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Coordinating ability of the iminophosphorane group in *ortho*-carborane derivatives.

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Abstract: The coordinating ability of the nitrogen donor atom of C-carboranyl iminophosphoranes was studied in different ligand systems. The analysis of organotin derivatives of the unsubstituted iminophosphorane **I1** (**$SnMe_3$I1** and **$SnClMe_2$I1**) and the comparison with the non-carboranyl analog (**$SnClMe_2$I3**), reveals the reduced donor capacity of the nitrogen atom by effect of the *closo*-carborane group. In order to promote the coordination of this weak donor atom, new phosphine-iminophosphorane ligands (**IP1** and **IP2**), with an extra -PPh_2 group on the other cage carbon atom, were synthesized and structurally characterized. The analysis of the products formed by reaction of these ligands and the metal precursor *cis*-[$PdCl_2(PhCN)_2$] reveals that the phosphine group promotes the coordination of the iminophosphorane nitrogen atom, yielding (P, N) chelates. However, this coordination mode activates the *closo*-carborane ligands towards deboronation, and the complexes evolve to the *nido* derivatives by effect of polar solvents. The activation is increased by the presence of extra donor groups, like in the tridentate ligand **IP2**, with an extra thioether group. The deboronation by coordination of (P, N) bidentate carboranyl ligands has never been reported, although it has been studied for other ligands, especially for chelating carboranyl diphosphines.

Introduction

Dicarbaboranes are cluster compounds with ten boron and two carbon atoms in an icosahedral arrangement. These bulky molecules have a close shell structure that gives them a remarkable thermal and chemical stability.[1] The thermal stability depends on the relative position of the carbon atoms, as they isomerize from *ortho*- to *meta*- and then to *para*-carborane on heating. This structural stability has been one of the most exploited properties of carboranes, and since the beginning of the development of carborane chemistry these molecules have been incorporated in other materials producing, for example, very robust polymers,[2] hybrid materials,[3] dendrimers[4] and, more recently, thermally stable metal-organic frameworks (MOFs).[5] Apart from their stability and bulkiness, the carborane clusters possess some particular electronic properties, like a σ-aromatic character and an irregular charge distribution, that have also found application in the design of compounds with interesting electronic properties.[6]-[7] The irregular charge distribution is responsible for the different inductive effect of substituted carboranes. The more electronegative carbon atoms make the C-carboranyl substituents electron-withdrawing groups, and due to their adjacent position in the *ortho*-carborane derivatives, the effect is more pronounced for these isomers. On the contrary, B-substituted carboranes show an electron-donating inductive effect, especially those substituted at the antipodal boron atoms. This is reflected in the chemical behavior of the *o*-carborane group, like in the acidity of the hydrogen atoms at the cage carbon atoms (Cc-H)[1] or in the different pK_a values of C- and B-carboranyl-thiols.[7(a)]

The structural and electron-withdrawing electronic properties of *o*-carboranes make them very attractive for ligand design.[8] The accessible functionalization of the *o*-carborane carbon[1] or boron[9] atoms with functional groups bearing donor atoms

has produced different *o*-carborane ligands that have been used for the production of *exo*-metallated carborane complexes with interesting properties and applications.[1a,10] Some *exo*-metallaboranes have found application in material science, for the production of luminescent materials[11] and as building blocks for polymers and macrocycles.[12] Other *exo*-metallaboranes have been used in medicinal chemistry[13] mainly for their hydrophobicity and/or high boron content (for Boron Neutron Capture Therapy). However, the main application for *exo*-metallated carborane derivatives is in the field of catalysis.[10, 14] Although the *o*-carborane moiety usually gets used because of its stability and bulky character,[8,15] the different inductive effects of the *o*-carborane moiety have also been used to modulate the coordinating ability of vicinal sulfur[16] and phosphorous[17] donor atoms in coordination compounds. Thus, a thioether group shows reduced donor ability when connected to a C-*m*-carboranyl moiety, but presents enhanced donor strength when connected to the antipodal boron atoms of *o*- and *m*-carborane groups.[16] It has also been shown that C-carboranyl phosphines present electron-poor character, while B9-*meta*-carboranyl phosphines are extremely electron-rich.[17] These studies have established the dichotomous character of carborane ligands.[8] Following this trend, we have recently studied the possibility of deactivating the donor ability of the nitrogen atom of an iminophosphorane group by attaching it to the cage carbon atom of an *o*-carborane group.[18] These studies contributed to the little explored chemistry of carborane-iminophosphorane derivatives,[19,20] and revealed that the thiolate **L1** [Figure 1(b)] derived from the parent carborane-iminophosphorane **I1** [Figure 1(a)] fails to promote the expected (S, N) chelation to palladium(II) or platinum(II) but, instead, evolves to different final products depending on the metal (Pd…H-B pseudo-agostic interaction

or Pt-B metalation). Thus, compounds with M-N bonds involving carborane-iminophosphorane ligands have not yet been described.

As a continuation of our studies on the coordination ability of carboranyl-iminophosphorane ligands, we now report some organotin compounds of the parent iminophosphorane **I1** [Figure 1(a)], which allow the study of the donor ability of the iminophosphorane nitrogen atom when is not affected by the presence of extra donor groups. To complete these studies, we have also designed the neutral phosphine-iminophosphoranes **IP1** and **IP2** [Figure 1(c)] that present an extra diphenylphosphino group (-PPh_2) on the other cage carbon atom, and should promote (P, N) chelation. In the case of the neutral ligand **IP2**, the extra thioether group should promote (P, N, S) tridentate coordination by chelate effect. Although these carboranyl derivatives are not known, non-carboranyl phosphine-iminophosphoranes are well known ligands that form stable (P, N) chelates with different metals.[21] Some of these hybrid ligands can reversibly change the coordination mode from (P, N) chelate to P-terminal (hemilabile behavior),[22] which explains the variety of applications that these ligands have found in homogeneous catalysis.[21]

Our new studies on carboranyl phosphine-iminophosphoranes also contribute to increase the knowledge on (P, N) carborane hybrid ligands. Although the (P, N) ligands are the most abundant types of non-carboranyl hybrid ligands,[23] in the field of carboranes only three examples of (P, N) donor ligands are known. The phosphine-amino ligand *closo*-1-PPh_2-2-CH_2NMe_2-1,2-$C_2B_{10}H_{10}$ was used to obtain rhodium and iridium complexes that were isolated and used in catalytic hydrogenation reactions;[24] the ligands 1-PR_2-2-(4-^{i}Pr-oxazolin-2-yl)-1,2-$C_2B_{10}H_{10}$, R= Ph, Cy, were also used in rhodium-catalyzed asymmetric hydrogenation processes,[25] although the metal complexes were not isolated; and finally, very recently, a (P, N) bis(phosphane)

derivative of carborane was used to obtain copper(I) and silver(I) complexes.[26] Besides, these few examples, the literature also describes some phosphine-imine and phosphite-imine carborane compounds that could be used as (P, N) chelating ligands, although no attempts have yet been made to obtain their metal complexes.[27] It is interesting to note that none of the literature examples presents both (P, N) donor atoms directly attached to the cage carbon atoms of the *o*-carborane moiety, so the new ligands **IP1** and **IP2** should provide an interesting comparison.

Results and Discussion

Synthesis and characterization of the carborane ligands

The carboranyl-iminophosphorane ligands **I1** and **I2** were obtained as described in the literature.[18] These compounds were used to obtain organotin derivatives (see below) and also as starting materials for the production of potentially bidentate phosphine-iminophosphorane ligands. Thus, the disubstituted carboranyl derivatives **IP1** and **IP2** were obtained by reaction of the carboranyl-lithium derivatives of the iminophosphorane precursors, **I1** and **I2**, with chlorodiphenylphosphine. The lithiated derivatives were prepared *in situ* by reaction of the iminophosphorane precursors and *n*-butyllithium (see Scheme 1). The new phosphine-iminophosphorane compounds, **IP1** and **IP2**, were obtained in very good yields (77% and 84%, respectively) and characterized by elemental analysis, standard spectroscopic techniques and X-ray diffraction analysis.

The disubstituted carboranes **IP1** and **IP2** are less stable compounds than the parent iminophosphoranes **I1** and **I2**.[18] The introduction of the phosphine group on the other cage carbon atom does not alter the stability of the iminophosphorane group, P=N, which is stable towards hydrolysis by dilute acids like HCl, or the stability of the *closo*-carborane cage, which does not show signs of deboronation

after reflux in common organic solvents, including polar alcohols. However, the weak point of the phosphine-iminophosphorane derivatives is the tendency towards aerial oxidation of the phosphine group. The thioether derivative **IP2** seems to be more sensitive and was isolated with a small amount of oxide impurity (after column chromatography). This is surprising, as *o*-carboranyl-phosphines, in contrast to organic phosphines, are usually stable towards oxidation in air or in presence of mild oxidizing agents, due to the electron-withdrawing character of the *o*-carborane group.[28]

The oxide impurity in **IP2** is revealed, for example, by ^{31}P NMR spectroscopy, which is the most informative characterization technique for these compounds in solution (see spectra in Supporting Information). The $^{31}P\{^{1}H\}$ NMR spectrum of the disubstituted thioether derivative **IP2** shows two major signals, due to the iminophosphorane group (3.5 ppm) and to the phosphine group (-0.5 ppm) of the non-oxidized compound **IP2**, along with two minor signals due to the oxidized impurity (7.6 ppm for P=N and 18.7 ppm for P=O). However, the $^{31}P\{^{1}H\}$ NMR spectrum of **IP1** only shows two peaks at 5.6 ppm (P=N) and at -0.7 ppm (phosphine), although it was subject of a similar purification by column chromatography. It is interesting to note that the signals of the iminophosphorane phosphorous atoms of **IP1** and **IP2** are shifted downfield respect to those of the parent iminophosphoranes **I1** (3.1 ppm) and **I2** (0.6 ppm).[18] This trend was also observed for the previously published sulfur derivatives of **I1** and **I2**, although in those cases the downfield shift was more pronounced.[18] It is also interesting to note that the values found for the diphenylphosphine groups (-PPh_2) are very shifted upfield respect to the value found for 1-diphenylphosphino-carborane (25.2 ppm),[29] due to the presence of the iminophosphorane group on the other cage carbon atom.

The value found for the phosphine oxide group in **IP2**, 18.7 ppm, is only slightly lower than the values found in the ^{31}P NMR spectra of other carboranyl-diphenylphosphine oxide derivatives described in the literature, like 1,2-$(OPPh_2)_2$-*closo*-$C_2B_{10}H_{10}$ (23.67 ppm)[28,30] or 1-$OPPh_2$-2-R-*closo*-$C_2B_{10}H_{10}$ [R= Me (19.28 ppm), Ph (19.65 ppm)][28].

