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Unconventional coordination modes of carboranyl phosphine–iminophosphorane ligands

José Luis Rodríguez-Rey, Irene Vázquez-Carballo and Antonio Sousa-Pedrares *

A series of new carboranyl phosphine–iminophosphorane ligands were obtained and characterized. The ligands present a flexible three-atom spacer between (P,N) donor atoms, derived from the diphosphine *dppe*. The ligands include examples of C-carboranyl derivatives (ligands **L1–L3**) and B₃-carboranyl derivatives (ligands **L4** and **L5**), to compare the different effect of these electron-withdrawing groups. An organic analog was also prepared (ligand **L6**) for comparison purposes. The analysis of the structures of their dichloride palladium(II) complexes using several techniques, including X-ray diffraction, reveals that the carboranyl group can affect the coordinating ability of the attached nitrogen atom. Thus, although organic phosphine–iminophosphorane ligands always show the (P,N) chelating mode, providing both sites are available, the new carboranyl ligands give rise to a surprising variety of coordination modes: the expected (P,N) chelating mode, the unusual P-terminal mode and the unprecedented (P,N) bridging mode. The comparison of these structures with organic analogues and with the carboranyl ligands derived from the diphosphine *dppm* indicates that the length of the spacer between the donor atoms is an important variable for the coordination mode of the ligand, once the coordinating strength of the nitrogen atom is reduced by effect of the carborane cage.

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Introduction

Ligands are crucial to the properties of coordination compounds and can determine their potential applications. The most straightforward way to influence the performance of a metal atom is through the steric and electronic properties of coordinated ligands. *ortho*-Carboranes are icosahedral clusters that combine both properties: steric bulk and an adjustable electronic inductive effect. Thus, they could be used for adjusting the donating properties of coordinating groups attached to them. Their bulkiness is comparable to adamantane,¹ and can be increased by the coupling of other steric groups in neighboring positions of the cluster. The irregular charge distribution of *ortho*-carboranes has been studied by several authors,² and is due to the presence in the cluster of two vicinal carbon atoms and ten more electropositive boron atoms. This is reflected in their electronic inductive effect, which changes from the electron-withdrawing character of C-carboranyles (more than a benzene ring) to the progressive electron-donating character of B-carboranyles, as the boron atom of attachment is further away from the carbon atoms of the cluster (Fig. 1). Thus, although the boron atoms connected to both carbon atoms (boron atoms B3/B6) still show an elec-

tron-withdrawing inductive effect on coordinated groups, the central boron atoms (B4, B5, B7, B11) present an electroneutral character, and the further boron atoms B8 and B10 and especially B9 and B12, clearly show an electron-donating effect. This varied inductive effect was first described by Teixidor and Viñas,³ and later exemplified by other authors, describing a progressive increase in donating strength of donor atoms attached to these positions.⁴

The first use of *ortho*-carboranes as ligands was through the dicarbollide dianion, derived from the *nido* open cluster.⁵ These anions are isolobal with the cyclopentadienyl ligand and coordinate to the metal atom through the five atoms of the open face (C₂B₃). Since then, a wide variety of metallaborane complexes of this type have been synthesized with almost

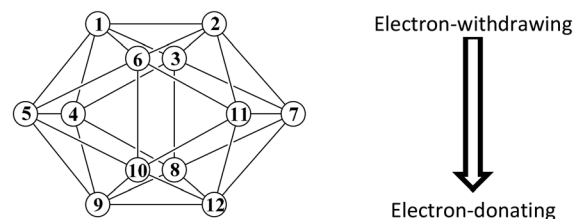


Fig. 1 Numbering scheme for *o*-carborane (1,2: carbon atoms; 3–12: boron atoms). Equivalent positions: (C1, C2), (B3, B6), (B4, B5, B7, B11), (B8, B9), (B9, B12).

Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain. E-mail: antonio.sousa.pedrares@usc.es



all transition and lanthanide metals.⁶ Besides, the functionalization of the *ortho-closo*-carborane cluster with donor groups produces ligands in which the cluster maintains its *closo* form, which allows us to take advantage of its electronic properties. These ligands are known as *closo*-carborane *exo*-ligands.⁷

A particular type of ligand in which the *closo*-carborane unit can show its modulating capacity through its electronic and steric effects are the hemilabile bidentate ligands, *i.e.* bidentate ligands that can reversibly dissociate one of the donor atoms. These ligands are very interesting in the field of homogeneous catalysis, due to their potential for creating vacant coordination sites that can accommodate the substrate.⁸ The usual combination is a soft phosphorus donor with a harder nitrogen or oxygen donor, to be used with a soft catalytically active metal atom. In this situation it is interesting to be able to modulate the donating properties of the hard (less coordinating) donor group, to achieve proper hemilabile behavior. The unique properties of the *ortho-closo*-carborane group make it an ideal choice for such modulation, although it has rarely been used for this purpose.⁹ In particular, the electron-withdrawing character of B3-carboranyl derivatives in conjunction with their modifiable steric effect has rarely been exploited to modulate a possible gradual decrease in the coordinating character of a donor group. In fact, most studies on the influence of the carborane cage on the coordinating strength of donor atoms have focused on the comparison of the extreme effects produced by C-carboranyl and B9-carboranyl derivatives.⁴

It is important to emphasize that in order to take advantage of the electron-withdrawing nature of the *ortho*-carborane group and thus be able to modulate the coordinating character of donor atoms connected to the cluster, it is essential that this unit maintains its closed *closo* structure, and that it does not evolve to the open *nido* form, associated with a strong electron-donating character.¹⁰ For this reason, the design of bidentate ligands with a potentially hemilabile character should not present two neutral donor atoms directly connected to the carbons of the carborane cage, since this arrangement tends to favor the evolution to *nido* derivatives by coordination to the metal atom in nucleophilic solvents such as alcohols. This evolution was firstly observed for *closo*-carboranyl-diphosphines,¹¹ and a lot of examples of *nido*-carboranyl-diphosphines obtained by complexation to metal atoms are now known.^{7,12} This behavior has also been reported for other carboranyl ligands with two neutral donor groups attached to the carbon atoms of *closo*-carborane, including bis(phosphine-oxide) ligands,¹³ bis(thioether) ligands,¹⁴ and phosphino-thioether ligands.¹⁵

Iminophosphoranes, $R_3P = NR$, are compounds that can act as ligands through their sp^2 -hybridized nitrogen donor atom. They have a strong σ -donor and relatively weak π -acceptor character, and the strength of their coordination depends on the metal atom they bind. Thus, although the coordination to electron-poor metal centers can be very strong,¹⁶ their weaker coordination to electron-rich metal centers makes them very interesting for homogeneous catalysis.¹⁷ Besides, the coordi-

nating character of the iminophosphorane can be modulated by the introduction of appropriate substituents on the N atom of the iminophosphorane,¹⁸ so attaching electron-withdrawing groups can make them less coordinating. This tunable character makes them very useful as the weak coordinating end of a hemilabile ligand. In fact, ligands combining an iminophosphorane group with other donor groups have found several applications in homogeneous catalysis.^{17,19–34} Despite their potential applications, iminophosphorane derivatives have been scarcely studied in the field of carboranes, although the *ortho*-carborane group is a good candidate for modulating the donor abilities of the nitrogen atom. Thus, although carboranyl-iminophosphorane derivatives are known,^{35–37} as well as related carboranyl-phosphazide derivatives,^{37,38} only our research group has explored the properties of carboranyl-iminophosphoranes as ligands.^{39–41} These studies revealed that the nature of the soft donor of the potentially bidentate hemilabile ligand has a great influence on the coordinating abilities of the iminophosphorane group. An anionic thiolate group connected to the other carbon atom of the cluster completely deactivates the nitrogen towards coordination,³⁹ making this group not suitable for modulation. A phosphine group attached to the other carbon of the cluster gives rise to (P,N) chelate coordination but promotes the evolution to the strong electron-donating *nido* form of the cluster,⁴⁰ as mentioned before for other carboranyl bidentate ligands with two neutral donor groups on the carbon atoms of the carborane cage. The positioning of the phosphine group on a side chain gave better results in terms of modulation of the coordinating character of the carboranyl-iminophosphorane group, as this situation allows the *closo* structure to be maintained and, thus, to express the electronic and steric influence of the carborane group. The phosphine-iminophosphorane ligands previously studied were 1,1'-bis(diphenylphosphino)methane (*dppm*) derivatives, with two atoms connecting the (P,N) donor atoms of the potentially bidentate ligands (see Fig. 2, $n = 1$).⁴¹ These ligands were used to obtain palladium complexes, which show the expected (P,N) coordination mode that is always found for non-carboranyl analogs, although the substitution of the other carbon atom of the C-carboranyl group gives rise to the unusual P-terminal coordination mode, regardless the electronic nature of the substituent ($R = Me, Ph$), proving that the

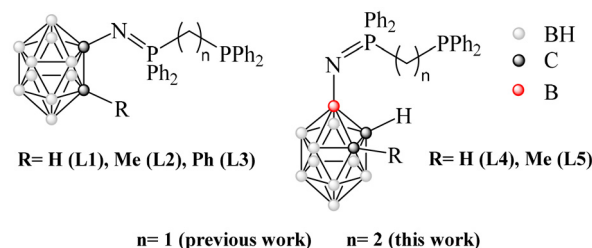


Fig. 2 Carboranyl phosphine-iminophosphorane ligands designed for this work, derived from the diphosphine *dppe* ($n = 2$), and related ligands reported previously, derived from the diphosphine *dppm* ($n = 1$).⁴¹



steric effect of the substituted electron-withdrawing C-carboranyl group can further tune its coordinating behavior. However, the less electron-withdrawing B3-carboranyl derivatives are less affected by the steric hindrance of the substituents, and the methyl-substituted B3-carboranyl group still promotes a (P,N) chelating mode.⁴¹

As a continuation of our research in the chemistry of carboranyl-iminophosphorane ligands, we now present the results found with the 1,1'-bis(diphenylphosphino)ethane (*dppe*) derivatives, with three atoms connecting the (P,N) donor atoms of the potentially bidentate ligands (see Fig. 2, $n = 2$). The results found for the new ligands show the uniqueness of the carborane group, since this presumably minor difference has led to unprecedented results.

Results and discussion

Synthesis and characterization of the carborane ligands

Five new carboranyl phosphine-iminophosphorane ligands were prepared with a three-atom spacer between the nitrogen and phosphorus donor atoms, derived from the diphosphine *dppe* (Fig. 2, $n = 2$). These ligands were obtained following the same methods used to prepare the previously reported ligands with a two-atom spacer between donor atoms, derived from the diphosphine *dppm* (Fig. 1, $n = 1$).⁴¹ Thus, in all cases the Staudinger method was used,⁴² by reaction of the corresponding carboranyl-azide with 1,1-bis(diphenylphosphino)ethane (*dppe*). In the case of C-carboranyl derivatives the corresponding C-carboranyl-azide was obtained *in situ* as described in the literature,^{37,39–41,43} *i.e.* by reaction of the corresponding lithiated carborane [$R = H$ (**L1**), Me (**L2**), Ph (**L3**)] with tosyl-azide. In the case of B3-carboranyl derivatives the B3-carboranyl-azide was obtained *in situ* from the corresponding carboranyl-amine [$R = H$ (**L4**), Me (**L5**)].⁴⁴

A non-carboranyl phosphine-iminophosphorane analogue was also obtained for comparison (**L6**), reacting the diphosphine *dppe* with 1-azido-2-phenylbenzene, obtained *in situ* from 2-phenyl-aniline, using the same method as for the B-carboranyl derivatives.⁴⁴

The carboranyl ligands **L1–L5** and the comparison organic ligand **L6** were characterized by solid state IR spectroscopy, ¹H, ³¹P and ¹¹B NMR spectroscopy, mass spectrometry and elemental analysis. In the case of ligand **L1**, it was also possible to study its crystal structure by X-ray diffraction analysis. The analysis of the ligands **L1–L5** confirmed the formation of the *closo*-carboranyl phosphine-iminophosphorane derivatives. The most relevant techniques are IR spectroscopy for the confirmation of the iminophosphorane bond formation and the *closo* nature of the cluster, ³¹P NMR for the confirmation of the presence of both phosphorus functionalities (phosphine and iminophosphorane), and ¹¹B NMR for the confirmation of the *closo* nature of the cluster.

