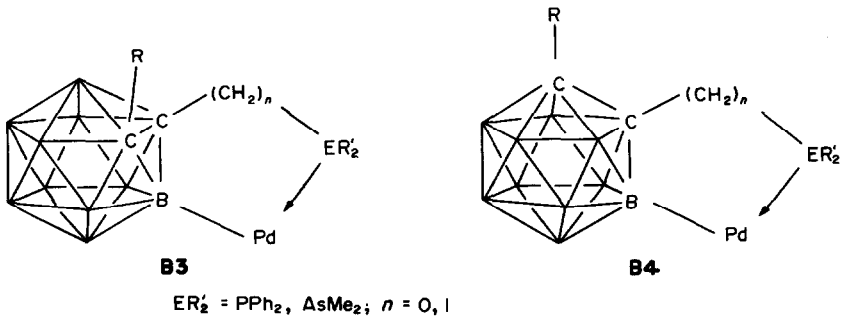
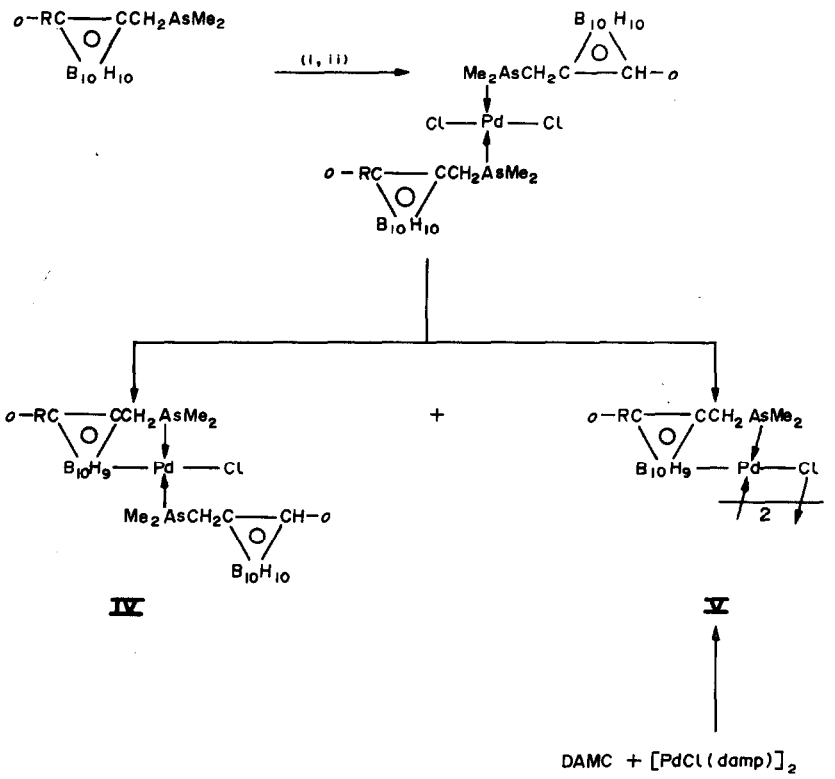


Fig. 2. Two possible isomers of the cyclopalladated *o*-carborane derivatives.

Table 2. Yields of the cyclopalladated *o*-carboranes and the bis-adducts in reactions with simple palladium salts and the corresponding analytical data