The ^1H NMR spectrum of the **IP1** shows signals only in the aromatic region, due to the protons of the triphenyliminophosphorane and diphenylphosphine groups. The spectrum of the thioether derivative **IP2** is similar, showing also the singlet signal of the thioether group (2.09 ppm). The ^1H NMR spectrum of **IP2** also shows minor peaks due to the oxide impurity present in the sample. The $^{11}B\{^1H\}$ NMR spectra of **IP1** and **IP2** are very similar, which indicates that the carborane cage is not affected to a great extent by the substitution by the -SMe group on a phenyl ring of the iminophosphorane moiety. They both display six broad resonances in the range (-2.9)-(-12.2) ppm, which are typical values for *closo*-carborane derivatives.

The analysis of solid samples of **IP1** and **IP2** by IR spectroscopy proves the presence in both compounds of the *closo*-carborane cage and the iminophosphorane group. Both compounds exhibit a very intense ν(B-H) multiple band around 2580 cm^{-1} typical of *closo*-carborane derivatives, almost in the same position as the parent compounds **I1** and **I2**.[18] The presence in both cases of a strong band at 1346 cm^{-1} (**IP1**) and 1332 cm^{-1} (**IP2**), attributable to the ν(PN) stretching frequency, proves the integrity of the iminophosphorane group in the disubstituted compounds. The shift to lower wavenumbers compared to the parent iminophosphoranes **I1** (1393 cm^{-1}) and **I2** (1384 cm^{-1})[18] accounts for a slight weakening of the P=N bond after functionalization with the diphenylphosphine group.

Elemental analysis and mass spectrometry (electronic impact) also confirmed the stoichiometries of the ligands **IP1** and **IP2** (see the Experimental Section). The crystal structures of these two compounds were studied by single crystal X-ray analysis.

Crystal structures of the iminophosphorane-phosphine derivatives IP1 and IP2

Both crystals were obtained by slow evaporation of solutions of the compounds in a mixture of dichloromethane and hexane. The crystallographic data can be found in Table 1. Selected bond lengths and angles for these compounds are collected in Table 2. The crystal structure of **IP2** contains two molecules of ligand per asymmetric unit, so the structural parameters appear twice. The x-ray analysis show that both compounds present distorted icosahedral carborane moieties substituted on the cage carbon atoms with a diphenylphosphino group and a triphenyliminophosphorane group (**IP1**, Figure 2) or a (2-SMe-phenyl)diphenyliminophosphorane group (**IP2**, Figure 3). In the case of compound **IP2**, the phosphorous atoms of the -PPh_2 groups of both molecules in the asymmetric unit are oxidized to a different extent, 15% and 50% (see Experimental Section).

The structural parameters that involve the cage carbon atoms are very interesting, as they reflect the interaction with the directly attached donor atoms. It is known that donor atoms on a cage carbon atom of an *o*-carborane group can engage in *exo* Cc-X π-bonding (X: donor atom), which leads to the lengthening of the Cc-Cc bond and to the shortening of the Cc-X bond, compared to unsubstituted carboranes.[31] Thus, the Cc-Cc values found for **IP1**, 1.785(2) Å, and for **IP2**, 1.828(3) (P=O 15%) Å and 1.776(3) (P=O 50%) Å, are all longer than the Cc-Cc distance reported in the literature for the unsubstituted iminophosphorane **I2**, 1.688(3) Å,[32] while the Cc-N distances [1.369(2) Å for **IP1** and 1.355(3) (P=O 15%)

and 1.368(3) (P=O 50%) Å for **IP2**] are all shorter than the value reported for the unsubstituted precursors **I1**, 1.373(3) Å, and **I2**, 1.368(2) Å.[18] The Cc-Cc and Cc-N distances found for **IP2** seem to be affected by the extent of oxidation of the phosphine phosphorous atom, as the phosphine oxide does not engage in *exo* π-bonding with the cage carbon atom, which results in shorter Cc-Cc bonds and longer Cc-N bonds. The literature also provides examples of shorter Cc-Cc distances for carboranyl phosphine oxide derivatives compared to analogous carboranyl phosphines. Thus, the Cc-Cc distance found for the literature compound 1-$OPPh_2$-2-Me-*closo*-$C_2B_{10}H_{10}$, 1.677(2) Å,[28] is shorter than the one found for the phosphine analog 1-PPh_2-2-Me-*closo*-$C_2B_{10}H_{10}$, 1.702(6) Å, as expected.[33]

The Cc-Cc values found for **IP1** and **IP2** are shorter than the literature values for the sulfur derivatives of carboranyl-iminophosphoranes (thiol, disulfide and trisulfide), in the range 1.832(5)-1.889(4) Å,[18] which indicates that the sulfur donor groups contribute more than the diphenylphosphino group to the lengthening of the Cc-Cc distance. This result had already been suggested by Teixidor et al through the structural analysis of a (P, S) carboranyl hybrid ligand, 1-PPh_2-2-S^{i}Pr-1,2-$C_2B_{10}H_{10}$.[34] The diphenylphosphino group of the literature ligand also shows the same pattern of P-C distances, i.e. longer for P-Cc bonds [range 1.858(2)-1.8758(17) Å for **IP1** and **IP2**] than for P-C_{Ph} bonds [range 1.817(2)-1.8331(18) Å for **IP1** and **IP2**].

The P=N bond distances of the iminophosphorane group [1.5800(15) Å for **IP1** and 1.5815(18) and 1.5812(18) Å for **IP2**] are very similar to the values found in the literature for other non-coordinated carboranyl iminophosphoranes,[18,20] and also similar to the values found for other free non-carboranyl triphenyliminophosphorane

derivatives [mean value of 1.586 Å, 170 structures, Cambridge Structural Database (Version 5.38, November 2016)].

Synthesis of metal complexes

Organotin derivatives of I1

The parent iminophosphorane **I1** presents an unsubstituted C-carboranyl group connected to the iminophosphorane nitrogen atom, with no extra donor atoms. The acidic Cc-H position can be used to obtain organometallic compounds, following a similar procedure as used for the preparation of the disubstituted compounds **IP1** and **IP2**. In the final products, the metal atom will be forced to be in the vicinity of the potentially donating nitrogen atom, which can result in an M-N interaction. We decided to obtain organotin derivatives of **I1**, as the final compounds were expected to be stable molecular compounds with good solubility in common organic solvents. These properties enable not only a structural characterization of the products in solid state by x-ray crystallography, but also a detailed characterization of the products in solution by NMR spectroscopy. The NMR studies are especially interesting for organotin derivatives, as they can be related to the coordination geometry around the metal atom (see below). Thus, these studies should give some insight on the coordinating ability of the iminophosphorane nitrogen atom when is not affected by the existence of extra donor atoms in the structure of the carboranyl ligand. Although the coordination of the iminophosphorane nitrogen atom to the tin atom is not geometrically favored in the final products, as it leads to the formation of a four-membered chelate ring, the availability of different tin precursors with different electrophilicities enables the study of the Sn…N interaction under different forcing conditions. Thus, we have synthesized derivatives of **I1** with -$SnMe_3$ and -$SnClMe_2$ organotin centers. The electronegative chlorine substituent on the tin atom enhances

its electrophilicity and promotes the coordination of the nitrogen atom. This strategy has already been described in the literature to promote the (Cc, N) coordination of an *o*-carboranylamino ligand to a tin metal center.[35]

The organotin derivatives **$SnMe_3I1$** and **SnClMe2I1** were easily prepared by reaction of the tin precursors, $SnMe_3Cl$ or $SnMe_2Cl_2$, and the lithiated derivative of **I1**, obtained *in situ* by reaction of **I1** and *n*-butyllithium in diethyl ether at -10ºC (see Scheme 1). After purification, the final tin compounds were obtained in good yields (62% and 50%, respectively) and characterized by IR spectroscopy, ^{1}H, ^{11}B, ^{31}P and ^{119}Sn NMR spectroscopy, mass spectrometry, elemental analysis and X-ray diffraction analysis. Elemental analysis and mass spectrometry confirmed the expected stoichiometries of the tin compounds (see the Experimental Section). The rest of the characterization techniques, not only confirmed the formation of the expected organotin compounds, but also gave information about the coordination environment of the tin atom, both in solution and solid state.

Although the literature reports several organotin(IV) compounds with nitrogen donor atoms, the information about iminophosphorane-tin(IV) compounds is very scarce. Due to the lack of appropriate bibliographic data for comparison, we decided to obtain the non-carboranyl analog of **$SnClMe_2I1$**. The organic analog, **$SnClMe_2I3$**, was obtained by reaction of the tin precursor $SnMe_2Cl_2$ with the lithiated derivative of the precursor N-(2-bromophenyl)-triphenyliminophosphorane (**I3-Br**), as depicted in Scheme 2 (experimental details in Supporting Information). This new tin compound was characterized by elemental analysis and standard spectroscopic techniques, and it will be used to trace the effect of the carboranyl group on the coordination ability of the nitrogen donor atom.

The IR spectra of the carboranyl-organotin complexes **$SnMe_3I1$** and **$SnClMe_2I1$** show the typical strong bands associated with *closo*-carborane cages [ν(B-H): 2613-2546 cm^{-1} (**$SnMe_3I1$**) and 2608-2561 cm^{-1} (**$SnClMe_2I1$**)]. These bands appear as multiple bands, like in the IR spectrum of the free ligand **I1**, and almost at the same position.[18] The spectra also show the intense band associated with the P=N stretching frequencies at 1327 cm^{-1} (**$SnMe_3I1$**) and at 1276 cm^{-1} (**$SnClMe_2I1$**). These values are both of them smaller than the value found for the free ligand (1393 cm^{-1}),[18] although to a different extent. The protonation[36] or the coordination to metal atoms[37] of the iminophosphorane nitrogen atom weakens the P-N bond, which shifts the ν(PN) stretching frequency to lower wavenumbers. However, the shift for the trimethyltin derivative ($\Delta\nu$= -66 cm^{-1}) is smaller than for **$SnClMe_2I1$** ($\Delta\nu$= -117 cm^{-1}), which indicates that the Sn…N interaction is stronger for the more electrophilic -$SnClMe_2$ group, as expected. The stronger interaction found in the solid state for **$SnClMe_2I1$** was confirmed by x-ray crystallography (see below). In the case of the organic analogue **$SnClMe_2I3$**, the value of the ν(PN) stretching frequency, 1205 cm^{-1}, is more shifted to lower wavenumbers from the value found for the organic precursor **I3-Br** (1336 cm^{-1}), $\Delta\nu$= -131 cm^{-1}. These results indicate stronger Sn…N interactions for the non-carboranyl derivatives in the solid state, which support the idea that a C-carboranyl group deactivates the donor ability of the iminophosphorane nitrogen atom. However, none of these ν(PN) values correspond to covalent Sn-N bonds, as a further shift is expected. Typical ν(PN) values reflecting a M-N covalent bond are provided by the palladium complexes described later on, in the range 1162-1181 cm^{-1} (see below).

The characterization in solution using different NMR spectroscopy techniques also provides interesting information about the coordination sphere of the tin centers.