The IR spectra of the carboranyl ligands show the presence of the *closo*-carborane group through a very intense band in the range 2570–2586 cm⁻¹ due to the $\nu(B-H)$ stretching. These

spectra also show an intense band in the range 1329–1406 cm⁻¹ due to the $\nu(P=N)$ stretching of the iminophosphorane group (Table 1). These ranges are similar to those presented by the already reported ligands derived from the diphosphine *dppm*.⁴¹ The organic analogue **L6** shows the $\nu(P=N)$ band at 1427 cm⁻¹, very similar to other phosphine-iminophosphorane ligands derived from the diphosphine *dppe*.^{45,46} These data show that the strength of the P=N bond increases in the order C-carboranyl (**L1–L3**) < B3-carboranyl (**L4, L5**) < organic (**L6**).

The ³¹P spectra of the carboranyl ligands **L1–L5** show two doublets: one at higher field due to the phosphine group [range (–14.9) to (–7.4) ppm] and one at lower field due to the iminophosphorane group [range 9.7–18.6 ppm], all with a similar coupling constant of 46.6–49.3 Hz. The non-carboranyl derivative **L6** shows a similar signal for the phosphine group, –14.4 ppm, although the signal for the iminophosphorane group appears at higher field, 3.1 ppm (coupling constant ² $J_{P-P} = 47.1$ Hz), due to the less electron-withdrawing nature of the organic group compared to the carborane moiety. The same pattern is followed by other unbound organic phosphine-iminophosphorane ligands derived from the diphosphine *dppe* found in the literature, with very similar values for the phosphine group, near –12 ppm, and a wider range of higher (positive) field values for the iminophosphorane group, 3.5–29 ppm, depending on the group attached to the nitrogen atom.^{22,34,45–48} The previously reported *dppm* carboranyl ligands show the signal due to the iminophosphorane group at similar values [range 5.8–9.1 ppm], but higher field values for the phosphine group [range (–30.9) to (–29.9) ppm], which is typical of *dppm* derivatives.⁴¹

The ¹H NMR spectra are the typical ones for this type of molecule. The ethylene spacer of all ligands **L1–L5** appears as two multiplet signals in the ranges 1.84–2.24 ppm and 2.30–2.60 ppm. It has been reported for other organic *N*-aryl phosphine-iminophosphoranes derived from *dppe* that the multiplet at higher field is due to the –CH₂P(III) group while the one at lower field corresponds to the –CH₂P(V) group.⁴⁷ The values found for the Cc–H groups (Cc: cage carbon atom) of the non-substituted carboranyl ligands (**L1, L4** and **L5**) show the same tendency found for the already reported *dppm* derivatives,⁴¹ *i.e.* an increasing highfield shift from the C-carboranyl

Table 1 Selected spectroscopic data (IR and ³¹P{¹H} NMR) for ligands **L1–L6**

	IR	³¹ P{ ¹ H} NMR ^a		
	$\nu(PN)/cm^{-1}$	–PPh ₂	P=N	³ $J_{P,P}$
L1	1340	–14.8	9.7	46.6
L2	1329	–14.7	11.1	46.7
L3	1338	–14.9	9.9	47.7
L4	1376	–7.4	18.6	49.3
L5	1406	–13.5	12.6	48.1
L6	1427	–14.4	3.1	47.1

^a Chemical shifts in ppm and coupling constants in Hz.



derivative **L1** (3.73 ppm) to the unsubstituted B-carboranyl derivative **L4** (3.34 ppm) and to the methyl-substituted B-carboranyl derivative **L5** (2.89 ppm).

The ^{11}B NMR spectra of the new *dppe* carboranyl ligands are very similar to those found for the previously reported *dppm* carboranyl ligands,⁴¹ *i.e.*, narrower ranges for the C-carboranyl derivatives **L1–L3** [range (–15.6) to (–3.9) ppm] and wider ranges for the B-carboranyl derivatives **L4, L5** [range (–23.3) to (1.8) ppm], with a single positive value due to the substituted B3 position. These values confirm the presence of a *closo*-carborane moiety in the ligands.

The solid-state structure of the free ligand **L1** was studied by single crystal X-ray diffraction. The crystals were obtained by slow evaporation of a solution of the compound in a mixture of dichloromethane and hexane. Crystallographic data can be found in Table S1 (SI). A selection of bond lengths and angles can be found in Table 2. The X-ray analysis shows that compound **L1** is the expected ligand, with a distorted icosahedral carborane moiety substituted on a cage carbon atom with a diphenylphosphine-ethyl-diphenyl-iminophosphorane group (Fig. 3). The iminophosphorane group, with a P–N–C bond angle of 129.62(15)°, is folded towards the ethylene spacer of the diphosphine. This conformation is the result of an intramolecular B–H...H–C interaction (“dihydrogen” bond) established between a partially negatively charged B–H group of the carborane moiety (B4–H4) and the partially positively charged C–H of a –CH₂– group of the spacer [$d(\text{H}\cdots\text{H})$: 2.368 Å, angle

(C–H...H): 171.88°, angle(B–H...H): 113.64°], as shown in Fig. 3.

The structural parameters that involve the nitrogen atom show typical values of a non-coordinated iminophosphorane group. The non-coordinated nitrogen atom can engage in *exo*- π -bonding with the carborane cage, which produces the elongation of the Cc–Cc distance and shortens the N–Cc bond.⁴⁹ Although the Cc–Cc distance for **L1** is artificially long due to the cluster disorder of the carborane cage (see crystallographic experimental details, SI),⁵⁰ the *exo*- π -bonding interaction is reflected in the short value of the N–Cc bond distance, 1.376(3) Å. This value is very similar to the values found in the literature for other non-coordinated C-carboranyl-iminophosphoranes [range: 1.339(2)–1.373(3) Å],^{37,39–41} including similar derivatives with no other donor groups on the other cage carbon atom [1.366(1)–1.373(3) Å],^{37,39} and derivatives with other donor groups like phosphine, [1.355(3)–1.369(2) Å],⁴⁰ and sulfur groups [1.339(2)–1.365(4) Å].³⁹ The non-coordination of the nitrogen atom is also reflected in the P–N distance of the iminophosphorane group, which presents a short value, 1.5845(17) Å, similar to those found in the literature for other free C-carboranyl-iminophosphoranes [range: 1.5659(17)–1.5870(16) Å].^{37,39–41} This value is also similar to the values found for non-coordinated organic (non-carboranyl) iminophosphorane ligands deposited in the Cambridge Structural Database (ConQuest Version 2024.3.0), either with C–N=PC₃ connection (408 structures, mean value: 1.580 Å) or with B–N=PC₃ connection (20 structures, mean value: 1.565 Å). Thus, the data indicate that the carborane cage does not affect the P–N bond to a great extent. The P–C bond distances depend on the oxidation state of the phosphorus atom. The iminophosphorane P(v)–C distances (average: 1.807 Å) are shorter than the phosphine P(III)–C distances (average: 1.842 Å). In both cases, the distances that involve the phenyl rings are always slightly shorter [P(v)–C(Ph): 1.805(2), 1.800(2) Å; P(III)–C(Ph): 1.835(2), 1.835(2) Å] than the corresponding distances that involve the aliphatic spacer [P(v)–C(CH₂): 1.817(2) Å; P(III)–C(CH₂): 1.858(2) Å]. The literature shows only one example of a free phosphine–iminophosphorane ligand derived from the diphosphine *dppe*,²² and four examples of free ligands derived from the diphosphine *dppm*.^{51,52} These examples show the same pattern of P–C bond distances, with very similar ranges for the same type of P–C distances [P(v)–C(Ph): 1.787–1.806 Å; P(v)–C(CH₂): 1.799–1.812 Å; P(III)–C(Ph): 1.826–1.845 Å; P(III)–C(CH₂): 1.847–1.864 Å].^{22,51,52}

Table 2 Selected bond lengths (Å) and angles (°) for **L1**

P=N	N–Cc	Cc–Cc ^a	P ^V –CPh
1.5845(17)	1.376(3)	1.710(3), 1.711(3)	1.805(2), 1.800(2)
PV–CCH ₂	P ^{III} –CPh	P ^{III} –CCH ₂	Cc–N–P
1.817(2)	1.835(2), 1.835(2)	1.858(2)	129.62(15)

^a Cluster disorder.

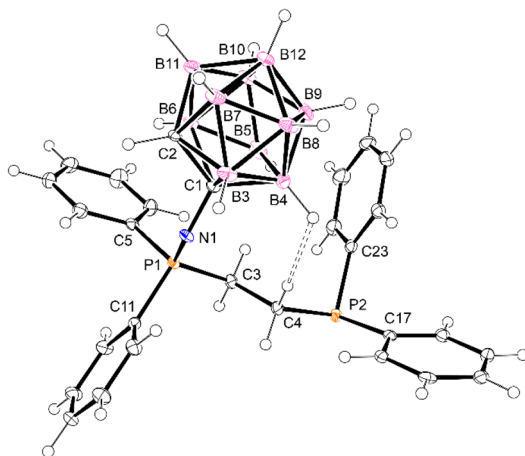
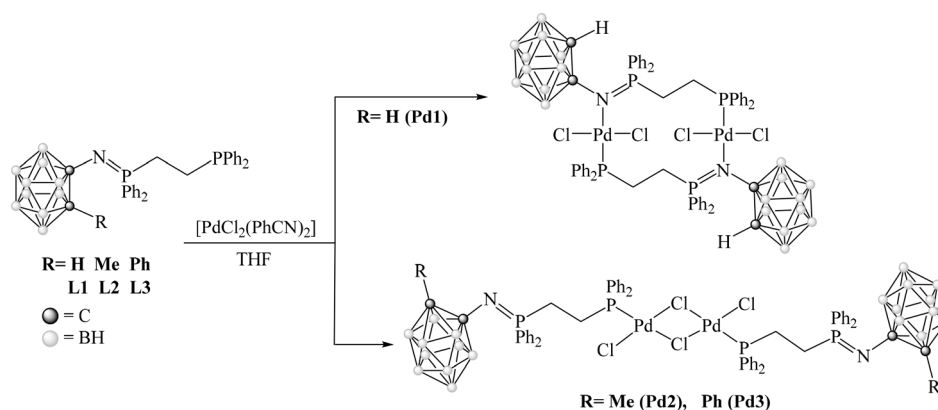


Fig. 3 Molecular structure of compound **L1**. Thermal ellipsoids are shown at the 40% probability level. Dotted line shows the intramolecular dihydrogen bond interaction (see values in text).

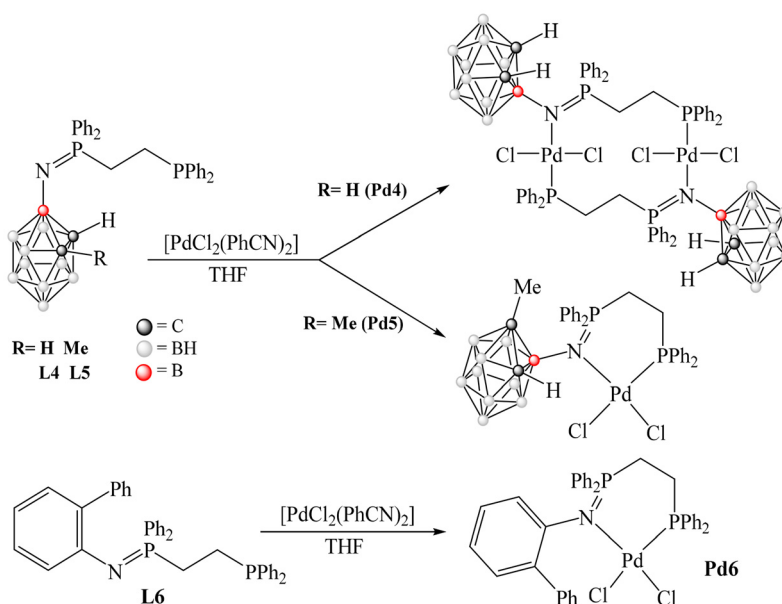
Synthesis and characterization of the palladium complexes

The new phosphine–iminophosphorane ligands **L1–L6** were used to obtain palladium chloride complexes by reaction with the precursor *cis*-[PdCl₂(PhCN)₂] (Schemes 1 and 2). In all cases, the reaction in a 1 : 1 molar ratio produced the substitution of the labile benzonitrile ligands giving rise to the complexes **Pd1–Pd6**, all with empirical formula [PdCl₂(P,N-ligand)]. The complexes were characterized by elemental analysis and spectroscopic techniques, which confirmed this stoichiometry. Although some of the spectroscopic techniques, like IR spec-





Scheme 1 Synthesis of palladium complexes **Pd1–Pd3** derived from the C-carboranyl phosphine–iminophosphorane ligands **L1–L3**.