Compound	Yield (%)	Brutto-formula	Calc./Found (%) C	H	B	Pd
$[PdCl_2(DPMC)_2]$	90–96	$C_{30}H_{46}B_{20}Cl_2P_2Pd \cdot C_6H_6$	45.9/46.0	5.9/5.6	22.9/23.0	10.8/11.3
$[PdCl_2(DPMMC)_2]$	96	$C_{32}H_{50}B_{20}Cl_2P_2Pd$	43.8/43.2	5.9/5.7	24.0/24.3	12.5/12.0
$[PdCl_2(DAMC)_2]$	93	$C_{10}H_{38}As_2B_{20}Cl_2Pd$	17.3/17.1	5.7/5.5	30.5/30.8	
Ia	90–95	$C_{30}H_{45}B_{20}ClP_2Pd \cdot \frac{1}{2}C_6H_6$	45.6/45.8	5.3/5.6	24.9/25.0	12.3/12.3
Ic	87–93	$C_{28}H_{41}B_{20}ClP_2Pd$	42.3/42.2	5.3/5.2	27.1/27.2	13.3/13.3
IIa	90–95	$C_{30}H_{44}B_{20}Cl_2P_2Pd_2$	37.1/37.3	5.0/4.6	22.1/22.4	21.9/22.0
IIb	99	$C_{32}H_{48}B_{20}Cl_2P_2Pd_2$	39.6/38.4	5.3/4.9	21.0/21.7	21.4/21.4
IIc[a]	13	$C_{28}H_{40}B_{20}Cl_2P_2Pd_2 \cdot \frac{1}{2}C_6H_6$	38.1/38.1	4.8/4.4	22.1/22.1	
IId	80	$C_{30}H_{44}B_{20}Cl_2P_2Pd_2 \cdot C_6H_6$	41.0/41.4	4.9/4.8	20.7/20.7	20.4/20.4
IIe	93–98	$C_{34}H_{52}B_{20}Cl_2P_2Pd_2$	40.1/39.9	5.1/5.1	21.0/21.1	20.6/20.8
IIf	91	$C_{30}H_{44}B_{20}Br_2P_2Pd_2$	34.6/34.1	4.5/4.2	20.4/20.5	20.1/20.2
IIg	95	$C_{30}H_{44}B_{20}I_2P_2Pd_2$	32.1/32.4	4.1/3.9	18.5/18.8	17.9/18.5
IIh	90	$C_{30}H_{44}B_{20}Br_2P_2Pd_2 \cdot \frac{1}{2}C_6H_6$	36.8/36.2	4.8/4.4	19.4/19.8	
IV	82	$C_{10}H_{37}B_{20}As_2ClPd$	18.2/18.1	5.6/5.6	32.4/32.5	
V	13	$C_{10}H_{36}B_{20}As_2Cl_2Pd_2$	14.5/14.9	4.4/4.5		

[a] Table 3, run 5.



Scheme 2. (i)—Na_2PdCl_4–MeOH; (ii)—$PdCl_2(PhCN)_2$–C_6H_6.

B(4) isomer of **IId** in MeOH, while a mixture of B(3) and B(4) in a ratio of 1 : 4 and 3 : 2 is seen in $CHCl_3$–HOAc (1 : 1) and benzene, respectively.

Interaction of DAMC *with palladium salts*

The transformations of DAMC in the presence of simple palladium complexes (Scheme 2) are much the same as those of the related phosphorus ligands DPMC and DPMMC. Thermal cyclopalladation of *trans*-$[PdCl_2(DAMC)_2]$ in *n*-propanol again gives a 1 : 1 mixture of B(3) and B(4) isomers identical to those in Fig. 2, as judged from the two sets of diastereotopic methyls at As of equal intensity.

Cyclopalladation of DPMC *and related ligands via the exchange of cyclopalladated ligands*

Dimers **II** can be very easily prepared in high yields by the ligand exchange strategy, eq. (2), developed by us previously for C,N-palladacycles.[6] In particular, DPMC and DPMMC react readily with an equimolar amount of chloro-bridged cyclopalladated N,N-dimethylbenzylamine, [PdCl (damp)]$_2$, at 70°C in a HOAc–$CHCl_3$ mixture, to afford five-membered palladacycles, **IIa** and **IIb**, respectively, without detectable amounts of monomers **I**, Table 3. As above, complexes **II** are a mixture of B(3) and B(4) palladated species. The

Table 3. Cyclopalladation of *o*-carborane derivatives via the exchange of cyclopalladated ligands in HOAc–$CHCl_3$ solvent