The $^{11}B\{^{1}H\}$ NMR spectra of the carboranyl organotin derivatives are similar to the spectrum of the free ligand **I1**,[18] displaying broad resonances in a similar range (-3.7)-(-12.3) ppm, typical of *closo*-derivatives. However, the spectrum of the trimethyltin derivative presents four broad signals and the chlorodimethyltin derivative presents five signals, indicating lower symmetry, perhaps due to the stronger Sn…N interaction. The $^{31}P\{^{1}H\}$ NMR spectra of the organotin derivatives present one signal due to the iminophosphorane group. Each spectrum presents a singlet signal, at 4.6 ppm (**$SnMe_3$I1**) and at 11.8 ppm (**$SnClMe_2$I1**), shifted downfield respect to the free ligand **I1** (3.1 ppm)[18]. The small shift found, accounts for a weak Sn…N interaction, especially in the case of the compound with the less electrophilic -$SnMe_3$ group. A comparison with the value found for the non-carboranyl analog **$SnClMe_2$I3** (17.5 ppm), more shifted respect to the organic precursor **I3-Br** (0.68 ppm), indicates again that the carboranyl derivatives show weaker Sn…N interactions. In any case, the shifts found for all the organotin compounds imply only weak Sn…N intramolecular interactions of different strength, as a proper M-N bond causes higher shifts, from 30 to 60 ppm, depending on the metal and its coordination geometry, as described in the literature for other cyclometalated iminophosphorane complexes.[38]

The ^{1}H NMR spectra of **$SnMe_3$I1** and **$SnClMe_2$I1** confirmed the formation of the desired organotin complexes by the disappearance of the Cc-H band found in the spectrum of the free ligand **I1** (3.82 ppm),[18] and by the appearance of a singlet signal due to the methyl groups on the tin atom (at 0.34 ppm for **$SnMe_3$I1** and at 0.77 ppm for **$SnClMe_2$I1**). The comparison non-carboranyl derivative also show the methyl groups as singlet signals at 0.08 ppm (**$SnClMe_2$I3**), slightly shifted upfield respect to the carboranyl analogs due to the higher electron-withdrawing character of

the carboranyl group compared to the phenyl one. The ^{1}H NMR spectra of methyltin(IV) compounds are structurally very informative, as the J coupling constants between the methyl groups and the ^{119}Sn nucleus, $^{1}J(^{119}Sn,^{1}H)$, can be related to the coordination number of the tin center.[39] The values found for the carboranyl compounds, 54 and 64 Hz, respectively, indicate that both compounds present tetrahedral (Td) geometry, although **SnClMe$_2$I1** is in transition to trigonal bipyramidal (TBP) geometry. The values found in the literature for other carboranyl-methyltin derivatives show coupling constants in the range 54.0-58.5 Hz for Td compounds[35,40] and in the range 67.5-101.1 Hz for TBP compounds.[35,41,42] The value found for the non-carboranyl analog **SnClMe$_2$I3** (58.1 Hz) is abnormally low, taking into account the rest of the characterization data. The main evidence for the coordination of the tin atoms in solution was provided by ^{119}Sn NMR spectroscopy.[43] The values found for the carboranyl-tin compounds (23.3 ppm for **SnMe$_3$I1** and 36.5 ppm for **SnClMe$_2$I1**) indicate Td geometry, as the normal range for this geometry is from 200 to -60 ppm.[43] The value found for the comparison non-carboranyl analog **SnClMe$_2$I3**, -21.5 ppm, also indicates Td geometry, although the negative value indicates a higher distortion towards TBP geometry.

In conclusion, the different characterization techniques, in solution and in solid state, indicate that the carboranyl organotin derivatives **SnMe$_3$I1** and **SnClMe$_2$I1** only show a weak Sn…N interaction, that is stronger for the more forcing –SnClMe$_2$ derivative. The comparison with the non-carboranyl analog **SnClMe$_2$I3** shows that the donor ability of the iminophosphorane nitrogen atom is slightly reduced by the effect of the C-carboranyl group.

Crystal structures of the tin complexes, SnMe$_3$I1 and SnClMe$_2$I1

The solid state structures of the tin derivatives **$SnMe_3I1$** and **$SnClMe_2I1$** were studied by single crystal X-ray analysis. Both crystals were obtained by slow evaporation of a solution of the compound in a mixture of diethyl ether and hexane. The crystallographic data can be found in Table 1. Selected bond lengths and angles are collected in Tables 3 and 4, respectively.

The organotin compounds **$SnMe_3I1$** and **$SnClMe_2I1$** present the C-carboranyl-iminophosphorane derivative **I1** functionalized on the other cage carbon atom with trimethyltin or chlorodimethyltin groups, respectively (see Figures 4 and 5). The analysis of the structural parameters (see below), indicates that the geometry around the tin centers should be described as distorted Td, with a weak Sn…N intramolecular interaction involving the iminophosphorane nitrogen atom. As expected, the distortion towards a five-coordinate TBP structure is more pronounced in the case of the chlorodimethyl derivative, **$SnClMe_2I1$**.

The strength of the Sn…N interaction can be estimated through the values of the Sn…N distances: 3.3458(14) Å for **$SnMe_3I1$** and 2.9240(13) Å for **$SnClMe_2I1$**. These distances are too long to be considered covalent bonds but are shorter than the sum of van der Waals radii (3.81 Å), so they should be considered as intramolecular interactions. The distances suggest a stronger interaction for the chlorodimethyl derivative, as expected. Examples of covalent Sn-N bonds can be found in the literature for three trigonal bipyramidal carboranyl-tin compounds with extra amine[35] or oxazoline[41] nitrogen donor groups, with Sn-N distances in the range: 2.503-2.701 Å.

The transition from Td to TBP geometry, by effect of the Sn…N interaction, produces other structural changes that reflect the degree of the interaction. The iminophosphorane group bends towards the tin atom, closing the Cc-Cc-N angle

from the theoretical value of 120º to 113.38(13)º for **$SnMe_3I1$** and to 110.34(12)º for **$SnClMe_2I1$**, and the tin atom also approximates the nitrogen atom, closing the Cc-Cc-Sn angle from the theoretical value of 120º to 118.01(10)º for **$SnMe_3I1$** and to 107.87(9)º for **$SnClMe_2I1$**.

In the case of the chloro-derivative **$SnClMe_2I1$**, the hypothetical Sn-N coordination would produce a distorted trigonal bipyramid with the nitrogen and chlorine atoms at the apical positions and the three carbon donor atoms (cage carbon and the two methyl groups) on the equatorial plane (see Figure 5). In the case of **$SnMe_3I1$**, the methyl group labeled C23 would occupy the other axial position (see Figure 4). The higher distortion towards five coordination of compound **$SnClMe_2I1$** compared to **$SnMe_3I1$** is reflected in equatorial C-Sn-C angles closer to 120º than to 107.5º (see Table 4) and in a smaller deviation of the tin atom from the equatorial plane (C2, C21, C22); 0.6499(12) Å for **$SnMe_3I1$** and 0.3541(10) Å for **$SnClMe_2I1$**. The literature reports the crystal structure of one carboranyl-trimethyltin derivative, [$SnMe_3$(1-pyridine-carborane)],[40] and several carboranyl-halodimethyltin derivatives (halogen: Cl, Br),[35,41,42] all of them bearing additional nitrogen (amine[35], oxazoline[41]), phosphorous (phosphine)[42] or oxygen (ether)[41] donor groups on the carboranyl moiety. All these halodimethyl derivatives present the halogen atom and the extra donor atom on the axial positions of the trigonal bipyramid, as described for **$SnClMe_2I1$**.

The Sn-Cl bond distance found in **$SnClMe_2I1$**, 2.3884(4) Å, provides an indirect evidence of the weakness of the Sn…N interaction is *trans* position, as it is shorter than the value of 2.458 Å of the Sn-Cl bond distance found in the only carborane derivative with a -$SnClMe_2$ group described in the literature, the five-coordinate compound [$SnClMe_2$(1-Me_2NCH_2-1,2-$C_2B_{10}H_{10}$)].[35]

Finally, the different degree of Sn…N interactions of **$SnMe_3I1$** and **$SnClMe_2I1$** is also shown in some structural parameters of the iminophosphorane-carborane ligand. As mentioned before, the engagement of the donor atom at a cage carbon atom in *exo* π-bonding, leads to the shortening of the Cc-X bond and to the lengthening of the Cc-Cc bond.[31] The coordination of the donor atom to a metal center competes with the *exo* π-bonding, producing the opposite effect; a lengthening of the Cc-X bond and a shortening of the Cc-Cc bond, compared to the free ligand. Thus, the Cc-Cc and Cc-N distances found in **$SnMe_3I1$**, 1.701(2) and 1.387(2) Å respectively, suggest no Sn…N interaction, in comparison to the free ligands [Cc-Cc: 1.688(3) Å for **I2** and Cc-N: 1.373(3) Å (**I1**) and 1.368(2) Å (**I2**)].[18,32] However, the data found for **$SnClMe_2I1$** [Cc-Cc: 1.677(2) Å and Cc-N: 1.4020(19) Å] suggests a weak interaction. Another structural parameter from the ligand that also gets affected by the strength of the Sn…N interaction is the value of the P-N distance of the iminophosphorane group, that increases from the value found in the free ligand **I1**, 1.5711(18) Å,[18] to 1.5755(15) Å for **$SnMe_3I1$** and to 1.5918(14) Å for **$SnClMe_2I1$**.

The Sn-C distances follow the same trend found for the other methyltin derivatives of carborane.[35,40-42] Thus, the Sn-Cc distances [2.1893(16) for **$SnMe_3I1$** and 2.1629(15) Å for **$SnClMe_2I1$**] are longer than the Sn-C(methyl) distances, in the range 2.1134(16)-2.1342(19) Å. All the Sn-C distances are slightly shorter for the chlorodimethyl derivative due to the presence of the more electronegative chlorine atom.

Palladium complexes of IP1 and IP2

The new disubstituted carborane derivatives **IP1** and **IP2** were used to obtained palladium complexes, in order to investigate the donor ability of the phosphine-iminophosphorane system. These ligands present a diphenylphosphino group on the

cage carbon atom adjacent to the iminophosphorane group, and could be used as (P, N) bidentate neutral ligands. *Closo*-carboranyl-phosphines are known to be good ligands towards late transition metals, and several metal complexes have been structurally characterized with both monodentate and bidentate *closo*-carboranyl-phosphines.[44] Thus, the diphenylphosphino group should function as a good first coordinating site for the soft palladium atom and promote the coordination of the iminophosphorane nitrogen atom by the formation of a five-membered ring (chelate effect). In the case of the ligand **IP2** the extra thioether group provides a third coordinating site, enabling it to act as a (P, N, S) tridentate ligand.