Scheme 2 Synthesis of palladium complexes **Pd4** and **Pd5** derived from the B3-carboranyl phosphine–iminophosphorane ligands **L4** and **L5**, and of palladium complex **Pd6** derived from the organic ligand **L6**.

troscopy, hint at the coordination modes of the ligands, these were revealed by X-ray diffraction studies of all complexes. These studies showed the full variety of coordination modes for these ligands: the expected P,N-chelating mode for the ligand **L5** and the organic analogue **L6**, the unusual P-terminal mode for the ligands **L2** and **L3** and the unprecedented P,N-bridging mode for the ligands **L1** and **L4** (Schemes 1 and 2).

The characterized compounds are stable in solid state and solution, and do not evolve to other species, as observed for other palladium complexes with carboranyl ligands with donor atoms in the vicinity of the carborane cage, that show metallation of the carborane cluster through B–H activation.⁵³

The IR spectroscopy is the best spectroscopic technique that reflects the coordination modes of the ligands in the complexes. They can be inferred from the analysis of the shift of the iminophosphorane stretching frequency found for the

complexes with respect to the values found for the free ligands, $\Delta\nu = \nu(\text{PN})_{\text{complex}} - \nu(\text{PN})_{\text{ligand}}$ (Table 3). The coordination of the iminophosphorane group to the palladium metal weakens the P–N bond and shifts its position to lower wavenumbers, giving negative values for $\Delta\nu$.⁵⁴ Besides, the extent of the shift reflects the strength of the Pd–N interaction that, in turn, suggests the coordination mode. The easiest case is that of the dimeric complexes **Pd2** and **Pd3**, with a P-terminal coordination mode of the ligands. In these cases, the small positive shift found for both complexes (2 and 11 cm^{-1} , respectively) agrees with a non-coordinated iminophosphorane group. A similar positive shift was also found for the palladium complexes of the already reported *dppm* analogues of these complexes, which also exhibit this unusual P-terminal coordination mode.⁴¹ In the case of the other complexes, with bonded iminophosphorane groups, the coordination modes



Table 3 Selected spectroscopic data (IR and $^{31}\text{P}\{^1\text{H}\}$ NMR) for the palladium complexes **Pd1–Pd6**.^a

	Coord. mode	IR/cm ⁻¹		$^{31}\text{P}\{^1\text{H}\}$ NMR ^b				
		ν (PN)	Δ (PN)	–PPh ₂	$\Delta\delta$	P=N	$\Delta\delta$	$^3J_{\text{P,P}}$
Pd1	(P,N)-bridging	1229	–111	24.3	39.1	37.6	27.9	73.6
Pd2	P-terminal	1331	2	32.1	46.8	10.7	–0.5	56.7
Pd3	P-terminal	1349	11	31.3	46.2	9.1	–0.8	56.6
Pd4	(P,N)-bridging	1255	–121	16.7	24.1	28.5	9.9	15.9
Pd5	(P,N)-chelate	1222	–184	15.6	29.1	28.4	15.8	17.5
Pd6	(P,N)-chelate	1221	–206	11.9	26.2	25.1	22.0	8.3

^a Δ values are the differences with respect to the corresponding free ligands. ^b Chemical shifts in ppm and coupling constants in Hz.

are reflected in the differences among the negative $\Delta\nu$ shifts. The more negative values of $\Delta\nu$ are found for the complexes with P,N-chelating ligands, *i.e.*, **Pd5** with the 1-Me-B3-carboranyl ligand ($\Delta\nu = -184 \text{ cm}^{-1}$) and the organic analogue **Pd6** ($\Delta\nu = -206 \text{ cm}^{-1}$). The values found for these two complexes show a higher donating strength for the iminophosphorane nitrogen atom of the organic ligand **L6**, as expected. A similar shift was also found for the already reported B3-ligands derived from *dppm*, both of them with a chelate coordination mode.⁴¹ It is interesting that although none of the new reported ligands with C-carboranyl ligands show the chelate mode, the already reported C-carboranyl ligand derived from *dppm* with no other substituents on the other cage carbon atom did show this coordination. In that case, the value of $\Delta\nu$ (-132 cm^{-1})⁴¹ was less negative than those found for B3-carboranyl ligands. Finally, the values found for the new complexes with the unexpected P,N-bridging mode, **Pd1** ($\Delta\nu = -111 \text{ cm}^{-1}$) and **Pd4** ($\Delta\nu = -121 \text{ cm}^{-1}$) also show negative values of $\Delta\nu$, but not as negative as those found for the chelating ligands. This result indicates that the P,N-bridging coordination involves a weaker Pd–N interaction, which is weaker for the more electron-withdrawing C-carboranyl bridging ligand (**Pd1**) than for the B3-carboranyl one (**Pd4**). In summary, considering the values found for the new *dppe* complexes and the already reported *dppm* complexes, the values of the $\Delta\nu$ shifts follow the order: P-terminal > C-carboranyl P,N-bridge > B3-carboranyl P,N-bridge > C-carboranyl P,N-chelate > B3-carboranyl P,N-chelate. The values suggest an increasing Pd–N interaction and, thus, an increasing donating strength of the iminophosphorane group.

All palladium complexes were characterized in solution by NMR spectroscopy (^{31}P , ^1H and ^{11}B). The ^{31}P NMR spectroscopy shows the presence of the ligands in the complexes but is not very useful to assign all the coordination modes of the ligands. In all cases, the spectrum consists of two doublets due to the phosphorus functional groups, phosphine and iminophosphorane (Table 3). The P-terminal complexes **Pd2** and **Pd3** are the easiest to assign, as the signal of the iminophosphorane group is not coordinated to the metal center and appears at almost the same position as for the free ligands (10.7 and 9.1 ppm, respectively). The signal for the phosphine group (32.1 and 31.3 ppm, respectively) is very similar in both cases and very shifted with respect to the phosphine signal of

the free ligands ($\Delta\delta_{\text{PPh}_2} = 46.8$ and 46.2 ppm, respectively), due to the coordination to the metal center. In fact, these P-terminal complexes show the highest phosphine group shift of all complexes presented in this paper. The coupling constants for both complexes **Pd2** and **Pd3** are also very similar (56.7 and 56.6 Hz, respectively). The shifts are similar to those reported for the already published analogous *dppm* derivatives,⁴¹ and comparable to the few literature examples of complexes with P-terminal phosphine–iminophosphorane ligands coordinated to a *cis*-PdCl₂ moiety.³³

The rest of the palladium complexes with (P,N) coordination, bridging or chelating, show similar ^{31}P spectra. In all cases, the doublet found at high field was assigned to the phosphine group, and the one at lower field was assigned to the iminophosphorane group, as reported for other literature examples.⁴¹ It is interesting to note that the ^{31}P spectrum of **Pd4** (16.7 ppm for PPh₂ and 28.5 ppm for P=N), with B3-carboranyl P,N-bridging ligands, and the one of **Pd5** (15.6 ppm for PPh₂ and 28.4 ppm for P=N), with a B3-carboranyl P,N-chelating ligand are almost identical, and both very similar to the spectrum of the organic analogue **Pd6** (11.9 ppm for PPh₂ and 25.1 ppm for P=N), also with a P,N-chelating ligand, as all the organic literature examples. This may indicate a change of coordination mode for **Pd4** in solution, from P,N-bridging to P,N-chelating. However, the ^{31}P spectrum of **Pd1**, with C-carboranyl P,N-bridging ligands, is different to all the rest (24.3 ppm for PPh₂ and 37.6 ppm for PN). Besides, the coupling constant for this complex is very high (73.4 Hz), compared to those found for the B3-carboranyl complexes (15.9 Hz for **Pd4** and 17.5 Hz for **Pd5**). This may indicate a retention of the P,N-bridging mode in solution for the C-carboranyl complex **Pd1**.

The ^1H NMR spectra of the palladium complexes are like those of the free ligands but with the signals shifted due to the coordination of the ligands to the metal atom. As discussed for the ^{31}P MNR spectra, the ^1H NMR spectra are not very useful for assigning the coordination modes of the ligands. In the case of the already reported *dppm* derivatives the increasing shift to lower field of the Cc–H signal was taken as evidence of the increasing P–N interaction.⁴¹ However, in the case of the complexes **Pd1–Pd5** with the new *dppe* derivatives, the shifts found ($\Delta = 1.36$ ppm for **Pd1**, $\Delta = 1.04$ ppm for **Pd4** and $\Delta = 3.28$ ppm for **Pd5**) do not follow the same pattern,



as the P–N interaction for **Pd4** is stronger than for **Pd1**, as judged by all the other techniques (IR spectroscopy, ^{31}P NMR and X-ray diffraction).

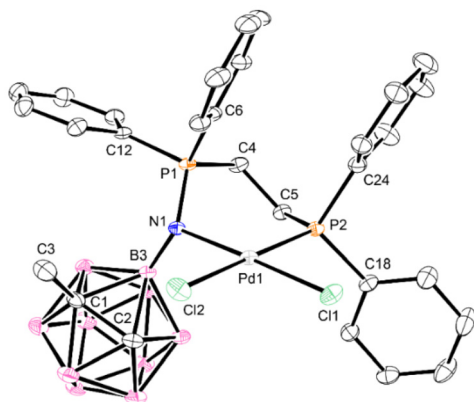


Fig. 4 Molecular structure of compound **Pd5**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

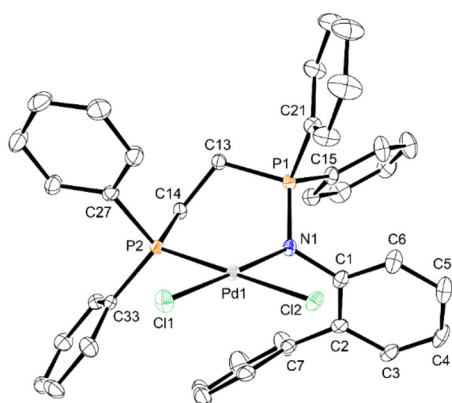


Fig. 5 Molecular structure of compound **Pd6**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

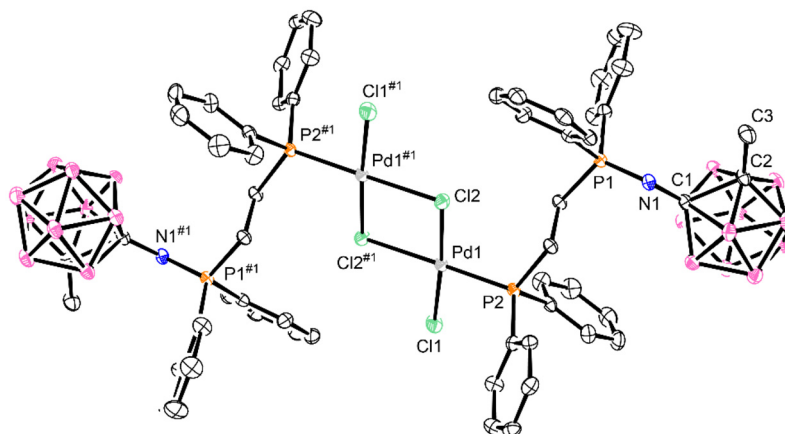


Fig. 6 Molecular structure of compound **Pd2**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

The ^{11}B NMR spectra of the complexes, although with low resolution, clearly show broad signals in similar ranges to the free ligands, typical of *closo*-carborane derivatives. In the case of compound **Pd5** it was possible to locate the band at low field due to the B3 boron atom (2.6 ppm), deshielded with respect to the signal of the free ligand (2.1 ppm), due to the coordination of the attached iminophosphorane group to the metal atom.

Description of the crystal structures of **Pd1**–**Pd6**

The spectroscopical analysis of the palladium complexes shows a vague relationship with the coordination modes of the ligands. Those modes could only be unequivocally assigned by the analysis of their crystal structures, using X-ray crystallography. Slow concentration of solutions of the complexes in dichloromethane and hexane provided the single crystals in all cases. Fig. 4–9 show the molecular structures of the complexes **Pd1**–**Pd6** and Tables 4–6 collect a selection of bond lengths and angles. Crystallographic data can be found in the Table S2.

The crystal structures comprise three different coordination modes of the ligands: the expected (P,N) chelate coordination, the unusual P-terminal coordination and the unprecedented (P,N) bridging coordination. The chelate coordination is the one found for the methyl-substituted B3-carboranyl ligand in complex **Pd5** and the organic analogue **Pd6**, like all the complexes with organic phosphine–iminophosphorane ligands reported in the literature with any metal, providing both coordination sites are available. The P-terminal coordination is the one found for the substituted C-carboranyl ligands in complexes **Pd2** and **Pd3**, which was also described for the already reported *dppm* analogues of these complexes.⁴¹ The (P, N)-bridging mode was found for the unsubstituted carboranyl ligands in complexes **Pd1** and **Pd4** and has never been described for phosphine–iminophosphorane ligands.