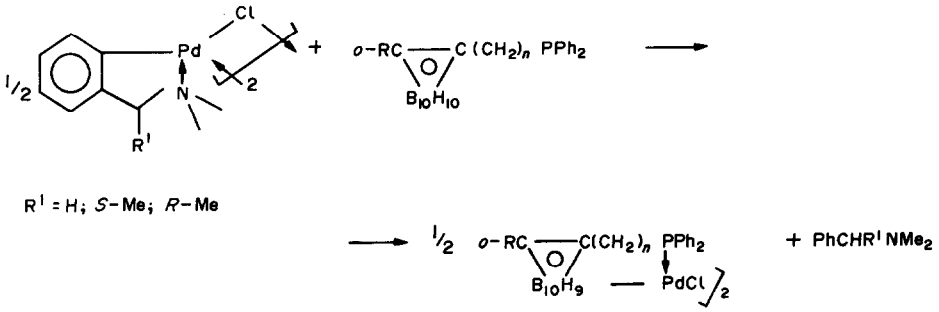
Run	Starting complex	Incoming ligand	*T*(°C)/Time (h)	Product	Yield (%)	Isomer ratio (%) [B(3)]	[B(4)]
1	$[PdCl(damp)]_2$	$HCB_{10}H_{10}CCH_2PPh_2$	70/25	**IIa**	83	80	20
2	$[PdCl(R\text{-daep})]_2$	$HCB_{10}H_{10}CCH_2PPh_2$	25/172	**IIa**	44		
3	$[PdCl(S\text{-daep})]_2$	$HCB_{10}H_{10}CCH_2PPh_2$	25/172	**IIa**	49		
4	$[PdCl(damp)]_2$	$MeCB_{10}H_{10}CCH_2PPh_2$	70/25	**IIb**	95	70	25
5	$[PdCl(damp)]_2$	$HCB_{10}H_{10}CPPh_2$	50/5	**IIc**	13		
6	$[PdCl(damp)]_2$	$MeCB_{10}H_{10}CPPh_2$	25/74	**IId**	74	20	80
7	$[PdCl(damp)]_2$	*iso*-$PrCB_{10}H_{10}CPPh_2$	25/60	**IIe**	40	0	100
8	$[PdCl(damp)]_2$	$HCB_{10}H_{10}CCH_2AsMe_2$	25/96	**IV**	66	50	50
9	**IIe**	$HCB_{10}H_{10}CCH_2PPh_2$	60/6	**IIa**	65		

relative amounts of these according to ^{31}P NMR of the monomeric d_5-py derivatives, are shown in Table 3. It should be pointed out that the "carborane version" of the exchange reaction is limited by the ligands with phosphorus donor atoms. Ligands with N-donors, namely *o*-$HCB_{10}H_{10}CCH_2NEt_2$ and *o*-$HCB_{10}H_{10}CN{=}NPh$, reduce palladium(II) in acetic acid medium, as carboranes without donor centres do reacting with palladium(II) acetate.[12]

According to ^1H NMR, the interaction between $[PdCl(damp)]_2$ and DPMC begins with the cleavage of chloro-bridges of the palladium dimer by the phosphorus donor. (No such cleavage occurs during the formation of the four-membered palladacycles, see below.) Since mono-substituted *o*-carborane is prochiral,[13] the reaction with optically active cyclopalladated *R* and *S* α-methyl-N,N-dimethylbenzylamine, $[PdCl(daep)]_2$, could afford optically active palladated DPMC. The product **IIa** proved to be racemic, confirming the previous conclusion that the exchange of cyclopalladated ligands proceeds by the dissociative route, i.e. the palladation of C—H and B—H bonds follows the complete departure of the leaving ligand.[6c]

Five-membered palladacycles incorporating the As donor atom are also available via the ligand exchange. In particular, DAMC reacts with $[PdCl(damp)]_2$ to give **V** without **IV**, Scheme 2.