The *closo*-disubstituted derivatives **IP1** and **IP2** were treated under inert gas with the palladium precursor *cis*-$[PdCl_2(PhCN)_2]$[45] in a 1:1 molar ratio in dry acetonitrile at room temperature (see Scheme 3). Although both reactions resulted in the formation of yellow solids, the analysis of the samples revealed their different nature. The characterization of the product precipitated from the reaction of ligand **IP1** (**Pd*closo*IP1**) by elemental analysis and standard spectroscopic techniques showed that it was the expected palladium complex depicted in Scheme 3, i.e. the $PdCl_2$ adduct of the chelating neutral *closo*-derivative **IP1**. The characterization by IR spectroscopy is very informative. The strong band at 2609-2565 cm^{-1} (multiple band), that can be assigned to the ν(B-H) stretching frequencies, is typical of *closo*-carborane derivatives, and almost identical to the value found for the free ligand **IP1** (2600-2569 cm^{-1}). The strong band associated with the stretching frequency of the P=N bond, 1181 cm^{-1}, is very shifted to lower wavenumbers respect to the ν(PN) signal found in the free ligand (1346 cm^{-1}), indicating that the iminophosphorane nitrogen atom is coordinated to the palladium metal. These two very important features shown by IR spectroscopy could be confirmed by other techniques. The

$^{11}B\{^{1}H\}$ NMR spectrum of **Pd*closo*IP1** shows a group of five broad signals in the range (-1.4)-(-14.8) ppm, which confirms the presence of the *closo*-carborane cage. The $^{31}P\{^{1}H\}$ NMR spectrum presents two singlet signals at 34.1 ppm (P=N) and 49.1 ppm (phosphine), both of them very shifted downfield by effect of the coordination of both donor groups. This technique confirms that the *closo*-**IP1** ligand is coordinated to the palladium metal as a (P, N) chelating ligand. The ^{1}H NMR spectrum of this compound is less informative, as it only shows signals in the aromatic region, due to the different phenyl rings of the ligand **IP1**. Elemental analysis and mass spectrometry (MALDI-TOF) further confirmed the stoichiometry of the complex (see Experimental Section).

The crystal structure of **Pd*closo*IP1** could not be studied, although its crystallization was tried from different solvents. All attempts to recrystallize the sample resulted in the formation of very fine yellow needles that did not give detectable diffraction of x-ray radiation. During the attempts to crystallize it from a mixture of methanol and dichloromethane, a different compound was obtained, **Pd*nido*IP1**. The analysis by x-ray diffraction of the orange crystals obtained (see below) revealed that the original complex had been deboronated, giving rise to the palladium dimer with *nido*-**IP1** ligands, $[Pd(\mu\text{-}Cl)(\textit{nido}\text{-}\mathbf{IP1}\text{-}\kappa^{2}P,N)]_2$, as depicted in Scheme 3. This product, **Pd*nido*IP1**, was also quantitatively obtained by refluxing the *closo*-derivative **Pd*closo*IP1** in a 1:1 mixture of methanol and dichloromethane (see Experimental Section).

The characterization of the solid precipitated from the reaction of the potentially tridentate ligand **IP2**, including x-ray diffraction studies (see below), showed that in this case the final product was the monomer complex [PdCl(*nido*-**IP2**-κ^{3}P,N,S)] (**Pd*nido*IP2**), depicted in Scheme 3. This product, very similar to the just

presented compound **Pd*nido*IP1**, is the deboronated product of the expected adduct. Apart from x-ray crystallography, both *nido*-derivatives **Pd*nido*IP1** and **Pd*nido*IP2** were also characterized by elemental analysis and standard spectroscopic techniques. The IR spectra of these compounds show strong ν(B-H) bands at 2536 cm^{-1} (**Pd*nido*IP1**) and at 2527 cm^{-1} (**Pd*nido*IP2**), shifted to lower wavenumbers respect to the *closo* precursors **IP1** and **IP2** or to the *closo* palladium complex **Pd*closo*IP1**. These bands indicate that the carborane cages in these two compounds are in the *nido* form. The IR spectra of these *nido* complexes also show the strong band associated with the ν(PN) stretching frequencies at 1162 and 1173 cm^{-1}, respectively. These values are slightly lower than the value found for the complex **Pd*closo*IP1** (1181 cm^{-1}) and are also indicative of the coordination of the nitrogen atom to the palladium atom in both *nido* complexes. Unfortunately, due to the low solubility of the two *nido* complexes in common solvents ($CDCl_3$, CD_2Cl_2, DMSO-d_6), it was not possible to confirm the presence of the *nido*-carborane cage in the complexes using ^{11}B NMR. It was only possible to register the ^{1}H and ^{31}P NMR spectra, with a bad signal to noise ratio (see Supplementary Material). The ^{1}H NMR spectra of these compounds show a complicated aromatic region and a broad absorption at -2.13 ppm (**Pd*nido*IP1**) and -2.85 ppm (**Pd*nido*IP2**), which implies a B-H-B interaction on the C_2B_3 open face of the carborane cage, proving the presence of the *nido*-derivatives in the complexes. The ^{31}P NMR spectra show two singlet signals that correspond to the iminophosphorane group [31.9 ppm for **Pd*nido*IP1** and 37.5 ppm for **Pd*nido*IP2**] and to the phosphine group [74.7 ppm for **Pd*nido*IP1** and 76.8 ppm for **Pd*nido*IP2**]. The degradation of the cage to *nido*-carborane shifts the signals of the phosphine phosphorous atoms downfield respect to the position in **Pd*closo*IP1** (49.1 ppm). The signals due to the iminophosphorane phosphorous atom are not affected by the

degradation and appear at a similar position as in **Pd*closo*IP1** (34.1 ppm). In any case, both signals appear shifted downfield respect to the signals of the free ligands, proving the coordination of the phosphorous and nitrogen donor atoms in both *nido*-complexes.[46] The literature presents several palladium adducts with the neutral diphosphine 1,2-$(PPh_2)_2$-*closo*-carborane, which present signals in ^{31}P NMR at around 80 ppm,[47,48] which are shifted to lower field in the *nido* derivatives.[49] Thus, the values found for the phosphine phosphorous atom of the *nido* derivatives **Pd*nido*IP1** and **Pd*nido*IP2** could be considered normal, but the value found for the *closo* derivative **Pd*closo*IP1** suggests a weaker Pd-P bond. According to the ^{31}P NMR data, the change from *closo* to *nido* results in an increase of the donor capacity of the phosphine group, although the iminophosphorane group seems less affected.

The dimeric nature of the complex **Pd*nido*IP1**, shown by x-ray diffraction (see below), could not be proved by mass spectrometry. The MALDI mass spectrum of **Pd*nido*IP1** only shows the peak associated with half the dimer, form by breakage of the chloro bridges.

The dimeric compound **Pd*nido*IP1** has resulted from the degradation of the adduct **Pd*closo*IP1** in methanol. The deboronation of the neutral *closo*-derivative **IP1** gives rise to the anionic *nido*-derivative, which results in the loss of a chloro ligand from the palladium adduct, and thus, in the dimerization of the complex by formation of the di-μ-chloro bridge, which is a very common motif for palladium(II) complexes.[50] The deboronation of coordinated *closo*-carborane ligands by the action of polar alcohols (methanol, ethanol) has already been described for other chelating *closo*-carboranyl ligands. This mild method of deboronation was firstly observed by Teixidor et al. in 1993 for *closo*-carboranyl-diphosphines,[51] and since then it has been extensively studied for different metal complexes with carboranyl-

diphosphines.[52,53] The use of low nucleophilic solvents (CH_2Cl_2, $CHCl_3$, toluene) can lead to the isolation of the *closo*-adducts, while more nucleophilic ones, like alcohols, promote the degradation to *nido*-derivatives. A pertinent literature example from palladium chemistry is the reaction of the diphosphine 1,2-$(P^iPr_2)_2$-$C_2B_{10}H_{10}$ with $[PdCl_2(COD)]$, COD: 1.5-cyclooctadiene, in dichloromethane, which produces the palladium adduct $[PdCl_2(1,2\text{-}(P^iPr_2)_2\text{-}C_2B_{10}H_{10})]$, which evolves to the dimeric *nido* compound $[Pd(\mu\text{-}Cl)(1,2\text{-}(P^iPr_2)_2\text{-}C_2B_{10}H_{10})]_2$ by reflux in acetonitrile.[47] Although the degradation of *closo*-carboranyl ligands to *nido*-derivatives by complexation to metal atoms has mainly been observed for carboranyl-diphosphines, it has also been described for other bidentate carboranyl ligands with two neutral donor groups on the cage carbon atoms. Thus, a related (O, O) bis(phosphine-oxide) ligand[54,55] and an (S, S) 1,2-bis(thioether)-carboranyl ligand[56] also evolve to the *nido* derivatives during complexation experiments in ethanol. Other known examples are two related (P, S) phosphine-thioether carboranyl ligands, that evolve to the *nido*-derivatives in ethanol by complexation to gold(I) and copper(I) metal centers,[57] or to rhodium atoms.[58]

The deboronation by complexation of a (P, N) bidentate carboranyl ligand has not been previously described. The isolation of the *closo* adduct **Pd*closo*IP1** and its deboronation product **Pd*nido*IP1** indicates that the process that has taken place is analogous to that experienced by *closo*-diphosphines, i.e. the cage gets activated by coordination to the metal center of both donor atoms at the cage carbon atoms. This reasoning leads us to think that the complex **Pd*nido*IP2** has been formed following a similar procedure: the ligand *closo*-**IP2** should form the expected (P, N) adduct in a first step and then suffer deboronation by the solvent (acetonitrile), evolving to the *nido*-derivative. The change from neutral *closo* to anionic *nido* produces the loss of a

chloro ligand, and its position is occupied by the extra thioether group, leading to the monomeric complex **Pd*nido*IP2**. The presence of the extra thioether group seems to further activate the sensitivity of the carborane cage to nucleophilic attack by the solvent, so the *closo*-adduct is not isolated.

The presented results indicate that the *closo* ligands **IP1** and **IP2** indeed coordinate the palladium atom as (P, N) chelating ligands in a first step. This means that the combination of the phosphine group with the iminophosphorane group at both carbon atoms of the carborane cage activates the donor ability of the iminophosphorane nitrogen atom. The tin complexes presented in the first part of this paper indicate that the iminophosphorane nitrogen atom, when is not affected by the presence of other donor atoms, presents reduced donor ability compared to non-carboranyl organic ligands, by effect of the electron-withdrawing C-carboranyl group. Thus, the use of the extra phosphine group seems to be a good way for promoting Pd-N bonds, although the (P, N) chelation of these ligands also promotes the evolution to the *nido*-derivatives. It is interesting to remember that our previous investigations on iminophosphorane-carborane ligands showed how the combination of the iminophosphorane group with an anionic thiolate group on the other cage carbon atom is not a good way for promoting Pd-N interactions, as those potential (S. N) ligands do not promote chelation.[18]

The characterization of the palladium complexes presented in this paper (see before) indicates that *closo*-**IP1** is less donating than the anionic *nido*-**IP1** ligand. However, the gain in donor strength is limited, and the final *nido*-ligands present similar donating abilities as non-carboranyl analogs. Although this was suggested by some characterization techniques, it is made clear by the x-ray analysis of the crystal structures of the *nido*-derivatives **Pd*nido*IP1** and **Pd*nido*IP1**, and the comparison

with the structural parameters of non-carboranyl palladium complexes (see below). The increase of donor strength experienced by donor atoms at the cage carbon atoms of deboronated *o*-carborane is an effect of the reduced electron-withdrawing character of the *nido*-carborane cage, and has already been exploited for increasing the donor capacity of bis(thioether)-carboranyl ligands.[59]

Crystal structures of the palladium complexes Pd*nido*IP1 and Pd*nido*IP2

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in chloroform (**Pd*nido*IP1**) or in a mixture of dichloromethane and hexane (**Pd*nido*IP2**). The crystallographic data can be found in Table 1. Selected bond lengths and angles for these compounds are collected in Tables 5 and 6, respectively.