(P,N) chelating ligands. Compounds **Pd5** (Fig. 4) and **Pd6** (Fig. 5) are neutral monomeric palladium(II) complexes in which the metal atom is coordinated to two *cis* terminal chlorine ligands and to the phosphorus and nitrogen donor atoms of a chelating phosphine–iminophosphorane ligand, which



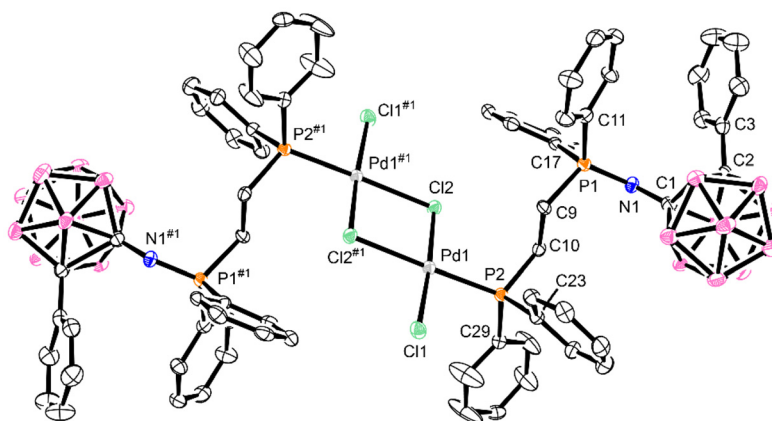


Fig. 7 Molecular structure of compound **Pd3**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

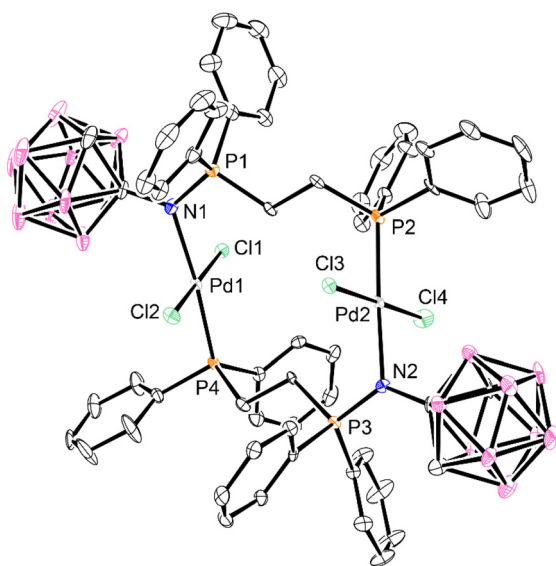


Fig. 8 Molecular structure of compound **Pd1**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

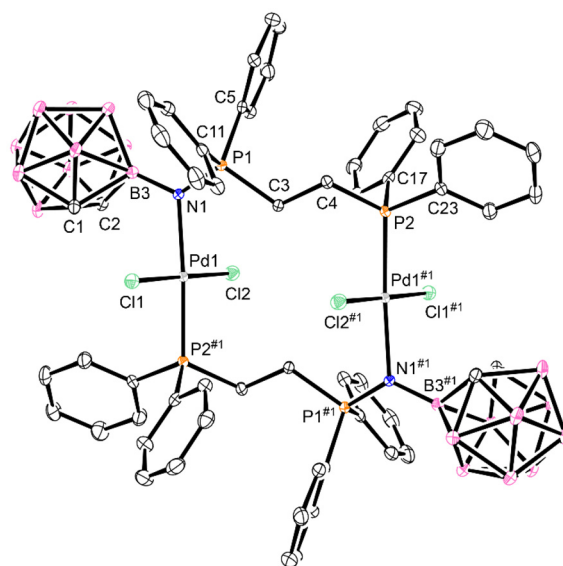


Fig. 9 Molecular structure of compound **Pd4**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

produces a six-membered chelate ring. This structure is found for the methyl-substituted B3-carboranyl ligand **L5**, and for the organic ligand **L6**. The flexible six-membered chelate ring adopts a twist-boat conformation which produces a minor distortion of the square-planar geometry of the palladium atom [94.76(4)° for **Pd5** and 92.27(9)° and 92.39(9)° for the two independent molecules of **Pd6**]. The N1–Pd1–P2–C fragment is planar [rms: 0.0881 Å for **Pd5** and 0.0529 and 0.0748 Å for **Pd6**] and forms an angle of 53.50(5)° for **Pd5** and of 56.52(14)° and 53.00(10)° for **Pd6** with the plane of the N1–P1–C–C fragment [rms: 0.1225 Å for **Pd5** and 0.0908 and 0.1617 Å for **Pd6**]. The deviations from the planarity of both four-atom groups are due to the twist-boat conformation, instead of the full planarity expected for a boat conformation. The coordination planes [PdNCl₂] are essentially planar [rms: 0.0407 Å for **Pd5**; 0.0148 Å and 0.0486 for **Pd6**], with the PdNP chelate angle only

slightly twisted with respect to the PdCl₂ angle [3.21(7)° for **Pd5**; 2.50(5)° and 4.15(15)° for **Pd6**]. In the structure of **Pd5**, the disposition of the carboranyl ligand **L5** is such that the Cc–H group establishes an intramolecular Cc–H⋯Cl interaction with one of the coordinated chlorine atoms [*d*(H⋯Cl): 2.473 Å], while a C–H bond of one of the phenyl rings of the phosphine group establishes an intramolecular C–H⋯H–B dihydrogen bond interaction with a B–H bond of the carborane cage [*d*(H⋯H): 2.032 Å, angle(C–H⋯H): 148.03°, angle(B–H⋯H): 160.88°].

The Pd–P distances (Table 4) are similar in both complexes, although shorter for the carboranyl complex **Pd5** than for the organic complex **Pd6**. The Pd–N distances are also similar, although longer for the carboranyl complex **Pd5**, reflecting a weaker interaction for the nitrogen atom attached to the B3-carboranyl moiety. The degree of the Pd–N interaction is



Table 4 Selected bond lengths (Å) for Pd1–Pd6

	Pd–N	Pd–P	Pd–Cl1	Pd–Cl2	Pd–Cl2 ^{#1}	P=N	N–Cc/B	Cc–Cc
Pd1	2.154(6)	2.217(2)	2.302(2)	2.2924(18)	—	1.619(6)	1.411(9)	1.698(10)/1.707(12) ^a
	2.181(6)	2.238(2)	2.2965(19)	2.3163(19)	—	1.627(6)	1.413(9)	1.693(12)/1.686(10) ^a
Pd2^b	—	2.2262(6)	2.2712(6)	2.3202(6)	2.4231(6)	1.577(2)	1.373(3)	1.767(3)
Pd3^b	—	2.2255(15)	2.2674(14)	2.3207(14)	2.4291(14)	1.575(5)	1.364(7)	1.795(8)
Pd4^b	2.148(2)	2.2339(7)	2.2948(7)	2.3114(6)	—	1.596(2)	1.441(3)	1.617(4)
Pd5	2.1203(14)	2.2278(5)	2.2883(5)	2.3940(5)	—	1.6165(15)	1.444(2)	1.623(3)
Pd6^c	2.072(3)	2.2334(10)	2.3074(9)	2.3670(10)	—	1.615(3)	1.434(5)	—
	2.076(3)	2.2272(10)	2.3145(9)	2.3644(10)	—	1.611(3)	1.442(4)	—

^a Cluster disorder. ^b Half molecule per asymmetric unit. Symmetry transformation used to generate equivalent atoms #1: $-x + 1, -y, -z$ (**Pd2**); #1: $-x + 2, y + 1, -z + 1$ (**Pd3**); #1: $-x + 1, -y + 1, -z + 1$ (**Pd4**). ^c Two molecules per asymmetric unit.

Table 5 Selected bond angles (°) for the monomeric complexes Pd1, Pd4–Pd6

	P–Pd–N	P–Pd–Cl1	P–Pd–Cl2	N–Pd–Cl1	N–Pd–Cl2	Cl1–Pd–Cl2	Cc/B–N–P
Pd1	174.93(16)	92.63(8)	87.33(7)	90.02(17)	90.10(16)	178.95(8)	124.9(5)
	174.60(17)	86.47(7)	94.79(7)	90.04(18)	88.84(17)	177.67(7)	124.1(5)
Pd4	175.35(6)	90.50(2)	88.88(2)	90.41(6)	90.19(6)	179.34(2)	125.71(18)
Pd5	94.76(4)	84.958(18)	174.793(18)	178.02(4)	89.77(4)	90.599(18)	122.92(12)
Pd6^a	92.27(9)	87.50(3)	175.64(3)	178.54(9)	91.56(8)	88.61(3)	117.3(2)
	92.39(8)	86.10(3)	173.47(3)	177.83(8)	92.91(8)	88.70(3)	117.0(2)

^a Two molecules per asymmetric unit.

Table 6 Selected bond angles (°) for the dimeric complexes Pd2 and Pd3

	P2–Pd–Cl1	P2–Pd–Cl2	P2–Pd–Cl2 ^{#1}	Cl1–Pd–Cl2	Cl1–Pd–Cl2 ^{#1}	Cl2–Pd–Cl2 ^{#1}	C1–N1–P1
Pd2	89.07(2)	94.95(2)	178.54(2)	175.51(2)	91.18(2)	84.75(2)	128.05(16)
Pd3	88.75(5)	94.13(5)	178.15(5)	175.30(5)	93.09(5)	84.04(5)	130.9(4)

reflected in a shorter Pd–Cl(*trans*-N) distance for **Pd5** [2.2883(5) Å] compared with the organic analogue **Pd6** [2.3074(9), 2.3145(9) Å]. The Pd–Cl distances *trans* to the phosphorus atom of the phosphine group are longer than the ones *trans* to the nitrogen atom of the iminophosphorane group (Table 4), as found for all the phosphine–iminophosphorane PdCl₂ complexes described in the literature.

The coordination of the nitrogen atom of the iminophosphorane group affects the bond distances of the ligand around the nitrogen atom.⁵⁴ Thus, the P=N distance lengthens, showing similar values for both complexes, either with a carboranyl ligand [1.6165(15) Å for **Pd5**] or with a non-carboranyl one [1.615(3) Å and 1.611(3) Å for **Pd6**], not reflecting in this case the differences in the Pd–N interaction.

In the case of the carboranyl ligand **L5** in complex **Pd5**, the position of the iminophosphorane group on the B3 boron atom does not influence the Cc–Cc distance, as this group cannot engage in *exo*- π -bonding with the carborane cage. Thus, the Cc–Cc distance is very short, 1.623(3) Å, even compared with the distance found for free *o*-carborane [Cc–Cc distance: 1.630 Å].⁵⁵

P-terminal ligands. Compounds **Pd2** (Fig. 6) and **Pd3** (Fig. 7) with substituted C-carboranyl ligands present this coordination mode. These structures are very similar to the ana-

logues of the already reported *dppm* complexes.⁴¹ The complexes are palladium dimers with a central [Pd₂(μ -Cl)₂] ring and two terminal chlorine ligands and two P-terminal ligands arranged in an *anti*-disposition, related by an inversion center. The coordination of the palladium atom [PdPCL₃] is essentially planar [rms: 0.0142 Å (**Pd2**) and 0.0142 Å (**Pd3**)], and the geometry around the metal atom is very close to the regular one. The central [Pd₂Cl₂] ring is the only source of distortion, with *cis* angles of 84.75(2)° for **Pd2** and 84.04(5)° for **Pd3**. The Pd–P and the Pd–Cl distances (Table 4) are the usual ones found in other palladium dimers with related terminal phosphines, as discussed for the already reported *dppm* complexes.⁴¹

As only the phosphorus atom of the phosphine group of the ligands is involved in the coordination to the metal atom, all the structural parameters of the ligands for both complexes are very similar, and also similar to the parameters of the free ligand **L1** (*vide supra*). The P=N bond distances [1.577(2) Å for **Pd2** and 1.575(5) Å for **Pd3**] are shorter than those found for the rest of the complexes with the Pd–N bond (Table 4) and are comparable to the value of 1.5845(17) Å found for the free ligand **L1**. Due to the lack of Pd–N bonding, the free nitrogen donor atom is engaged in *exo*- π -bonding with the carborane cage, which is reflected in short N–Cc distances and long Cc–Cc distances,⁴⁴ as described for the free ligand **L1**. The value



of the Cc–Cc distance is longer for the complex **Pd3**, 1.795(8) Å, than for **Pd2**, 1.767(3) Å, as the phenyl substituent of **Pd3** can also engage in *exo*- π -bonding with the carborane cage.⁴⁹ The P–C bond distances show the same pattern discussed for the free ligand **L1**, with shorter bond distances for the P(iminophosphorane)–C distances than for the P(phosphine)–C distances.