Four-membered cyclopalladated carboranes can also be prepared in the same way even under milder conditions, Table 3. In particular, DPIC and $[PdCl(damp)]_2$ react in a HOAc–$CHCl_3$ mixture at room temperature to give **IIe** in an isolated 40% yield. No pre-equilibrium bridge-cleavage by these incoming ligands takes place, obviously, due to their large cone angles. Remarkably, the ^{31}P NMR spectrum of dimeric **IIe** contains only two signals at δ 13.2 and 13.4 as expected for the mixture of *ab–hg* and *ab–gh* isomers. Addition of d_5-py, which monomerizes the dimer, transforms the two signals into one at δ 14.8, as expected for the one-linkage isomer. We believe that the palladacycle formed is the B(4) isomer, since the B(3) position is sterically hindered by the bulky isopropyl group, Fig. 2. Isopropyl C—H bonds are not metallated, and one can observe two doublets of diastereotopic methyls at δ 0.45 and 1.13 (J = 7 Hz) in the case of **IIIe**. Contrary to five-membered palladacycles **IIa,b,f,g**, the ^{11}B NMR spectroscopy of four-membered species **IIc–e,h** gives direct evidence for the presence of the Pd—B bond. In particular, the ^{11}B NMR spectrum of **IIe** contains a well separated signal shifted



(2)

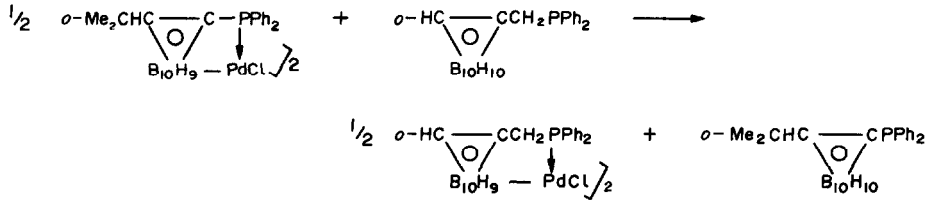
upfield at δ −19.3, the area under which corresponds to one boron. It should be pointed out that we never observed such separated ^{11}B signals in the related five-membered complexes.

DP2MC reacts with $[PdCl(damp)]_2$ like DPIC giving, however, a mixture of B(3) and B(4) palladated products. There are two corresponding signals both in the ^{31}P (δ −1.4 and 13.1) and ^{11}B (δ −16.6 and −18.9) NMR spectra of the monomeric complex obtained from **IId** and d_5-py. It is clear that the less sterically demanding methyl group allows the palladation of the B^3—H bond as well giving B(3) and B(4) products in a molar ratio of 1 : 4. Under the same conditions DPC also gives **IIc** in a low yield but without monomer **Ic**.

The ligand exchange in P-*donor* B-*palladated complexes*

In the previous section we considered the palladium(II) transfer from an N-donor ligand to a P-donor one. It was interesting to find out whether such an exchange from a P-donor ligand is possible. Reaction (3), between the four-membered cyclopalladated chloro-bridged dimer derived from DPIC (**IIe**) and free DPMC, shows that this is the case yielding the five-membered B-palladated chloro-bridged dimer **IIa** in 65% yield. It should be pointed out that the exchange takes place when only DPMC is the incoming ligand. No migration of palladium(II) from **IIe** was observed when $PhCH_2PPh_2$ or *o*-$PhCB_{10}H_{10}CN{=}NPh$ were tested as palladium(II) scavengers. At the same

time the reaction between $[PdCl(dmap)]_2$ and $PhCH_2PPh_2$ yields the cyclopalladated product $[PdCl(o\text{-}C_6H_4CH_2PPh_2)]_2$ in 21% yield (see Experimental). Note that palladation of $PhCH_2PPh_2$ by $Pd(OAc)_2$ gives the corresponding acetato palladacycle in 19% yield.[14] possibly indicating different mechanisms of the two rearrangements. By measuring the concentration of α-methylstyrene liberated, one could follow the reaction kinetics by GLC (Fig. 3). It is seen that the initial rate of dissociation is practically independent



(3)

Palladation of DPMC *by* η^3*-allyl palladium*(II) *dimers*

We have recently presented evidence[15] that $[PdCl(\eta^3\text{-allyl})]_2$ complexes are very resistant to protolytic cleavage, and the departure of the η^3-bonded allyl in acetic acid takes place in the monomeric phosphine complex $[PdCl(\eta^3\text{-}2\text{-}PhC_3H_4)(PPh_3)]$ when the latter is thermolysed at 80°C in the presence of lithium chloride:

$$[PdCl(\eta^3\text{-}2\text{-}PhC_3H_4)(PPh_3)] + HOAc + LiCl \longrightarrow \tfrac{1}{2}[PdCl_2(PPh_3)]_2 + H_2C{=}CMePh + LiOAc. \quad (4)$$