Compound **Pd*nido*IP1** (Figure 6) is a neutral dinuclear palladium(II) complex with a di-μ-chloro bridge and two equivalent ***nido*-IP1** ligands. This compound presents a two-fold rotation axis that is perpendicular to both middle points of the lines than join the two metal atoms and two chlorine atoms [symmetry operation #1: -x+3/2, -y, z]. The equivalent anionic *nido*-carborane ligands chelate the metal atom through their nitrogen and (phosphine) phosphorous donor atoms, forming five-membered chelate rings. Each palladium atom completes its distorted square planar geometry with two chlorine ligands that bridge the two metal atoms, forming a [(μ-$Cl)_2Pd_2$] four-membered ring. This central ring is not planar, as the two $PdCl_2$ units form and angle of 47.62(4)º. Both (P, N) chelating ligands are disposed *anti* to each other, around the central Pd_2Cl_2 ring, as imposed by the two-rotation axis. The main sources of distortion with respect to the ideal square planar geometry are the formation of the rings: the (P, N) chelate ring with the *nido*-**IP1** ligand [P-Pd-N: 79.15(12)º] and the central [(μ-$Cl)_2Pd_2$] ring [Cl-Pd-$Cl^{\#1}$: 84.45(5)º], both of them

forcing *cis* angles lower than 90º. The simultaneous formation of the two opposed rings affects the planarity of the coordination sphere of the palladium atom (rms: 0.1521 Å), as the N-Pd-P plane is rotated 13.89(11)º respect to the Cl-Pd-Cl$^{\#1}$ plane.

Compound **Pd*nido*IP2** (Figure 7) is a neutral monomeric palladium(II) complex. In this case, the palladium atom is coordinated to a terminal chlorine atom and to the nitrogen, (phosphine) phosphorous and (thioether) sulfur donor atoms of the *nido* derivative of the ligand **IP2**, that behaves as an anionic (P, N, S) tridentate chelating ligand. The chlorine atom is located *trans* to the nitrogen donor atom. The (P, N) coordination forms a five-membered ring while the (N, S) coordination forms a six-membered ring. These rings are the main sources of distortion respect to the ideal square planar geometry, forcing low *cis* angles [(P, N) chelate angle of 81.50(4)º and (N, S) chelate angle of 86.64(4)º]. However, the simultaneous formation of the two adjacent chelate rings does not affect the planarity of the coordination sphere of the palladium atom (rms: 0.0326 Å).

In both complexes, the five-membered (P, N) chelate rings have an envelope disposition: the N-Cc-Cc-P carborane fragment is planar [rms: 0.0036 Å for **Pd*nido*IP1** and 0.0324 Å for **Pd*nido*IP2**] and forms and angle of 40.1(2)º (**Pd*nido*IP1**) and 32.53(7)º (**Pd*nido*IP2**) with the N-Pd-P plane.

The bond lengths that involve the metal atom are very interesting, as they reflect the coordinating abilities of the donor atoms. The iminophosphorane nitrogen atom is located in both palladium complexes *trans* to a chlorine atom, which modulates the value of the Pd-N bond distance (*trans* influence). The values of the Pd-Cl bond distances depend on the coordinating mode of the ligand (terminal or bridging). In the case of the monomeric complex **Pd*nido*IP2**, the terminal Pd-Cl bond [2.2834(5) Å] and the Pd-N bond [2.0447(13) Å] present values that are similar

to those found for other palladium complexes with a terminal Pd-Cl bond *trans* to a non-carboranyl iminophosphorane ligand (Pd-N) deposited in the Cambridge Structural Database (37 structures, CCDC Version 5.38, November 2016). In the literature examples, the mean values found for the Pd-Cl bonds, 2.303 Å, and for the Pd-N bonds, 2.062 Å, are only slightly longer than those found for **Pd*nido*IP2**.

The dimeric complex **Pd*nido*IP1** presents an asymmetric chloro bridge, which is a reflection of the higher *trans* influence of the phosphine group compared to the iminophosphorane one. Thus, the Pd-Cl bond distance *trans* to the phosphine phosphorous atom is longer, 2.4783(13) Å, and the Pd-Cl bond distance *trans* to the iminophosphorane nitrogen atom is shorter, 2.3213(13) Å. The Pd-N bond distance is 2.072(4) Å. The literature shows five related structures with non-carboranyl iminophosphorane ligands.[60] All the literature examples are palladium dimers with a central asymmetric [$(\mu\text{-Cl})_2Pd_2$] ring and metallated iminophosphorane ligands that act as (N, C) chelating ligands. In these structures, the mean values of the Pd-Cl and Pd-N bond distances *trans* to each other (2.333 Å and 2.050 Å respectively) are very similar to those discussed for the dimeric complex **Pd*nido*IP1**. In conclusion, the analysis of the bond distances involving the palladium atom suggests that the nitrogen donor atom of the iminophosphorane group attached to a *nido*-carborane cage has similar donor strength as an organic, non-carboranyl, iminophosphorane ligand.

The Cc-Cc distances of the *nido*-carborane cages [1.566(7) Å for **Pd*nido*IP1** and 1.569(2) Å for **Pd*nido*IP2**] are much shorter than those found in the free *closo* derivatives **IP1** [1.785(2) Å] and **IP2** [1.828(3) and 1.776(3) Å]. This is the result of two Cc-Cc shortening effects: the evolution from *closo* to *nido* and the coordination to the palladium metal. Although there are no examples of carborane derivatives with

phosphorous and nitrogen donor atoms at the cage carbon atoms, this is made clear by comparison with published data for carboranyl-diphosphines. Thus, the free ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$, presents a Cc-Cc distance of 1.697(4)[61(a)]-1.722(4)[61(b)] Å, that is reduced to 1.61(2) Å by evolution to the *nido* derivative.[55] The coordination of the *nido*-derivative to palladium in the dimeric complex [Pd(μ-Cl)(1,2-$(PPh_2)_2$-*nido*-carborane]$_2$, similar to **Pd*nido*IP1**, further reduces the Cc-Cc distance to 1.556(13)[62(a)]-1.570(6)[62(b)] Å. Another effect of the evolution from *closo* to *nido* is the elongation of the Cc-N and the Cc-P distances.

As mentioned before, the coordination of the iminophosphorane nitrogen atom to the metal weakens the P-N bond,[37] which is reflected in longer P-N distances [1.611(5) Å for **Pd*nido*IP1** and 1.6100(14) Å for **Pd*nido*IP2**] compared to the free ligands [range 1.5800(15)-1.5815(18) Å]. However, the P-N values in the complexes are very similar to those found for $PdCl_2$ adducts of neutral non-carboranyl phosphine-iminophosphoranes that form five-membered chelate rings with the palladium atom, in the range 1.601-1.627 Å,[63] suggesting again a similar strength of the Pd-N bond.

Conclusions

As a continuation of our investigations on carboranyl-iminophosphoranes, we have isolated and characterized organotin derivatives of 1-triphenyliminophosphorane-*o*-carborane **I1** (**$SnMe_3$I1** and **$SnClMe_2$I1**) in which the nitrogen atom directly attached to the *o*-carborane cage, not affected by the presence of other donor atoms, is forced to interact with the metal atom. These studies show that the nitrogen atom has a tendency to interact with the tin atom, and that the Sn…N intramolecular interactions can be strengthened by increasing the electrophilicity of the tin atom. The comparison with the non-carboranyl analog **$SnClMe_2$I3**, with stronger Sn…N

interactions, indicates that the reduction of donor capacity is a genuine effect of the electron-withdrawing character of the carborane cage.

In order to exploit the weak tendency of the carboranyl-iminophosphorane group towards coordination to metal atoms, it was combined with a diphenylphosphino group, -PPh_2, on the other cage carbon atom, producing new phosphine-iminophosphorane compounds (**IP1** and **IP2**) that are potential (P, N) chelating ligands. In the case of **IP2**, the presence of an extra thioether group, -SMe, on a phenyl ring of the iminophosphorane group makes it a potential (P, N, S) chelating ligand. The isolation of the $PdCl_2$ adduct of the neutral ligand *closo*-**IP1**, **Pd*closo*IP1**, shows that the phosphine group can promote the coordination of the nitrogen atom to the palladium atom, forming (P, N) chelates. The evolution of this complex to the dimeric complex **Pd*nido*IP1**, in which the neutral ligand *closo*-**IP1** has evolved to the anionic ligand *nido*-**IP1** by effect of methanol, proves that the (P, N) coordination of the phosphine-iminophosphorane ligand activates the carborane cage towards deboronation. The deboronation of coordinated carboranyl ligands has already been observed for other neutral donor groups, especially diphosphines, but has never been observed for (P, N) carboranyl hybrid ligands. In the case of the tridentate ligand **IP2**, the presence of the extra –SMe group further activates the deboronation of the carborane cage, and the *closo* adduct is not isolated. However, the complexes isolated with ligand **IP1** suggest that the complex **Pd*nido*IP2** should be an evolution of the expected $PdCl_2$ adduct with *closo*-**IP2**, by effect of the solvent. It is also interesting to note that this ligand **IP2** shows a tendency towards aerial oxidation, which is not common for carboranyl-phosphines.

It is interesting to remember that the only studies found in the literature on the coordination chemistry of carboranyl-iminophosphorane ligands, recently published

by our research group,[14] indicate that the combination of the iminophosphorane group with a thiolate group on the other cage carbon atom does not produce (N, S) chelating ligands, as the donor capacity of the iminophosphorane nitrogen atom is completely deactivated. The new results show that the use of donor groups less involved in *exo* π-bonding with the carborane cage, like a phosphine group, can promote the coordination of the iminophosphorane nitrogen atom. The analysis of the new palladium complexes reveals that the (P, N) coordination of the *closo* phosphine-iminophosphorane ligand is rather weak, but gets reinforced by the evolution to the *nido* derivative, which shows a similar strength in the interaction with the palladium metal as other non-carboranyl phosphine-iminophosphorane analogs.