(P,N) bridging ligands. Compounds **Pd1** (Fig. 8) and **Pd4** (Fig. 9) are neutral dinuclear palladium(II) complexes in which each palladium atom is coordinated to two *trans* terminal chlorine ligands and to the phosphorus and nitrogen donor atoms of two different carboranyl phosphine–iminophosphorane ligands (**L1** and **L4**, respectively), which act as (P,N) bridging ligands between the two palladium atoms of the dimer. The carboranyl ligands that show this coordination mode present the phosphine–iminophosphorane substituent on one cage carbon atom (**L1**) or on the B3 boron atom (**L4**), and no other substituents on the cage carbon atoms. The coordination of both bridging carboranyl ligands forms a twelve-membered ring. In the case of compound **Pd4**, the palladium dimer shows an inversion center at the middle point of the line that joins the two palladium atoms. Thus, the coordination environments of both metal atoms in **Pd4** are symmetry equivalent. Each palladium atom presents a [PNCl₂] coordination environment in a square planar geometry. There are no obvious sources of distortion, so the geometries in both cases are close to a regular square-planar coordination, especially in the case of the symmetric dimer **Pd4**. The only distortion, in both cases, is that the Pd–P bonds are slightly bent with respect to the coordination plane, outward from the central twelve-membered ring. Thus, the *trans* P–Pd–N angles are more distorted [174.60(18)–175.35(6)°] than the *trans* Cl–Pd–Cl angles [177.65(7)–179.34(2)°]. Due to the center of inversion of **Pd4**, the coordination planes of both metal atoms are parallel (rms: 0.0411 Å; angle between planes: 0°), and perfectly aligned (torsion angle Cl1–Pd1–Pd1#1–Cl1#1: 180°), while in the case of **Pd1**, the coordination planes are not parallel [rms–Pd(1): 0.0480 Å; rms–Pd(2): 0.0536 Å; angle between planes: 13.10(11)°] nor aligned [torsion angle Cl1–Pd1–Pd2–Cl3: 149.45(8)°].

The terminal chlorine ligands, *trans* to each other, show Pd–Cl distances in the range 2.2922(19)–2.3166(19) Å, mean value: 2.3067 Å, very close to the mean value of 2.3032 Å found in the Cambridge Structural database for mutually *trans* terminal Pd–Cl bonds. The values of the mutually *trans* Pd–N [range: 2.148(2)–2.180(6) Å, mean value: 2.160 Å] and Pd–P [range: 2.217(2)–2.238(2) Å, mean value: 2.2296 Å] bond distances can be compared with those found in the CSD for palladium(II) complexes with a *trans*-[PNCl₂] environment, involving phosphine ligands and sp²-nitrogen donor ligands (48 structures). The values found in the literature for the Pd–N distances, 2.078–2.207 Å, are slightly shorter than those found for **Pd1** and **Pd4**, and the values found for the Pd–P distances, 2.219–2.271 Å, are slightly longer, although some literature examples include more donating terminal trialkylphosphines. Thus, the data indicate that the carboranyl iminophosphorane

nitrogen atom presents a reduced coordinating ability compared with organic nitrogen donating ligands, which is reflected in longer Pd–N bonds and in shorter *trans*-Pd–P bonds. In fact, the Pd–P distances found for **Pd1** and **Pd4** are similar to those found in the palladium dimers with P-terminal ligands [2.2262(6) Å for **Pd2** and 2.2255(15) Å **Pd3**], *trans* to bridging chlorine atoms, which are very weak donors. A detailed analysis of the Pd–N distances shows that the interaction in **Pd1** (Cc–N=P ligand) is weaker [2.154(6) and 2.181(6) Å] than the one found in **Pd4** (B3–N=P ligand) [2.148(2) Å], as expected.

As commented before for the complexes with chelating ligands, the Pd–N coordination weakens the P–N bond,⁵⁴ which is reflected in P–N bond distances [1.596(2)–1.626(6) Å] that are longer than those found for non-coordinated carboranyl-iminophosphoranes, like the known literature examples [1.5659(17)–1.5870(16) Å],^{37,39,40} the free ligand **L1**, 1.5845(17) Å, or the P-terminal complexes **Pd2** [1.577(2) Å] and **Pd3** [1.575(5) Å]. A more detailed analysis also reveals minor differences between the derivative **Pd1**, with a Cc–N=P connection [P–N: 1.619(6) Å, 1.627(6) Å], and the derivative **Pd4**, with a B3–N=P connection [P–N: 1.596(2) Å]. The same trend was also described for the already published *dppm* complexes,⁴¹ as the Cc–N=P derivatives tend to show longer P–N distances than the B3–N=P ones, although the Pd–N interaction is weaker.

In the case of compound **Pd1**, with a Cc–N=P connection, the Pd–N coordination also affects the Cc–Cc and the Cc–N bond distances, as it competes with the *exo*- π bonding to the cage carbon atoms. The Cc–Cc distances will not be commented on due to the presence of cluster disorder (see crystallographic experimental section, SI),⁵⁰ but the long values of the Cc–N bonds [1.411(9), 1.413(9) Å] compared to those found for the free ligand **L1** [1.376(3) Å] and for the literature examples of free C-carboranyl-iminophosphoranes [range: 1.339(2)–1.373(3) Å]^{37,39,40} clearly indicate this competition. In the case of compound **Pd4**, with a B3–N=P connection and no donor atoms on the cage carbon atoms, the Cc–Cc distance is very short, 1.617(4) Å, similar to the value found for the chelate complex **Pd5** discussed before, 1.623(3) Å, and shorter than the value found for free *o*-carborane [Cc–Cc distance: 1.630 Å].⁵⁵

The 12-membered rings formed by the dimeric structures of **Pd1** and **Pd4** do not leave usable free space inside. A “space-fill” image of the ring for **Pd4** (Fig. S1, SI) shows very little free space inside the ring.

Discussion

In order to show the uniqueness of the coordinating properties of the carboranyl-phosphine–iminophosphorane ligands presented in this paper, it is important to review the structures of all known coordination complexes with non-carboranyl phosphine–iminophosphorane ligands that have been structurally characterized by X-ray diffraction. All known organic ligands present the (P,N) chelate mode providing the coordination



sites around the metal atom are available, regardless of the number of atoms in the spacer that join the P (phosphine) and the N (iminophosphorane) donor atoms. The Cambridge Structural Database (ConQuest Version 2024.3.0) collects 38 structures of metal complexes with chelating phosphine–iminophosphorane ligands with a 2-atom spacer between donor atoms (forming 5-membered chelate rings),^{25–34,41,47,48,51,52,56–66} most of them derived from the diphosphine *dppm* (33 structures); 20 structures with a 3-atom spacer (6-membered chelate rings),^{23,24,67–72} and one example of a PdCl₂ complex with a rigid 4-atom spacer (7-membered chelate ring).⁷³ Incidentally, the PdCl₂ complexes are very common, as 17 of the 59 total structures are complexes of this type.^{33,34,41,45,47,48,56,57,67–69,72,73}

Of the 20 structures with a 3-atom spacer, 17 comprise a rigid phenyl spacer,^{23,24,68–71} one a rigid ethene spacer,⁶⁷ one of them a flexible propyl spacer,⁷² and only one a flexible –PPh₂–CH₂–CH₂– spacer derived from the diphosphine *dppe*,⁴⁵ which is the spacer used for the structures presented in this paper. The *dppe* literature complex is an example of an organic phosphine–iminophosphorane ligand with low steric hindrance around the nitrogen donor atom, with the substituent –CH₂–CN. Due to the lack of data for comparison, we decided to synthesize the PdCl₂ complex **Pd6**, with a biphenyl group on the nitrogen atom, as an example of an organic *dppe* derivative with high steric hindrance around the donor atom. As described before, even in this case the chelate coordination is observed.

In addition to these examples, the literature presents 5 structurally characterized complexes in which the phosphine–iminophosphorane ligand presents a P-terminal coordination mode.^{25,28,33,56} In all cases the ligands present a two-atom spacer between donor atoms, as the ligands are derived from the diphosphine *dppm*. However, in all cases this coordination mode is forced. Two examples are palladium complexes in which the nitrogen atom of an originally chelating phosphine–iminophosphorane ligand to a PdCl₂ moiety has been displaced by stronger donors.³³ Another example is a ruthenium complex with a N-protonated P-terminal phosphine–iminophosphorane ligand with no neutral coligands susceptible to being displaced.²⁸ In fact, the coordination compound presents the same ligand in a (P,N) chelating mode. Another example is a ruthenium complex also with no coordination sites available.²⁵ The same ligand has been structurally characterized as a (P,N) chelating ligand in a PdCl₂ complex.⁵⁷ The other example is a rhodium complex with two equal phosphine–iminophosphorane ligands, one showing a (P,N) chelating mode and the other a P-terminal mode, as there are no other coordination sites available.⁵⁶ The ligand of this last example is very interesting for comparison, as the nitrogen atom is connected to a phenyl ring that is fluorinated in four of its five available positions. Although the electron-withdrawing effect of a C-carboranyl group has been usually compared with the one exerted by a fluorinated aryl group,^{4b,d} this ligand still shows a (P,N) chelating mode when the coordination sites around the metal atom are available.

In summary, the only known coordination mode for organic phosphine–iminophosphorane ligands is the (P,N)

chelation, providing both sites are available. This is in clear contrast with the variety of coordination modes exhibited by the carboranyl phosphine–iminophosphorane ligands presented in this paper. In the field of carboranes, the unexpected P-terminal coordination mode was also described for the *dppm* analogues of the dimers **Pd2** and **Pd3**,⁴¹ showing a tendency for substituted C-carboranyl-phosphine–iminophosphorane ligands to present this coordination mode. However, to our knowledge, the (P,N) bridging coordination mode described for **Pd1** and **Pd4** has never been observed for any phosphine–iminophosphorane ligands. That is not to say that this kind of dimeric structure with other (P,N) bridging ligands is not known. Thus, the Cambridge Structural Database collects 14 dimeric PdCl₂ complexes with (P,N) bridging ligands: 2 structures with a 1-atom spacer between (P,N) donor atoms,⁷⁴ 5 structures with a 3-atom spacer,⁷⁵ 4 structures with a 4-atom spacer,⁷⁶ one structure with a 5-atom spacer,^{76b} and 2 structures with an 8-atom spacer.⁷⁷

The variety of coordination modes exhibited by the carboranyl phosphine–iminophosphorane ligands presented in this paper (complexes **Pd1–Pd5**) cannot only be explained by the balance between the donating strength of the iminophosphorane nitrogen atom directly attached to the carborane cage and the steric hindrance around this donor atom. The comparison of these structures with those published for their *dppm* analogues⁴¹ indicates that an additional variable that must be considered is the length of the spacer between donor atoms.