Wishing to carry out the reaction of type (4) with DPMC as a tertiary phosphine, we have found that the compound $[PdCl_2(DPMC)]_2$ does not form, but complex **IIa** is obtained instead [eq. (5)]. The reaction course is independent of whether the η^3-allyl dimer and DPMC or prepared before the monomer $[PdCl(\eta^3\text{-allyl})(DPMC)]$ has been introduced into the reaction (Table 4). The ratio of B(3) and B(4) isomers formed (Table 4) differed from that observed above in reaction (2) in acetic acid solvent, of the nature of added salt. We have also found that reaction (5) occurs even in the absence of added salts and the highest yield of **IIa** (75%) is achieved in this case. It is noteworthy that a palladacycle from the η^3-allylpalladium moiety was obtained by

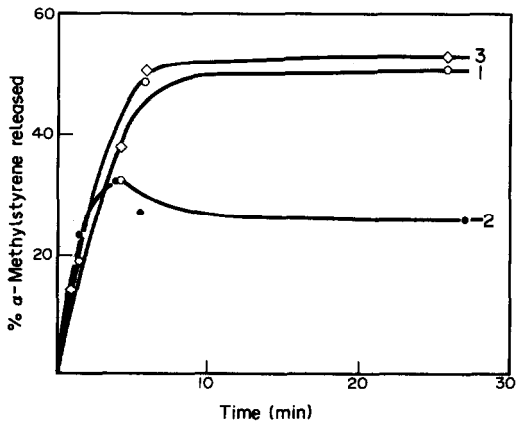


Fig. 3. Kinetic curves of reaction (5), as followed by measuring the liberation of α-methylstyrene from **VIb** by GLC: 1—LiCl, 2—LiBr and 3—LiI; 80°C, HOAc–$CHCl_3$.

Table 4. Cyclopalladation of 1-diphenylphosphinomethyl-*o*-carborane derivatives via the exchange of η^3-allyl ligands in HOAc–$CHCl_3$ solvent at 80°C

Starting complex	Added salt[a]	Time (h)	Product	Yield (%)	Isomer ratio (%) [B(3)]	[B(4)]
VIa	—	24	**IIa**	74.5	50	50
VIa[b]	LiCl	48	**IIa**	48	—	—
VIb	LiCl	48	**IIa**	47	64	36
VIb	LiBr	48	**IIf**	39	72	28
VIb	LiI	48	**IIg**	23	> 90	< 10

[a] Three-fold excess with respect to the starting complex.