Experimental section

Instrumentation. Elemental analysis were performed using a Thermo Finnigan Flash 1112 microanalyzer. IR spectra for **IP1**, **$SnMe_3I1$** and **$SnClMe_2I1$** were recorded as KBr mulls with a BrukerIFS-66V spectrophotometer. ATR-IR spectra for the rest of the compounds were recorded on a high-resolution spectrometer FT-IR Perkin Elmer Spectrum Two. The ^{1}H NMR and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer. The ^{11}B NMR and ^{119}Sn NMR spectra were recorded on a Varian Inova 500. All NMR spectra were recorded in $CDCl_3$ solutions at 25ºC. Chemical shift values for ^{1}H NMR were referenced to $SiMe_4$ (TMS), those for ^{31}P were referenced to 85% H_3PO_4, those for $^{11}B\{^{1}H\}$ NMR were referenced to external $BF_3{\cdot}OEt_2$ and those for ^{119}Sn NMR were referenced to $SnMe_4$. 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 organic derivatives were determined on a Micromass Autospec instrument (positive electronic impact). Mass spectra of the metal complexes were determined on a Bruker Microtof instrument in

the ESI+ mode, except in the case of compounds **SnClMe$_2$I1**, **Pd*closo*IP1** and **Pd*nido*IP1** for which the MALDI-TOF mass spectra were recorded in negative-ion mode on a Bruker Autoflex instrument.

Materials. All reactions were performed under atmosphere of dinitrogen employing standard Schlenk techniques. Toluene and diethyl ether were purchased from Merck and distilled from sodium benzophenone previously to use. Acetonitrile was purchased from Merck and distilled from P_4O_{10} previously to use. Commercial grade diethyl ether, ethyl acetate, hexane, chloroform and dichloromethane were used without further purification. Demineralized water was used in the aqueous stages of synthesis. The iminophosphorane derivatives **I1** and **I2**[18] and the metal precursor $[PdCl_2(PhCN)_2]$[45] were synthesized according to the literature. Compounds chlorodiphenylphosphine, 2-bromoaniline, triethylamine, the metal precursors trimethyltin chloride and dimethyltin dichloride and *n*-BuLi solution (1.6 M in hexanes) were purchased from Aldrich and used as received.

Synthesis of IP1. To a solution of **I1** (0.50 g, 1.19 mmol) in dry diethyl ether (50 mL) at -10ºC was added dropwise a solution of *n*-BuLi 1.6 M in hexanes (0.78 mL, 1.25 mmol). The mixture was stirred for ninety minutes at the same temperature and then chlorodiphenylphosphine (0.23 mL, 1.25 mmol) was added dropwise. The reaction mixture was stirred at room temperature overnight (16 hours). The organic layer was then washed with water (3 x 15 mL), dried over $MgSO_4$ and evaporated. The crude mixture was purified by silica column chromatography (4:1, hexane:ethyl acetate). Yield: 0.56 g (77%); white solid. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.80 (m, 6H, *o*-P*Ph$_3$*), 7.67 (m, 4H, *o*-P*Ph$_2$*), 7.57 (m, 3H, *p*-P*Ph$_3$*), 7.45 (m, 6H, *m*-P*Ph$_3$*), 7.39 (m, 2H, *p*-P*Ph$_2$*), 7.34 (m, 4H, *m*-P*Ph$_2$*), 3.00-1.00 (bm, 10H, B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$) δ (ppm): -2.9, -4.8, -8.9, -10.1, -12.2. ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 5.6 (*P*Ph$_3$), -0.7

(*P*Ph$_2$). IR (KBr, ν/cm^{-1}): 3431m, 3059w, 2600s, 2569s ν(B-H), 1436vs, 1346vs ν(P=N), 1107vs, 1072s, 743m, 719s, 692vs, 544m, 525s, 507m, 492m. MS (EI, m/z): 603.0 (100%) [M-H]$^+$, 526.0 (5%) [M-Ph]$^+$, 418.0 (8%) [M-PPh$_2$]$^+$, 261.9 (54%) [PPh$_3$]$^+$, 182.9 (46%) [PPh$_2$-H]$^+$, 108.0 (25%) [PPh]$^+$. Elemental analysis calcd (%) for $C_{32}H_{35}B_{10}NP_2$: C 63.6, H 5.8, N 2.3; found: C 63.3, H 6.0, N 2.4.

Synthesis of IP2. This compound was prepared in a similar manner as compound **IP1**, i.e. by lithiation of **I2** (0.30 g, 0.65 mmol) in dry diethyl ether (50 mL) with *n*-BuLi (0.40 mL, 0.65 mmol), followed by addition of chlorodiphenylphosphine (0.12 mL, 0.68 mmol). The crude oily mixture was treated with diethyl ether yielding a solid that was separated by filtration. Yield: 0.35 g (84%); white solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.46 (m, 1H), 7.90 (m, 4H, *o*-N=P*Ph$_2$*), 7.66 (m, 4H, *o*-P*Ph$_2$*), 7.56 (m, 3H: 2H *p*-N=P*Ph$_2$* + 1H), 7.45 (m, 4H, *m*-N=P*Ph$_2$*), 7.39 (m, 4H: 2H *p*-P*Ph$_2$* + 2H), 7.33 (m, 4H, *m*-P*Ph$_2$*), 3.00-1.00 (bm, 10H, B*H*), 2.09 (s, 3H, SC*H$_3$*). ^{11}B{^{1}H} NMR ($CDCl_3$) δ (ppm): -3.2, -8.8, -10.5, -12.1. ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 3.5 (N=*P*Ph$_2$PhSMe), -0.5 (*P*Ph$_2$). IR (ATR, ν/cm^{-1}): 3051w, 2590vs, 2566s ν(B-H), 1435s, 1362vs, 1332vs ν(P=N), 1256m, 1103s, 1072m, 741m, 727m, 689vs, 531m, 501s. MS (EI, m/z): 649.0 (35%) [M-H]$^+$, 635.0 (91%) [M-Me]$^+$, 602.0 (6%) [M-SMe]$^+$, 573.9 (17%) [M-Ph]$^+$, 559.0 (29%) [M-Ph-Me]$^+$, 292.9 (100%) [PPh$_3$S]$^+$, 261.9 (60%) [PPh$_3$]$^+$, 214.9 (38%) [PPh$_2$S]$^+$, 182.9 (40%) [PPh$_2$-H]$^+$, 108.0 (14%) [PPh]$^+$. Elemental analysis calcd (%) for $C_{33}H_{37}B_{10}NP_2S$: C 60.9, H 5.7, N 2.2, S 4.9; found: C 59.9, H 5.9, N 2.1, S 4.5.

Synthesis of SnMe$_3$I1. The carborane precursor **I1** (0.15 g, 0.36 mmol) was dissolved in dry diethyl ether (10 mL) and treated with *n*-BuLi (0.24 mL, 0.38 mmol) at -10ºC. The reaction mixture was stirred at the same temperature for one hour and then a solution of trimethyltin chloride (0.075 g, 0.38 mmol) in 5 mL dry diethyl ether was

added. The reaction mixture was stirred overnight (16 hours) at room temperature. The organic layer was then washed with water (3 x 15 mL), dried over $MgSO_4$ and evaporated. The residue was recrystallized from commercial diethyl ether. Yield: 0.13 g (62%); white solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.67 (m, 6H, *o*-P*Ph*$_3$), 7.56 (m, 3H, *p*-P*Ph*$_3$), 7.46 (m, 6H, *m*-P*Ph*$_3$), 2.80-1.30 (bm, 10H, B*H*); 0.34 (s, 9H, Sn(C*H*$_3$)$_3$, with Sn satellites $^{2}J_{119Sn-H}$= 57 Hz, $^{2}J_{117Sn-H}$= 54 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$) δ (ppm): -3.9, -8.2, -10.0, -12.3. ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 4.6. ^{119}Sn NMR ($CDCl_3$) δ (ppm): 23.3. IR (KBr, ν/cm^{-1}): 3060w, 2916w, 2613s, 2546s ν(B-H), 1483w, 1439s, 1327vs ν(P=N), 1190m, 1107s, 1074s, 779m, 715s, 696s, 570m, 544s, 525s, 509s. MS (ESI, m/z): 583.3 (100%) $[M+H]^+$. Elemental analysis calcd (%) for $C_{23}H_{34}B_{10}NPSn$: C 47.4, H 5.8, N 2.4; found: C 47.1, H 6.0, N 2.2.

Synthesis of SnClMe$_2$I1. This compound was prepared in a similar manner as **SnMe$_3$I1**, by reaction of the precursor **I1** (0.15 g, 0.36 mmol) with *n*-BuLi (0.24 mL, 0.38 mmol) at -10ºC, followed by addition of dimethyltin dichloride (0.080 g, 0.38 mmol). The pure compound was obtained by recrystallization from diethyl ether of the solid residue obtained after work up. Yield: 0.11g (50%); white solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.62 (m, 9H, *o*,*p*-P*Ph*$_3$), 7.52 (m, 6H, *m*-P*Ph*$_3$), 3.00-1.10 (bm, 10H, B*H*), 0.77 [s, 9H, Sn(C*H*$_3$)$_3$, with Sn satellites $^{2}J_{119Sn-H}$= 67 Hz, $^{2}J_{117Sn-H}$= 64 Hz]. ^{11}B{^{1}H} NMR ($CDCl_3$) δ (ppm): -3.7, -7.2, -9.6, -11.7, -12.3. ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 11.8. ^{119}Sn NMR ($CDCl_3$) δ (ppm): 36.5. IR (KBr, ν/cm^{-1}): 2608s, 2561s ν(B-H), 1460m, 1438s, 1276vs ν(P=N), 1107vs, 1076s, 783m, 751m, 719s, 695s, 577m, 547m, 525s, 509m. MS (MALDI-TOF, m/z): 604.3 (1%) $[M+H]^+$, 567.3 (8%) $[M-Cl]^+$, 420.3 (100%) $[M-SnMe_2Cl+H]^+$. Elemental analysis calcd (%) for $C_{22}H_{31}B_{10}ClNPSn$: C 43.8, H 5.1, N 2.3; found: C 44.1, H 5.3, N 2.3.

Synthesis of Pd*closo*IP1. The ligand **IP1** (100 mg, 0.17 mmol) and the metal precursor bis(benzonitrile)palladium(II) chloride, $[PdCl_2(PhCN)_2]$, (63 mg, 0.16 mmol) were suspended in dry acetonitrile (20 mL) and stirred at room temperature overnight (16 hours). The yellow precipitate was filtered, washed with diethyl ether and dried under vacuum. Yield 115 mg (90%), yellow solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.32 (m, 4H, *o*-P*Ph*$_2$), 7.84 (bs, 6H, *o*-N=P*Ph*$_3$), 7.71 (m, 2H, *p*-P*Ph*$_2$), 7.65 (m, 7H: 4H *m*-P*Ph*$_2$ + 3H *p*-N=P*Ph*$_3$), 7.51 (bs, 6H, *m*-N=P*Ph*$_3$), 2.80-0.90 (bm, 10H, B*H*). ^{11}B{^{1}H} NMR ($CDCl_3$) δ (ppm): -1.4, -5.2, -8.8, -12.0, -14.8. ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 49.1 (*P*Ph$_2$), 34.1 (N=*P*Ph$_3$). IR (KBr, ν/cm^{-1}): 3077w, 3057w, 2609s, 2589s, 2565vs ν(B-H), 1482m, 1437s, 1315w, 1181vs ν(P=N), 1102vs, 1043w, 998m, 965w, 891w, 751m, 718s, 688vs, 644m, 600m, 565m, 501s, 480m. MS (MALDI, m/z): 745.2 (100%) $[M\text{-}Cl]^+$. Elemental analysis calcd (%) for $C_{32}H_{35}B_{10}Cl_2NP_2Pd$: C 49.2, H 4.5, N 1.8; found: C 48.8, H 4.3, N 1.7.