The palladium precursor, *cis*-[PdCl₂(PhCN)₂], with two adjacent labile benzonitrile ligands, is a widely used precursor to produce PdCl₂ complexes, especially with neutral bidentate chelating ligands. The more donating (and softer) phosphine functionality of the phosphine–iminophosphorane ligands is expected to be the first to bind the palladium atom, replacing one of the labile ligands of the palladium precursor. The immediate substitution of the second benzonitrile ligand by the iminophosphorane nitrogen atom produces a monomeric *cis* complex with a (P,N) chelating ligand. This is the route followed by all organic phosphine–iminophosphorane ligands. Indeed, the organic ligand **L6** shows this coordination mode in complex **Pd6** (Fig. 5). However, in the case of the carboranyl ligands presented in this paper only ligand **L5** (the B3-substituted ligand with a methyl group on one of the cage carbon atoms) follows this path, forming a six-membered chelate ring (Fig. 4). In contrast, most of the already published *dppm* analogues show this coordination mode, forming 5-membered chelate rings: the unsubstituted C-carboranyl analogue **L1-dppm** and both the B3-carboranyl analogues, either unsubstituted (**L4-dppm**) or methyl substituted (**L5-dppm**).⁴¹

In the case of the substituted C-carboranyl ligands **L2** (R = Me) and **L3** (R = Ph) the non-coordinating nature of the nitrogen atom of the iminophosphorane group gives rise to the formation of dimers with chlorine bridges (Fig. 6 and 7). The nitrogen atom is not capable of displacing the second benzonitrile molecule and the ligand is forced to show the unusual P-terminal mode. This mode, which is never found for organic phosphine–iminophosphorane ligands in complexes with



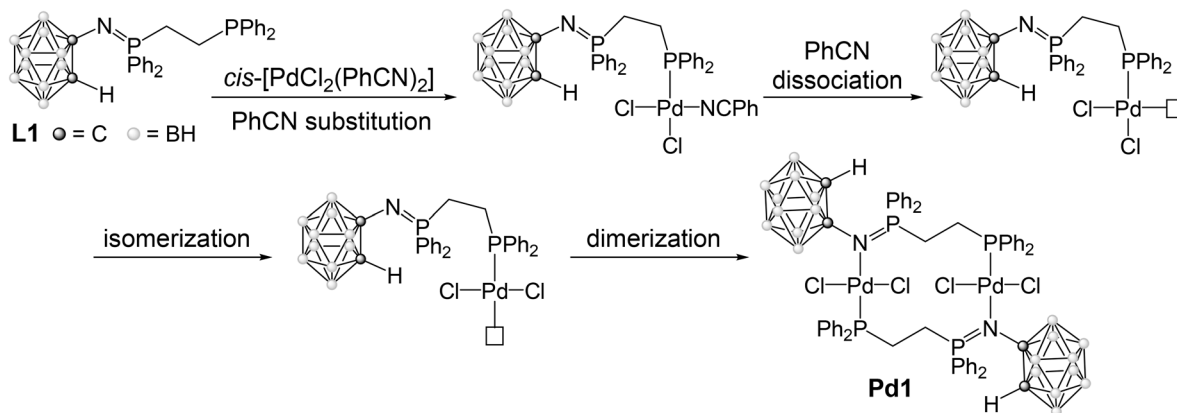
available metal sites, was also described for the *dppm* analogues of these complexes, **Pd2-dppm** and **Pd3-dppm**.⁴¹ In that case, the electronic properties of the carboranyl *dppm* ligands were revealed by the Mulliken charges on the nitrogen atoms, calculated using DFT calculations. These calculations did not show any surprises, indicating the expected electronic effects: the C-carboranyl moiety is more electron-withdrawing than the B3-carboranyl one;² the methyl group attached to a cage carbon atom is associated with an increase of the donating strength of the nitrogen atom; and the phenyl group attached to a cage carbon atom is associated with a decrease of its donating strength. Thus, the non-coordinating nature of the nitrogen atom of the substituted C-carboranyl derivatives was attributed to the steric effect of the group on the other cage carbon atom, phenyl (**Pd3-dppm**) or even the small and donating methyl group (**Pd2-dppm**).⁴¹ Obviously, the same principle operates for the new *dppe* derivatives, which explains the P-terminal coordination mode of the complexes **Pd2** and **Pd3**.

The structures of the new palladium complexes with methyl substituted ligands **L3** (Me-C-carboranyl, P-terminal mode) and **L5** (Me-B3-carboranyl, chelate mode) reflect the more electron-withdrawing nature of the C-carboranyl group compared with the B3-carboranyl one, as the (small) steric hindrance of the methyl substituent has no effect on the chelate structure of the more donating B3-carboranyl ligand.

The unprecedented (P,N) bridging mode found in the dimers **Pd1** (Fig. 8) and **Pd4** (Fig. 9) deserves special attention. The ligands involved are the unsubstituted C-carboranyl derivative **L1** and the unsubstituted B3-carboranyl derivative **L4**. It is interesting to remember that the *dppm* analogues of these compounds, **Pd1-dppm** and **Pd4-dppm**, show the expected (P,N) chelate mode, which is entropically favored (chelate effect). Taking into account the similar electronic and steric properties of corresponding *dppm* and the *dppe* ligands, that should give them the same coordinating ability, the bridging mode is a reflection of the lower stability of the six-membered chelate ring that would be produced by the chelation of

the *dppe* ligands compared with the five-membered chelate ring produced by the chelate coordination of the *dppm* ligands. The sole effect of the six-membered chelate ring is not enough to explain the formation of the bridging mode, as the organic analogue **Pd6**, with a bulky biphenyl group on the nitrogen atom, and other literature organic examples with flexible three-atom spacers,^{67,72} indicate that the (P,N) chelation is the preferred coordination mode for these linkers. Besides, the sole effect of the electron-withdrawing nature of the C- and B3-carboranyl groups is also not enough to explain the bridging mode, as the *dppm* analogues show the chelate mode.⁴¹ Therefore, the bridging mode is the result of the combination of the lower stability of the six-membered chelate ring and the reduced coordinating ability of the nitrogen atom by effect of the electron-withdrawing carboranyl group.

Another interesting difference between the dimeric bridging complexes **Pd1** and **Pd4** and the monomeric chelate analogues **Pd1-dppm** and **Pd4-dppm** is the relative orientation of the terminal chloride ligands. The (P,N) bridging mode is associated with a more stable *trans* disposition of the terminal chlorine ligands, while the chelate coordination of the ligand forces a *cis* disposition. The palladium precursor, *cis*-[PdCl₂(PhCN)₂], with two adjacent labile benzonitrile ligands, promotes a *cis* disposition in the final substituted complex. Thus, as shown in Scheme 3, after the initial substitution of a benzonitrile ligand by the phosphine group of the ligand, the failure of the iminophosphorane nitrogen atom to immediately substitute the second benzonitrile ligand to produce a chelate complex should result in the dissociation of the second benzonitrile ligand, producing a “*cis*-like” three-coordinate T-shape intermediate that can isomerize to the more stable “*trans*-like” intermediate.⁷⁸ This species can be finally stabilized by Pd–N bond formation, giving rise to palladium dimers, as found for **Pd1** and **Pd4**. The formation of the dimeric compounds can be taken as proof of the hemilabile character of ligands **L1** and **L4**, as they temporarily show P-terminal coordination (for the *cis* to *trans* isomerization) to



Scheme 3 Rationalization of the formation of the (P,N) bridging mode for complex **Pd1**. A similar route is proposed for the B3-carboranyl complex **Pd4**.



finally coordinate the nitrogen atom to another palladium metal. This behavior is very relevant for their potential applications, especially in homogeneous catalysis.⁸

The novel results presented in this work, resulting from the modulation of donor atoms by the effect of the carborane unit, indicate that it may be interesting to extend these investigations to other diphosphines. The use of carboranyl diphosphines for the formation of phosphino–iminophosphorane ligands could allow further modulation of the donor characteristics of the donor atoms (N,P), which could result in interesting catalytic activities. In particular, diphosphines in which the phosphine groups are connected to boron and carbon atoms of the same carborane unit,^{79,80} whose synthesis has been described by B–H activation methods,^{79–81} could be especially interesting since the combination of the Cc-donor atom and B-donor atom connections in the same ligand can lead to novel and interesting results, as the present work demonstrates.

Conclusions

We have extended our studies on carboranyl phosphine–iminophosphorane ligands by synthesizing five new ligands derived from the diphosphine *dppe*, with a three-atom spacer between donor atoms. The ligands include examples of C-carboranyl derivatives (ligands **L1–L3**) and B3-carboranyl derivatives (ligands **L4** and **L5**), to compare the different effect of these electron-withdrawing groups. Due to the scarcity of literature data for comparison, an organic analogue was also prepared (ligand **L6**), with a bulky biphenyl group attached to the nitrogen atom. The ligands were used to prepare PdCl₂ complexes. The analysis of the final structures using several techniques, including X-ray diffraction, shows the whole variety of coordination modes that this kind of potentially (P,N) donating ligand can show. Surprisingly, only one of the carboranyl ligands show the expected (P,N) chelating mode (ligand **L5**, Cc-methyl substituted B3-carboranyl), which is the mode found for the organic analogue **L6** and all the organic literature examples, providing both coordination sites are available. In contrast, the substituted C-carboranyl ligands **L2** (R = Me) and **L3** (R = Ph) show the unusual P-terminal coordination, indicating that the substitution of the other carbon atom hinders the coordination of the nitrogen atom, even with small donating groups like a methyl group. This coordination mode was not completely unexpected for this kind of substituted carboranyl derivative as the already published *dppm* counterparts also show this type of P-terminal coordination.⁴¹ The findings for the unsubstituted ligands **L1** (C-carboranyl) and **L4** (B3-carboranyl) were more striking, as they show the unprecedented (P,N) bridging mode, forming palladium dimers with a *trans* configuration of the PdCl₂ moiety. The fact that the corresponding *dppm* analogues (with similar donating character and steric bulk) show the usual chelating mode indicates that other variables like the length of the (P,N)-spacer can influence the final coordination mode, once the coordinating strength of the

nitrogen atom is reduced by effect of the carborane cage. Besides, the *trans* disposition of the terminal chloride ligands in the bridged dimers **Pd1** and **Pd4** can be taken as an indication of hemilabile character of the ligands.

The discovery that the length of the spacer between donor atoms is an appropriate variable for the tunability of carboranyl phosphine–iminophosphorane ligands extends the possibilities of these ligands for potential catalytic applications. This is especially true in the case of the *dppe* B3-derivatives, for which the modulation can be increased with the combination of different groups that may substitute the cage carbon atoms.

All in all, the novelty of the performance of the new carboranyl phosphine–iminophosphorane compounds as ligands reflects the uniqueness of the carborane cage as a modifying group of the coordinating abilities of donor atoms.

Experimental section

General

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Tetrahydrofuran, acetonitrile and dichloromethane were purchased from Merck and distilled from sodium benzophenone, P₄O₁₀ and calcium hydride, respectively, prior to use. Commercial grade diethyl ether, ethyl acetate, hexane and dichloromethane were used without further purification. Demineralized water was used in the aqueous stages of synthesis. The precursors tosyl azide,⁸² bis(benzonitrile)palladium(II) chloride, *cis*-[PdCl₂(PhCN)₂],⁸³ and 1-R-3-NH₂-1,2-*ortho*-carborane, R = H, Me,⁸⁴ were synthesized according to the literature. *o*-Carborane precursors, *o*-1-R-C₂B₁₀H₁₁ R = H, Me, Ph, were supplied from KatChem Ltd (Prague) and used as received. The precursors *tert*-butyl nitrite, trimethylsilyl azide, 2-phenylaniline, bis(diphenylphosphino) ethane (*dppe*) and *n*-BuLi solution (1.6 M in hexanes) were purchased from Aldrich and used as received. No uncommon hazards are noted.

Analytical methods

Elemental analyses were performed using a Thermo Finnigan Flash 1112 microanalyzer. Solid-state ATR-IR spectra were recorded on a high-resolution spectrometer FT-IR PerkinElmer Spectrum Two. The ¹H NMR spectra were recorded on a Varian Mercury 300 spectrometer (¹H 300 MHz). The ³¹P NMR and the ¹¹B NMR spectra were recorded on a Varian Inova 500 spectrometer (³¹P 202 MHz; ¹¹B 160 MHz). All NMR spectra were recorded in CDCl₃ solutions at 25 °C. Chemical shift values for ¹H NMR were referenced to SiMe₄ (TMS), those for ³¹P were referenced to 85% H₃PO₄, and those for ¹¹B NMR were referenced to external BF₃·OEt₂. Chemical shifts are reported in units of parts per million downfield from the reference and all coupling constants are reported in Hertz. Mass spectra of the ligands **L1–L6** were determined on a Micromass Autospec instrument (positive electronic impact). MALDI-TOF mass spectra of the metal complexes **Pd1–Pd6** were recorded in negative-ion mode on a Bruker Autoflex instrument.



Synthesis of C-carboranyl iminophosphoranes, L1–L3

The compounds were synthesized in a similar way, following the literature procedure described for other C-carboranyl iminophosphoranes.^{37,39–41} To a solution of *ortho*-carborane in dry THF (40 mL) at $-10\text{ }^{\circ}\text{C}$ was added dropwise a solution of *n*-BuLi 1.6 M in hexanes. The mixture was stirred for 30 minutes and then tosyl azide was added. The reaction mixture was stirred at $-10\text{ }^{\circ}\text{C}$ for 30 minutes and then 30 minutes at room temperature. Then, a solution of *dppe* in dry THF (10 mL) was added dropwise. The reaction mixture was heated to reflux for 1.5 hours (evolving nitrogen gas). The cold reaction mixture was evaporated to dryness to yield a brown oil. The crude mixture was purified by silica column chromatography (90 : 10, hexane : ethyl acetate).