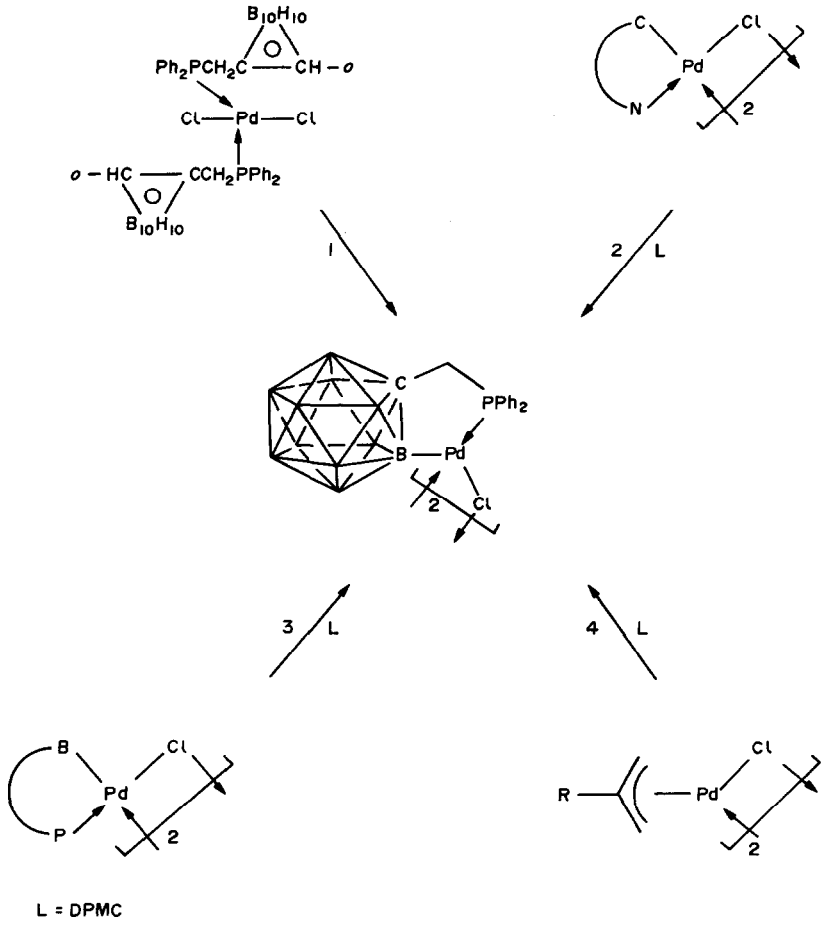
[b] The $[PdCl(\eta^3\text{-}C_3H_5)(DPMC)]$ complex was introduced into the reaction mixture.

us only in the case of the carborane with a tertiary phosphine group in a side chain. No migration of palladium(II) from η^3-allyls to azobenzene, 2-phenylpyridine, N,N-dialkylbenzylamines as well as the exchange between dimeric η^3-allyls and corresponding allylic alkenes occurs.

VI [R = H (a), Ph (b)]

DISCUSSION

The cyclopalladated derivative of DPMC can be prepared in several ways as shown in Scheme 3. Of particular interest are pathways 2–3 which occur in acidic media. Our previous mechanistic investigation of the exchange of cyclopalladated C,N ligands[6c] revealed that at equilibrium, palladium(II) is preferably bound to a ligand which is the most resistant to the acidic cleavage, in particular, by acetic acid. The results of the present study clearly show that C,N-palladacycles are less protolytically stable than C,P, B,P and B,As ones; the four-membered B,P-carboranyl palladacycles are less stable than the corresponding five-membered ones. But the most surprising was the migration of palladium(II) from η^3-allyls which are very strongly bound to the central atom. It is clear that the lability of η^3-allyls is profoundly increased by the coordinated tertiary phosphines, since no exchange is observed in the case of 2-phenylpyridine, although the latter readily cleaves chloro-bridges of $[PdCl(\eta^3\text{-}2\text{-}PhC_3H_4)]_2$ to yield $[PdCl(\eta^3\text{-}2\text{-}PhC_3H_4)(2\text{-}Phpy)]$ with an equilibrium constant of 1.8×10^3 M^{-1} in $CHCl_3$ at 25°C. At the same time, one should assume that **IIa** itself must be very unreactive



Scheme 3.

towards acidic solvents. This was shown[6c] to be the driving force of the exchange of σ-bound ligands in palladium(II) complexes in protic solvents. Palladacycle **IIa** thus appears to be a deep "potential well" in acidic media, since the σ-bond metathesis leads to this particular compound in all cases studied.

EXPERIMENTAL

Instrumentation

IR spectra in the 400–4000 cm^{-1} region were recorded on a JASCO A-200 spectrophotometer with KBr pellets; those in the far-IR region were obtained on a Bruker JFS-113 instrument in Nujol mulls. ^1H NMR spectra were obtained using Tesla BS-467 (60 MHz) and Bruker WP-200 SY (200 MHz) spectrometers using TMS as internal standard. Chemical shifts are given in the δ scale and J are in Hertz throughout. ^{11}B and ^{31}P spectra were recorded on the Bruker instrument with BF_3–Et_2O and 85% H_3PO_4 as external standards, respectively.