Synthesis of Pd*nido*L1. A solution of compound **Pd*closo*IP1** (50 mg, 0.06 mmol) in 10 mL of a 1:1 mixture of methanol and dichloromethane was refluxed for four hours. The color changed from yellow to orange and an orange solid precipitated. The solid was filtered, washed with diethyl ether and dried under vacuum. Yield 46 mg (98%), orange solid. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.50-7.00 (bm, aromatic CH), -2.13 (bs, B-*H*-B). ^{31}P{^{1}H} NMR ($CDCl_3$) δ (ppm): 74.7 (*P*Ph$_2$), 31.9 (N=*P*Ph$_3$). IR (KBr, ν/cm^{-1}): 3055w, 2536vs ν(B-H), 1587w, 1482w, 1435s, 1312vw, 1162m ν(P=N), 1102s, 1044m, 998m, 834w, 743m, 717m, 687s, 592w, 562w, 505m, 474w. MS (MALDI, m/z): 1434,4 (3 %) $[M\text{-}Cl]^+$; 734,2 (100 %) $[M_{1/2}]^+$. Elemental analysis calcd (%) for $C_{64}H_{70}B_{18}Cl_2N_2P_4Pd_2$: C 52.3, H 4.8, N 1.9; found: C 52.1, H 4.9, N 1.9.

Synthesis of Pd*nido*L2. The ligand **IP2** (100 mg, 0.15 mmol) and $[PdCl_2(PhCN)_2]$ (59 mg, 0.15 mmol) were dissolved in dry acetonitrile (20 mL) and stirred at room temperature overnight (16 hours). The precipitate was filtered, washed with diethyl ether and dried under vacuum. Yield 100 mg (83%), yellow solid. . ^{1}H NMR ($CDCl_3$) δ (ppm): 8.50-7.00 (bm, aromatic CH), -2.85 (bs, B-*H*-B). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 76.8 (PPh_2), 37.5 ($N{=}PPh_3$). IR (KBr, ν/cm^{-1}): 3060w, 2951m, 2922m, 2854m, 2527vs ν(B-H), 1573w, 1482w, 1435s, 1312w, 1173m ν(P=N), 1102s, 1051m, 998w, 964w, 835w, 742m, 724m, 689m, 519m, 477w. MS (ESI, m/z): 780.2 (17%) $[M]^+$, 744.2 (28%) $[M\text{-}Cl]^+$, 667.3 (59%) $[M\text{-}Cl\text{-}Ph]^+$, 381.3 (100%) $[PdNPPh_3]^+$. Elemental analysis calcd (%) for $C_{33}H_{37}B_9ClNP_2SPd$: C 50.7, H 4.7, N 1.8, S 4.1; found: C 50.3, H 4.9, N 1.7, S 3.8.

X-Ray Crystallography. Intensity data sets for all compounds were collected with the use of a Bruker X8 Kappa APEXII diffractometer (Mo Kα radiation, λ = 0.71073 Å) equipped with a graphite monochromator. All crystals were measured at 100 K. The omega and phi scans technique was employed to measure intensities in all crystals. No decomposition of the crystals occurred during data collection. The intensities of all data sets were corrected for Lorentz and polarization effects. Absorption effects in all compounds were corrected using the program SADABS.[64] The crystal structures of all compounds were solved by direct methods. Crystallographic programs used for structure solution and refinement were those of SHELXL-2014[65] installed on a PC clone. Scattering factors were those provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2, using anisotropic displacement parameters for all non-hydrogen atoms. The positions of hydrogen atoms attached to

the boron atoms of the open face of the *nido* derivatives **Pd*nido*IP1** and **Pd*nido*IP2** were located in the difference Fourier maps and refined without any constraints. The rest of the hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C-C bonds for methyl groups, with C-H distances of 0.95-0.99 Å and B-H distances of 1.12 Å. The calculated hydrogen atoms were refined with U_{iso} constrained at 1.2 (for non-methyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The crystal structure of the ligand **IP2** contains two independent molecules of the phosphine-iminophosphorane derivative. Each molecule is oxidized to phosphine oxide to a different extent (15 and 50%) as suggested by the refinement of the occupancy of the oxygen atoms. One of the independent molecules presents a minor disorder of the thioether group (5%). This disordered was not modelled, leaving a residual peak of 1.60 $eÅ^{-3}$. The crystal structure of **Pd*nido*IP1** contains three chloroform molecules per asymmetric unit. One of them presents a minor disordered that was handled by introducing split positions for the disordered chlorine atoms in the refinement with the respective occupancies (70/30). The other two molecules of chloroform were very disordered and were removed using the Squeeze program,[66] implemented in Platon.[67] The crystal structure of **Pd*nido*IP2** also contains large voids with disordered solvent that was also removed using the Squeeze program. In this case, the attempts to model the solvent molecules suggest the presence of one molecule of hexane in the asymmetric unit.

Table 1 summarizes pertinent details of the data collection and the structure refinement of the crystal structures. The program ORTEP3[68] was used to generate the pictures of all the molecular structures. CCDC reference numbers: 1546606-1546611.

Supporting Information Available: Supporting information for this article is available on the WWW under http://dx.doi.org/XXX. It contains the synthesis and characterization data for the non-carboranyl analogs **I3-Br** and **SnClMe$_2$I3**, and all the NMR and spectra.

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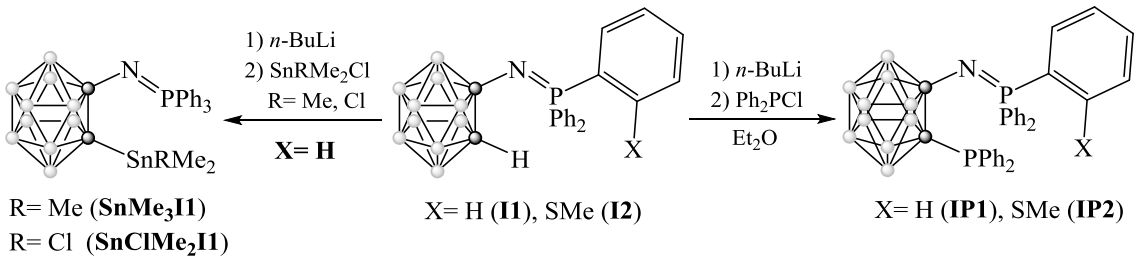
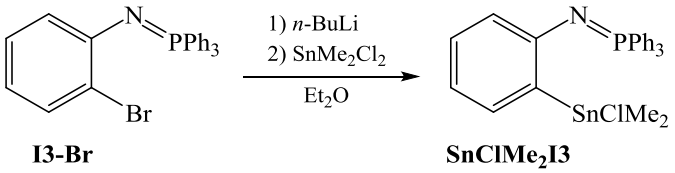
Keywords: *o*-carborane ligands, phoshine-iminophosphoranes, tin, palladium.

Figures and schemes

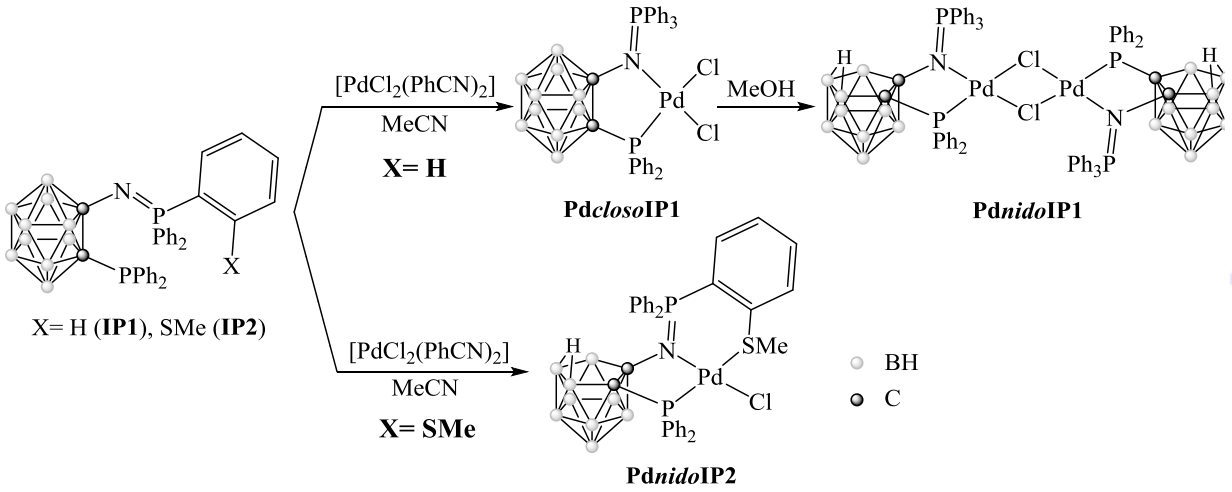
Scheme 1. Synthesis of derivatives of iminophosphoranes **I1** and **I2**: phosphine-iminophosphoranes **IP1** and **IP2**, and organotin compounds **SnMe$_3$I1** and **SnClMe$_2$I1**.



Scheme 2. Synthesis of the organotin compound **SnClMe$_2$I3**.



Scheme 3. Synthesis of the palladium complexes **Pd*closo*IP1**, **Pd*nido*IP1** and **Pd*nido*IP2**.



10.1002/ejic.201700487

Figure 1. (a) Unsubstituted carboranyl-iminophosphorane **I1**, previously reported;[14] (b) carboranyl iminophosphorane-thiolate **L1**, previously reported;[14] (c) new carboranyl phosphine-iminophosphorane ligands **IP1** and **IP2**.