Synthesis of L1. Reaction mixture: *ortho*-carborane (0.50 g, 3.47 mmol), *n*-BuLi 1.6 M in hexanes (2.28 mL, 3.65 mmol), tosyl azide (0.60 mL, 3.68 mmol), *dppe* (1.50 g, 3.76 mmol). Yield: 0.68 g (35%); white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 1.07–3.27 (bm, 10H, BH), 2.00 (m, 2H, $\text{CH}_2\text{-P(III)}$), 2.45 (m, 2H, $\text{CH}_2\text{-P(V)}$), 3.73 (bs, 1H, $\text{C}_{\text{cage}}\text{-H}$), 7.31 (m, 10H, PPh_2), 7.48 (m, 10H, PPh_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , ppm): δ -14.8 (d, $^3J_{\text{PP}} = 46.6$ Hz, $-\text{CH}_2\text{PPh}_2$), 9.7 (d, $^3J_{\text{PP}} = 46.6$ Hz, $\text{P}=\text{N}$); $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , ppm): δ -15.6 , -13.2 , -12.2 , -11.0 , -5.8 . IR (ATR, ν/cm^{-1}): 3059m, 2910w, 2562vs $\nu(\text{B-H})$, 1482m, 1436s, 1400m, 1340vs $\nu(\text{P}=\text{N})$, 1267m, 1137m, 1112m, 1072m, 1012m, 748m, 721s, 692s, 530m, 506m, 490m; MS (EI, m/z): 555 (7.8%) $[\text{L}]^+$, 478 (2.0%) $[\text{L-Ph}]^+$, 370 (7.4%) $[\text{L-PPh}_2]^+$, 342 (21.4%) $[\text{L-CH}_2\text{CH}_2\text{PPh}_2]^+$, 262 (73.8) $[\text{PPh}_3]^+$, 212 (100.0%) $[\text{CH}_2\text{CH}_2\text{PPh}_2\text{-H}]^+$. EA (%): calculated for $\text{C}_{28}\text{H}_{35}\text{B}_{10}\text{NP}_2$: C 60.5, H 6.3, N 2.5; found: C 59.8, H 6.3, N 2.6.

Synthesis of L2. Reaction mixture: *ortho*-1-Me-carborane (0.50 g, 3.14 mmol), *n*-BuLi 1.6 M in hexanes (2.15 mL, 3.45 mmol), tosyl azide (0.55 mL, 3.45 mmol) and *dppe* (1.44 g, 3.61 mmol). Yield: 0.57 g (32%); white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 1.40–2.94 (bm, 10H, BH), 2.11 (m, 2H, $\text{CH}_2\text{-P(III)}$), 2.09 (s, 3H, $\text{C}_{\text{cage}}\text{-CH}_3$), 2.60 (m, 2H, $\text{CH}_2\text{-P(V)}$), 7.36 (m, 10H: 8H *m*- PPh_2 , 2H *p*- PPh_2), 7.49 (m, 4H, *o*- PPh_2), 7.58 (m, 6H, 4H *o*- PPh_2 , 2H *p*- PPh_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , ppm): δ -14.7 (d, $^3J_{\text{PP}} = 46.7$ Hz, $-\text{CH}_2\text{PPh}_2$), 11.1 (d, $^3J_{\text{PP}} = 46.7$ Hz, $\text{P}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , ppm): δ -12.2 , -11.6 , -6.8 , -6.3 . IR (ATR, ν/cm^{-1}): 3055w, 2581vs $\nu(\text{B-H})$, 1587w, 1481w, 1435m, 1377m, 1329vs $\nu(\text{P}=\text{N})$, 1167w, 1114m, 1090m, 1026w, 999w, 874w, 722m, 694s, 560w, 518w, 497w. MS (EI, m/z): 569 (28.4%) $[\text{L}]^+$, 384 (100.0%) $[\text{L-PPh}_2]^+$, 356 (42.6%) $[\text{L-CH}_2\text{CH}_2\text{PPh}_2]^+$, 262 (22.6%) $[\text{PPh}_3]^+$, 212 (92.2%) $[\text{CH}_2\text{CH}_2\text{PPh}_2\text{-H}]^+$. EA (%): calculated for $\text{C}_{29}\text{H}_{37}\text{B}_{10}\text{NP}_2$: C 61.1, H 6.5, N 2.5; found: C 60.7, H 6.2, N 2.7.

Synthesis of L3. Reaction mixture: *ortho*-1-Ph-carborane (0.50 g, 2.26 mmol), *n*-BuLi 1.6 M in hexanes (1.55 mL, 2.49 mmol), tosyl azide (0.39 mL, 2.49 mmol) and *dppe* (1.04 g, 2.60 mmol). Yield: 0.51 g (36%); white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 1.22–3.20 (bm, 10H, BH), 1.84 (m, 2H, $\text{CH}_2\text{-P(III)}$), 2.30 (m, 2H, $\text{CH}_2\text{-P(V)}$), 7.16 (m, 4H *m*- PPh_2), 7.28 (m, 6H, 4H *o*- PPh_2 , 2H *p*- PPh_2), 7.34 (m, 8H,

2H *m*-Ph, 2H *p*- PPh_2 , 4H *m*- PPh_2), 7.45 (t, 1H, *p*-Ph), 7.52 (m, 4H, *o*- PPh_2), 7.67 (d, 2H, *o*-Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , ppm): δ -14.9 (d, $^3J_{\text{PP}} = 47.7$ Hz, $-\text{CH}_2\text{PPh}_2$), 9.9 (d, $^3J_{\text{PP}} = 47.7$ Hz, $\text{P}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , ppm): δ -14.8 , -13.1 , -11.7 , -10.7 , -7.0 , -4.7 , -3.9 . IR (ATR, cm^{-1}): 3433vs, 3059w, 2910w, 2586s $\nu(\text{B-H})$, 1635w, 1435s, 1338vs $\nu(\text{P}=\text{N})$, 1169m, 1115s, 1072s, 731s, 692s, 525m, 496m. MS (EI, m/z): 631 (5.5%) $[\text{L}]^+$, 446 (3.1%) $[\text{L-PPh}_2]^+$, 418 (18.7%) $[\text{L-CH}_2\text{CH}_2\text{PPh}_2]^+$, 341 (1.5%) $[(\text{L-CH}_2\text{CH}_2\text{PPh}_2)\text{-Ph}]^+$, 262 (42.9%) $[\text{PPh}_3]^+$, 212 (100.0%) $[\text{CH}_2\text{CH}_2\text{PPh}_2\text{-H}]^+$. EA (%): calculated for $\text{C}_{34}\text{H}_{39}\text{B}_{10}\text{NP}_2$: C 64.6, H 6.2, N 2.2; found: C 62.3, H 6.1, N 2.3.

Synthesis of B-carboranyl iminophosphoranes, L4 and L5

The compounds were synthesized in a similar way, following the literature procedure described for other B3-carboranyl iminophosphoranes.⁴¹ To a solution of 3-NH₂-1,2-*ortho*-carborane in dry acetonitrile (40 mL) at $0\text{ }^{\circ}\text{C}$ was added dropwise *tert*-butyl nitrite and trimethylsilyl azide. The yellow solution was stirred at room temperature for 1.5 hours and then a solution of *dppe* in dry THF (10 mL) was added dropwise. The reaction mixture was heated to reflux for 2 hours (evolving nitrogen gas). The cold reaction mixture was evaporated to dryness to yield a brown oil which was purified by silica column chromatography (90 : 10, hexane : ethyl acetate).

Synthesis of L4. Reaction mixture: 3-NH₂-1,2-*ortho*-carborane (0.20 g, 1.25 mmol), *tert*-butyl nitrite (0.22 mL, 1.84 mmol), trimethylsilyl azide (0.24 mL, 1.84 mmol) and *dppe* (0.73 g, 1.83 mmol). Yield: 0.45 g (65%); white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 1.04–2.58 (bm, 9H, BH), 2.20 (m, 2H, $\text{CH}_2\text{-P(III)}$), 2.41 (m, 2H, $\text{CH}_2\text{-P(V)}$), 3.34 (s, 2H, $\text{C}_{\text{cage}}\text{-H}$), 7.33 (m, 10H, PPh_2), 7.44 (m, 4H, *m*- PPh_2), 7.55 (m, 6H, 2H *p*- PPh_2 , 4H, *o*- PPh_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , ppm): δ -7.4 (d, $^3J_{\text{PP}} = 49.3$ Hz, $\text{CH}_2\text{-PPh}_2$), 18.6 (d, $^3J_{\text{PP}} = 49.3$ Hz, $\text{P}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , ppm): δ -23.3 , -16.9 , -15.2 , -13.5 , -7.2 , 1.8. IR (ATR, ν/cm^{-1}): 3056m, 2908w, 2570s $\nu(\text{B-H})$, 1481w, 1430w, 1376vs $\nu(\text{P}=\text{N})$, 1112m, 1027m, 1010w, 982w, 750w, 724m, 690s, 524m, 506m. MS (EI, m/z): 555 (44.4%) $[\text{L}]^+$, 478 (26.4%) $[\text{L-Ph}]^+$, 370 (9.8%) $[\text{L-PPh}_2]^+$, 342 (70.1%) $[\text{L-CH}_2\text{CH}_2\text{PPh}_2]^+$, 262 (83.0%) $[\text{PPh}_3]^+$, 212 (100.0%) $[\text{CH}_2\text{CH}_2\text{PPh}_2\text{-H}]^+$. EA (%): calculated for $\text{C}_{28}\text{H}_{35}\text{B}_{10}\text{NP}_2$: C 60.5, H 6.3, N 2.5; found: C 60.4, H 5.8, N 2.4.

Synthesis of L5. Reaction mixture: 1-Me-3-NH₂-1,2-*ortho*-carborane (0.20 g, 1.15 mmol); *tert*-butyl nitrite (0.22 mL, 1.84 mmol); trimethylsilyl azide (0.24 mL, 1.84 mmol) and *dppe* (0.84 g, 2.11 mmol). Yield: 0.40 g (61%); white solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 1.02–2.80 (bm, 10H, BH), 1.94 (s, 3H, $\text{C}_{\text{cage}}\text{-CH}_3$), 2.24 (m, 2H, $\text{CH}_2\text{-P(III)}$), 2.41 (m, 2H, $\text{CH}_2\text{-P(V)}$), 2.89 (bs, 1H, $\text{C}_{\text{cage}}\text{-H}$), 7.33 (m, 10H, PPh_2), 7.45 (m, 4H, *m*- PPh_2), 7.54 (m, 2H, *p*- PPh_2), 7.59 (m, 4H, *o*- PPh_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , ppm): δ -13.5 (d, $^3J_{\text{PP}} = 48.1$ Hz, $\text{CH}_2\text{-PPh}_2$), 12.6 (d, $^3J_{\text{PP}} = 48.1$ Hz, $\text{P}=\text{N}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , ppm): δ -22.3 , -17.5 , -15.0 , -13.6 , -12.9 , -10.5 , -7.9 , 2.1. IR (ATR, ν/cm^{-1}) 3053 m, 2576vs $\nu(\text{B-H})$, 1584w, 1420vs, 1406vs $\nu(\text{P}=\text{N})$, 1163w, 1111m, 1093m, 1066w,



870w, 737m, 714m, 694s, 527m, 514w, 477w. **MS** (EI, m/z): 569 (6.5%) $[L]^+$, 492 (2.7%) $[L-Ph]^+$, 384 (1.8%) $[L-PPh_2]^+$, 356 (39.4%) $[L-CH_2CH_2PPh_2]^+$, 262 (31.1%) $[PPh_3]^+$, 212 (100.0%) $[CH_2CH_2PPh_2-H]^+$. **EA** (%): calculated for $C_{29}H_{37}B_{10}NP_2$: C 61.1, H 6.5, N 2.5; found: C 60.3, H 6.3, N 2.6.