Materials

Palladium(II) cyclopalladated complexes $[PdCl(damp)]_2$ and $[PdCl(daep)]_2$, were prepared as described in refs 16 and 17, respectively. $PhCH_2PPh_2$ was obtained according to ref. 18. Precursors of the four-membered B,P-palladacycles DPC, DPIC and DP2MC were prepared as described in ref. 19. Diphenylphosphinomethyl carborane derivatives and DAMC were synthesized according to the procedures of Zakharkin *et al.*,[19,20] respectively. Preparation of palladium(II) η^3-allyl complexes is described in detail elsewhere.[15]

General procedure for the synthesis of bis-adducts trans-$[PdCl_2L_2]$, *the precursors of five-membered palladacycles*

To a solution of DPMC, DPMMC or DAMC (1.6 mmol) in 5 cm^3 of benzene (or 10 cm^3 of methanol), 0.75 mmol of $PdCl_2(PhCN)_2$ in 10 cm^3 of benzene (or Na_2PdCl_4 in 10 cm^3 of methanol) was added and the mixture was stirred for 3 h at room temperature. The precipitate formed was filtered, washed with hexane and dried *in vacuo*. Yields and analytical data of the compounds formed are summarized in Table 2.

Cyclopalladation of trans-$[PdCl_2(DPMC)_2]$ *in toluene*

The bis-adduct (0.43 g, 0.46 mmol) was refluxed in 15 cm^3 of toluene. In a matter of 20 min the reaction mixture turned colourless from dark yellow; 20–25 cm^3 of heptane was added and the mixture cooled. The crystals formed were filtered, washed with hexane and dried to yield 100 mg (45%) of dimeric compound **IIa**. The mother liquor was evaporated *in vacuo* and the residue was crystallized from benzene–hexane to yield 178 mg (45%) of monomeric compound **Ia**. The corresponding characteristics are given in Tables 1 and 2.

Cyclopalladation of trans-$[PdCl_2(DAMC)_2]$ *in toluene*

This was performed as described above to yield 30 mg (13%) of **V** and 310 mg (82%) of **IV** from 0.40 g (0.57 mmol) of the starting material. For data see Tables 1 and 2.

General procedure for the cyclopalladation of trans-$[PdCl_2(DPMC)_2]$ *and* trans-$[PdCl_2(DPMMC)_2]$ *in* n-*propanol*

A mixture of 0.50 g of the complex and a 10-fold excess of lithium bromide or sodium iodide in 20 cm^3 of *n*-propanol was refluxed until the solution faded. The precipitate formed after cooling was filtered, washed consequently with water, methanol and hexane, and dried to yield **IIa,b**. For data see Tables 1 and 2.

Non-metathetical cyclopalladation of 1-*diphenylphosphino*-o-*carboranes*

To 1.0 mmol of DPC, DPIC or DP2MC dissolved in 5–10 cm^3 of the corresponding solvent (MeOH, C_6H_6), 0.5 mmol of the palladium(II) compound (Li_2PdCl_4, Na_2PdCl_4, $PdCl_2(PhCN)_2$), dissolved in 15–20 cm^3 of the same solvent, was added and the mixture was mixed at room temperature until it became colourless. The precipitate which formed was filtered, washed with hexane and recrystallized from benzene–hexane to yield either monomer **Ic** or dimers **IId,e**. The bromo-bridged dimer can be obtained by performing the reaction in methanol in a 10-fold excess of LiBr. For data see Tables 1 and 2.

Di-μ-chlorobis[(2-*diphenylphosphinomethylphenyl*-C^1,P)*palladium*(II)]

To a mixture of $[PdCl(damp)]_2$ (0.095 g, 0.17 mmol) and $PhCH_2PPh_2$ (0.096 g, 0.34 mmol) in 3 cm^3 of chloroform, acetic acid (3 cm^3) was added. The reaction solution was kept for 4 days at room temperature and then 20:20 cm^3 of $CHCl_3$–H_2O was added. The organic layer was separated, twice

washed with 10 cm^3 water and dried over $MgSO_4$. The solution was then concentrated *in vacuo* and column-chromatographed (SiO_2–$CHCl_3$). The first band was separated, the solvent removed, and the residue recrystallized from hexane–benzene to afford pale yellow crystals of [PdCl(*o*-$C_6H_4CH_2PPh_2$)]$_2$ (0.030 g, 21%). Found: C, 56.0; H, 4.2. Calc. for $C_{19}H_{16}ClPd \cdot 1/6C_6H_6$: C, 55.8; H, 4.0%. Spectral data were as reported in ref. 14.