Synthesis of L6. The non-carboranyl derivative **L6** was obtained following the same procedure used for the preparation of the B3-carboranyl derivatives, starting from 2-phenylaniline. Reaction mixture: 2-phenylaniline (0.30 g, 1.77 mmol), *tert*-butyl nitrite (0.25 mL, 2.12 mmol), trimethylsilyl azide (0.28 mL, 2.12 mmol) and *dppe* (1.06 g, 2.65 mmol). Purification: silica column chromatography (80:20, hexane: ethyl acetate) Yield: 0.45 g (45%); white solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 1.95–2.00 (m, 2H, P- CH_2-CH_2-P), 2.27–2.33 (m, 2H, P- CH_2-CH_2-P), 6.34–6.36 (m, 1H, HAr), 6.69–6.71 (m, 1H, HAr), 6.79–6.82 (m, 1H, HAr), 7.10–7.13 (m, 4H, *m*-PPh₂), 7.16–7.19 (m, 6H, 4H *m*-PPh₂ + 2H *m*-Ph), 7.21–7.22 (m, 2H, 1H *p*-Ph + 1H), 7.24–7.27 (m, 2H, *p*-PPh₂), 7.28–7.32 (m, 4H, *o*-PPh₂), 7.38–7.41 (m, 2H, *p*-PPh₂), 7.49–7.53 (m, 4H, *o*-PPh₂), 7.64–7.66 (m, 2H, *o*-Ph); **$^{31}P\{^1H\}$ NMR** (202 MHz, $CDCl_3$, ppm): δ -14.4 (d, $^3J_{PP} = 47.1$ Hz, CH_2-PPh_2), 3.1 (d, $^3J_{PP} = 47.1$ Hz, P=N). **IR** (ATR, ν/cm^{-1}): 3047m, 3014w, 1739m, 1583m, 1471s, 1427s $\nu(P=N)$, 1311vs, 1263m, 1241m, 1164m, 1112s, 1059m, 1034m, 1003w, 871w, 800w, 755m, 735m, 719s, 692s, 560w, 514m, 492w. **MS** (EI, m/z): 565 (11.5%) $[M]^+$, 488 (28.3%) $[M-Ph]^+$, 412 (3.0%) $[M-PPh_2]^+$, 380 (2.5%) $[M-PPh_2]^+$, 352 (100.0%) $[M-CH_2CH_2PPh_2]^+$, 262 (7.3%) $[PPh_3]^+$. **EA** (%): calculated for $C_{38}H_{33}NP_2$: C 80.7, H 5.8, N 2.5; found: C 81.0, H 6.1, N 2.4.

Synthesis of the palladium complexes, Pd1–Pd6

To a solution of the metal precursor bis(benzonitrile)palladium(II) chloride, *cis*-[PdCl₂(PhCN)₂] in dry acetonitrile (15 mL) was added dropwise a solution of ligand in dry dichloromethane (10 mL). The reaction mixture was stirred overnight (16 hours) at room temperature. The mixture was concentrated to half of its volume under reduced pressure. Commercial hexane (5 mL) was added to the solution, precipitating a yellow solid. The solid was filtered, washed with diethyl ether and dried under vacuum.

Synthesis of Pd1. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.10 g, 0.27 mmol); ligand **L1** (0.15 g, 0.27 mmol). Yield: 0.047 g (24%), yellow solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 1.10–3.00 (bm, 10H, BH), 1.96 (m, 2H, $CH_2-P(III)$), 4.53 (m, 2H, $CH_2-P(V)$), 5.09 (s, 1H, C_{cage-H}), 7.29 (m, 4H, *m*-PPh₂), 7.48 (m, 2H, *p*-PPh₂), 7.62 (m, 8H, 4H *o*-PPh₂, 4H *m*-PPh₂), 7.66 (m, 2H, *p*-PPh₂), 8.10 (m, 4H, *o*-PPh₂). **$^{31}P\{^1H\}$ NMR** (202 MHz, $CDCl_3$, ppm): δ 24.3 (d, $^3J_{PP} = 73.6$ Hz, CH_2-PPh_2), 37.6 (d, $^3J_{PP} = 73.6$ Hz, P=N). **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$, ppm): δ -12.6, -10.4, -8.8, -7.4. **IR** (ATR, ν/cm^{-1}): 3034w, 2565vs $\nu(B-H)$, 2358w, 1484w, 1435s, 1405w, 1229s $\nu(P=N)$, 1179w, 1104s, 1067m, 994m, 887s, 729vs, 689vs, 655m, 511s, 484s. **MS** (MALDI, m/z): 697.4 [PdLCl-H], 555.7 [L]. **EA** (%): calculated for $C_{56}H_{70}B_{20}N_2P_4Cl_4Pd_2$: C 45.9, H 4.8, N 1.9; found: C 45.7, H 4.9, N 1.8.

Synthesis of Pd2. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.10 g, 0.27 mmol) and ligand **L2** (0.10 g, 0.18 mmol). Yield: 0.031 g (24%); yellow solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 0.71–2.23 (bm, 10H, BH), 1.92 (s, 3H, $C_{cage-CH_3}$), 2.26 (m, 2H, $CH_2-P(III)$), 2.77 (m, 2H, $CH_2-P(V)$), 7.46 (m, 4H, *m*-PPh₂), 7.49 (m, 2H, *p*-PPh₂), 7.53 (m, 4H, *o*-PPh₂), 7.57 (m, 4H, *m*-PPh₂), 7.61 (m, 2H, *p*-PPh₂), 7.70 (m, 4H, *o*-PPh₂). **$^{31}P\{^1H\}$ NMR** (202 MHz, $CDCl_3$, ppm): δ 10.7 (d, $^3J_{PP} = 56.7$ Hz, P=N), 32.1 (d, $^3J_{PP} = 56.7$ Hz, CH_2-PPh_2). **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$, ppm): δ -12.3, -11.3, -10.5, -9.6, -9.1, -6.2, -5.2. **IR** (ATR, ν/cm^{-1}): 2918w 2849w, 2576m $\nu(B-H)$, 1482w, 1435m. 1331s $\nu(P=N)$, 1173m, 1102m, 1043w, 1026m, 998m, 878w, 733s, 723s, 690vs, 561w, 537s, 509s, 483s, 467s. **MS** (MALDI, m/z): 1494.3 [Pd₂L₂Cl₄], 747.1 [PdLCl₂], 710.2 [PdLCl-H]. **EA** (%): calculated for $C_{58}H_{74}B_{20}N_2P_4Pd_2Cl_4$: C 46.6, H 5.0, N 1.9; found: C 47.3, H 5.2, N 1.8.

Synthesis of Pd3. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.061 g, 0.16 mmol) and ligand **L3** (0.10 g, 0.16 mmol). Yield: 0.027 g (26%); yellow solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 1.00–2.50 (bm, 10H, BH), 2.10 (m, 2H, $CH_2-P(III)$), 2.65 (m, 2H, $CH_2-P(V)$), 7.16 (m, 4H, *m*-PPh₂), 7.28 (m, 2H, *p*-PPh₂), 7.31 (m, 4H, *o*-PPh₂), 7.36 (m, 1H, *p*-Ph), 7.50 (m, 8H, 4H *m*-PPh₂, 2H *o*-Ph, 2H *p*-Ph), 7.59 (m, 2H, *p*-PPh₂), 7.66 (m, 4H, *o*-PPh₂). **$^{31}P\{^1H\}$ NMR** (202 MHz, $CDCl_3$, ppm): δ 9.1 (d, $^3J_{PP} = 56.6$ Hz, P=N), 31.3 (d, $^3J_{PP} = 56.6$ Hz, CH_2-PPh_2). **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$, ppm): δ -13.8, -11.6, -5.7. **IR** (ATR, ν/cm^{-1}): 3057w, 2919m, 2851w, 2579vs $\nu(B-H)$, 1589w, 1484w, 1435s, 1349vs $\nu(P=N)$, 1279m, 1176m, 1115s, 1074m, 1027w, 998w, 872vw, 724s, 689vs, 575w, 527w, 509m, 485m. **MS** (MALDI, m/z): 773.3 [PdLCl-H]. **EA** (%): calculated for $C_{68}H_{78}B_{20}N_2P_4Pd_2Cl_4$: C 50.5, H 4.9, N 1.7; found: C 50.8, H 5.0, N 1.6.

Synthesis of Pd4. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.06 g, 0.14 mmol) and ligand **L4** (0.08 g, 0.14 mmol). Yield: 0.037 g (35%); yellow solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 1.02–2.75 (bm, 10H, BH), 2.14 (m, 2H, $CH_2-P(III)$), 2.61 (m, 2H, $CH_2-P(V)$), 4.38 (bs, 2H, C_{cage-H}), 7.23–7.25 (m, 1H), 7.46 (m, 15H), 7.99 (m, 3H), 8.29 (m, 1H). **$^{31}P\{^1H\}$ NMR** (202 MHz, $CDCl_3$, ppm): δ 16.7 (d, $^3J_{PP} = 15.9$ Hz, CH_2-PPh_2), 28.5 (d, $^3J_{PP} = 15.9$ Hz, P=N). **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$, ppm): δ -17.1, -14.6, -12.0, -5.4, -3.6, -1.4. **IR** (ATR, ν/cm^{-1}): 3037m, 2597s, 2572s $\nu(B-H)$, 1484w, 1435s, 1405w, 1255vs $\nu(P=N)$, 1179m, 1115s, 1104s, 1027m, 975s, 879m, 728vs, 690s, 584w, 518m, 476 m. **MS** (MALDI, m/z): 1430.2 (4.8%) [Pd₂L₂Cl₃-H]⁺, 1396.5 (3.9%) [Pd₂L₂Cl₂-2H]⁺, 697.1 [PdLCl-H], 555.4 [L]. **EA** (%): calculated for $C_{56}H_{70}B_{20}N_2P_4Pd_2Cl_4$: C 45.9, H 4.8, N 1.9; found: C 46.1, H 4.9, N 1.8.

Synthesis of Pd5. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.07 g, 0.18 mmol) and ligand **L5** (0.10 g, 0.18 mmol). Yield: 0.042 g (32%); yellow solid.

1H NMR (300 MHz, $CDCl_3$, ppm): δ 0.92–2.55 (bm, 10H, BH), 2.14 (s, 3H, $C_{cage-CH_3}$), 2.87 (m, 2H, $CH_2-P(III)$), 3.51 (m, 2H, $CH_2-P(V)$), 6.17 (bs, 1H, C_{cage-H}), 7.42 (m, 2H), 7.61 (m, 14H), 7.88 (m, 2H), 8.45 (bm, 2H). **$^{31}P\{^1H\}$ NMR** (202 MHz,



CDCl₃, ppm): δ 15.6 (d, $^3J_{\text{PP}} = 17.5$ Hz, CH₂PPh₂), 28.4 (d, $^3J_{\text{PP}} = 17.5$ Hz, P=N). $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl₃, ppm): δ -21.4, -16.8, -14.2, -12.8, -10.5, -9.6, -7.2, -6.1, -0.8, 2.6. IR (ATR, ν/cm^{-1}): 3052w, 2986vs, 2607s, 2579s $\nu(\text{B-H})$, 2562vs $\nu(\text{B-H})$, 2543s, 1589w, 1485w, 1435s, 1405w, 1336w, 1277m, 1222vs $\nu(\text{P=N})$, 1192m, 1110s, 1100s, 1001m, 975m, 952m, 909w, 862w, 793w, 740m, 719s, 684s, 593w, 551m, 540m, 517w. MS (MALDI, m/z): 711.2 [PdLCl-H]. EA (%): calculated for C₂₉H₃₇B₁₀NP₂PdCl₂: C 46.6, H 5.0, N 1.9; found: C 46.9, H 5.1, N 1.8.

Synthesis of Pd6. Reaction mixture: bis(benzonitrile)palladium(II) chloride (0.10 g, 0.27 mmol) and ligand L6 (0.15 g, 0.27 mmol). Yield: 0.047 g (24%); yellow solid.

^1H NMR (300 MHz, CDCl₃, ppm): δ 2.75 (bm, 2H, CH₂-P(III)), 3.01 (m, 2H, CH₂-P(V)), 6.99 (m, 2H), 7.14 (m, 2H), 7.39 (m, 3H), 7.56 (m, 18H), 7.69 (m, 2H), 8.02 (m, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl₃, ppm): δ 11.9 (bs, CH₂PPh₂), 25.1 (bd, $^3J_{\text{PP}} = 8.3$ Hz, P=N). IR (ATR, ν/cm^{-1}): 3054m, 2966w, 2911vw, 2866vw, 1642vw, 1588w, 1474w, 1435m, 1256w, 1221m $\nu(\text{P=N})$, 1109m, 996m, 922vw, 869w, 824w, 744m, 727s, 703s, 690vs, 672s, 613w, 549m, 533s, 520s, 486s. MS (MALDI, m/z): 742 [PdLCl₂], 706 [PdLCl-H], 670 [PdL-2H]. EA (%): calculated for C₃₈H₃₃NP₂PdCl₂: C 61.4, H 4.4, N 1.8; found: C 61.8, H 4.5, N 1.7.

Author contributions

J. L. R.-R.: experimental work; I. V.-C.: experimental work and manuscript preparation; A. S.-P. research conception, research supervision, single crystal X-ray analysis and manuscript preparation.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: crystallographic details and selected bonds and angles for all crystal structures. NMR and IR spectra for all compounds. See DOI: <https://doi.org/10.1039/d5dt02122g>.

CCDC 2451931–2451937 (L1, Pd1, Pd2, Pd3, Pd4, Pd5 and Pd6) contain the supplementary crystallographic data for this paper.^{85a-g}

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