Metathetical preparation of di-μ-chlorobis[(1-*diphenylphosphinomethyl- and -2-methyl-*o*-carboranyl*-B^{3,4},P)*palladium*(II)] (**IIa** *and* **IIb**)

(a) *From* [PdCl(damp)]$_2$ *or* [PdCl(daep)]$_2$. Acetic acid (4 cm^3) was added to a mixture of [PdCl(damp)]$_2$ (0.0975 g, 0.175 mmol) and DPMC (0.121 g, 0.35 mmol) dissolved in 4 cm^3 of chloroform. The solution was thermostatted at 70°C for 25 h. Cooling to room temperature afforded white scaly crystals which were washed subsequently with $CHCl_3$–HOAc (1:1), HOAc, HOAc–H_2O (1:1) and pure water. Product **IIa** was then dried *in vacuo* over NaOH. Yield 83% (0.142 g). **IIb** was obtained in 95% yield in a similar way.

(b) *From di-μ-chlorobis*[(1C-*diphenylphosphino*-2C-*isopropyl*-*o*-*carboranyl*-B^4,P)*palladium*(II)] (**IIe**). Acetic acid (2 cm^3) was added to a solution of **IIc** (0.078 g, 0.077 mmol) and DPMC (0.060 g, 0.176 mmol) in 2 cm^3 of chloroform. The mixture was thermostatted for 6 h at 60°C to produce fine white crystals of **IIa**. The mixture was cooled to −5°C and after 30 min the crystals were filtered and treated as above. Yield 65% (0.048 g).

(c) *From di-μ-chlorobis*[(η^3-*allyl*)*palladium*(II)]. Acetic acid (4 cm^3) was added to a mixture of [PdCl(η^3-C_3H_5)]$_2$ (0.143 g, 0.39 mmol) and DPMC (0.116 g, 0.34 mmol). The resulting solution was kept at 80°C for 24 h to produce white crystals of **IIa** which were treated as above. The runs with [PdCl(η^3-2-PhC_3H_4)]$_2$ in the absence and in the presence of lithium chloride, bromide and iodide were obtained in a similar way. Data are given in Table 4.

Metathetical preparation of di-μ-chlorobis[(1-*diphenylphosphino*-2-*isopropyl*-*o*-*carboranyl*-B,P)*palladium*(II)] (**IIe**) *from* [PdCl(damp)]$_2$

Acetic acid (9 cm^3) was added to a mixture of DPIC (0.260 g, 0.690 mmol) and [PdCl(damp)]$_2$ (0.190 g, 0.345 mmol). This mixture was kept for 60 h at room temperature and then 20:20 cm^3 $CHCl_3$–H_2O was added. The organic layer was separated, washed twice with water (10 cm^3) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was crystallized from benzene–hexane. White crystals of **IIe** were filtered, washed with hexane and dried. Yield 40% (0.141 g). Data are given in Tables 1 and 2.

Metathetical preparation of di-μ-chlorobis[(1-*diphenylphosphino*-2-*methyl*-*o*-*carboranyl*-B,P)*palladium*(II)] (**IIf**)

A solution of [PdCl(damp)]$_2$ (0.263 g, 0.746 mmol) and DP2MC (0.212 g, 0.746 mmol) in 9 cm^3 of chloroform was mixed with 9 cm^3 of HOAc. The mixture was filtered and allowed to stand for 48 h at room temperature. White crystals which formed were filtered, washed consequently with HOAc–$CHCl_3$ (1:1), HOAc, HOAc–H_2O (1:1), H_2O and air-dried to yield 0.130 g of **IIf** (35%). An additional crop of less pure **IIf** (0.146 g) can be obtained by slow evaporation of chloroform from the initial filtrate, the total yield being 74%. Data are given in Tables 1 and 2.

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