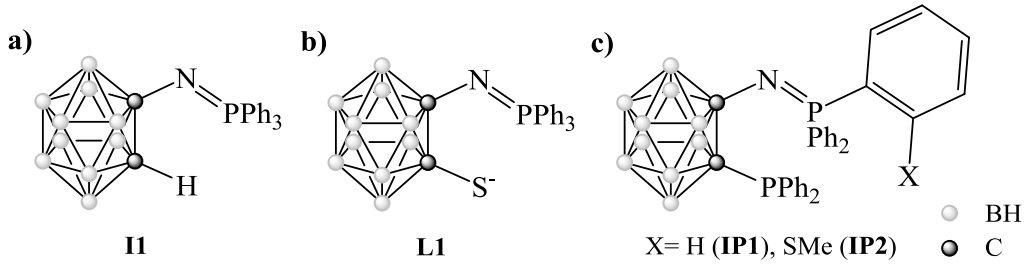
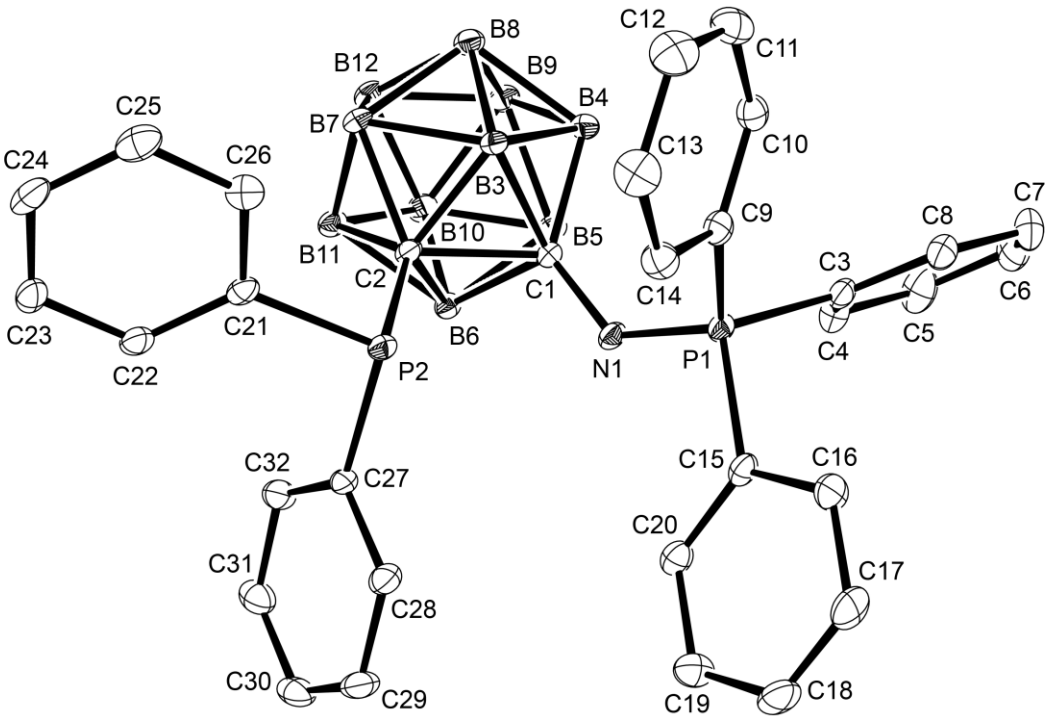


Figure 2. Molecular structure of compound **IP1**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms omitted for clarity.



10.1002/ejic.201700487

Figure 3. Molecular structure of compound **IP2**. The phosphine phosphorous atom P2 is 15% oxidized to phosphine oxide (oxygen atom not shown). Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms omitted for clarity.

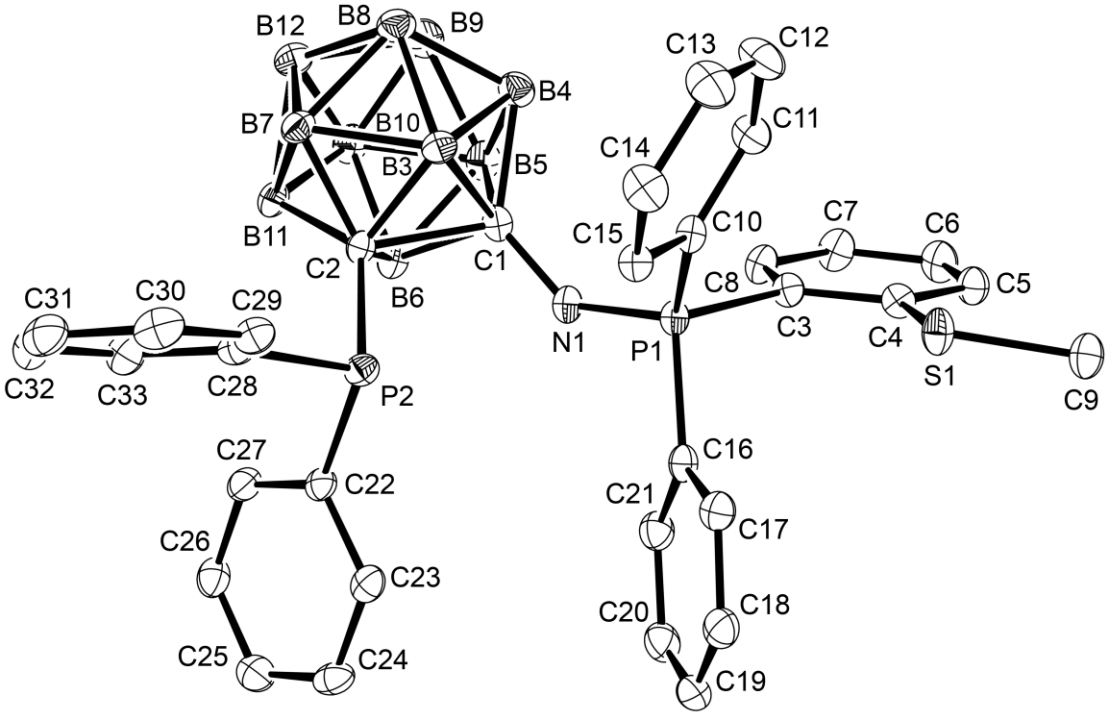


Figure 4. Molecular structure of compound **$SnMe_3I1$**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms omitted for clarity.

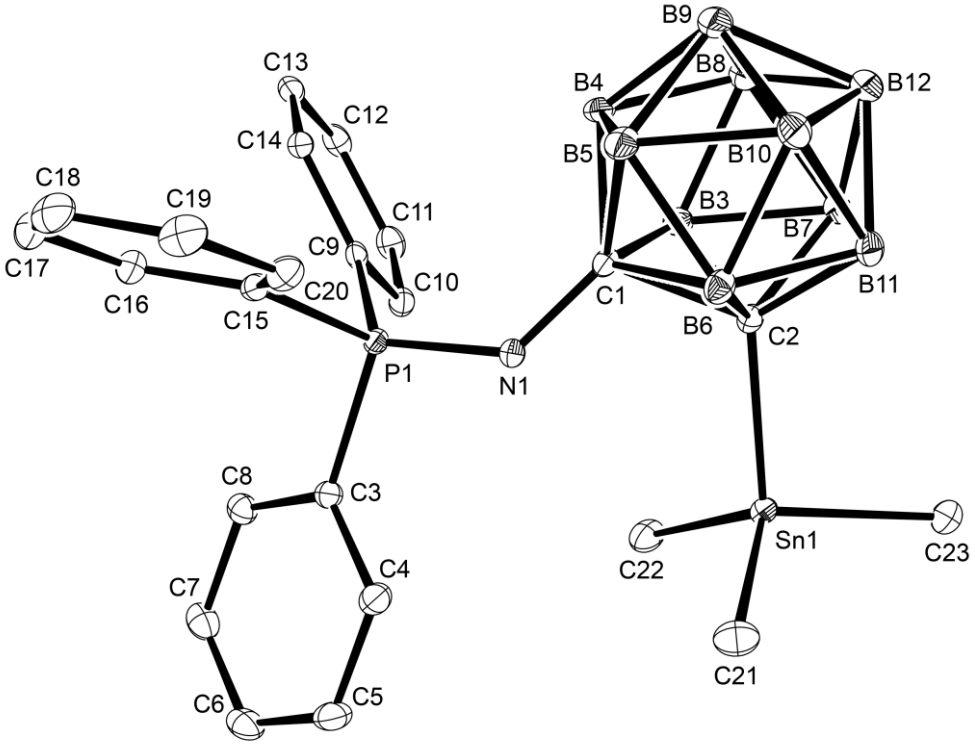


Figure 5. Molecular structure of compound **SnClMe$_2$I1**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms omitted for clarity.

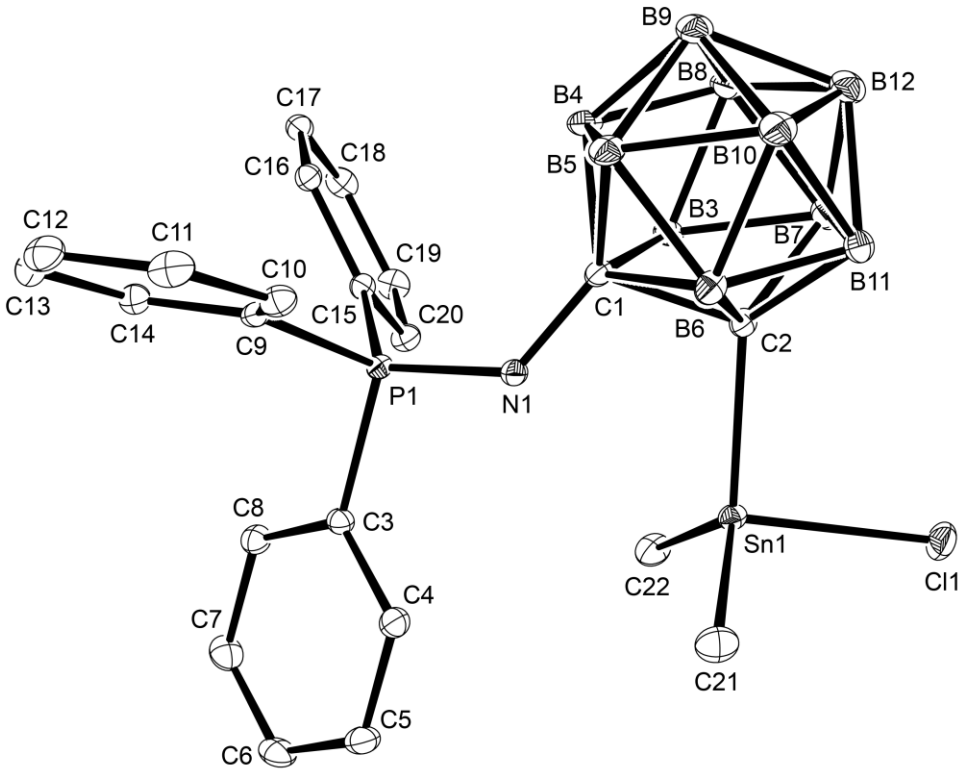


Figure 6. Molecular structure of compound **Pd*nido*IP1**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms and phenyl rings on the phosphorous atoms (P1, P2, P1$^{\#1}$ and P2$^{\#1}$) omitted for clarity. Symmetry operation used to generate equivalent atoms #1 -x+3/2, -y, z.

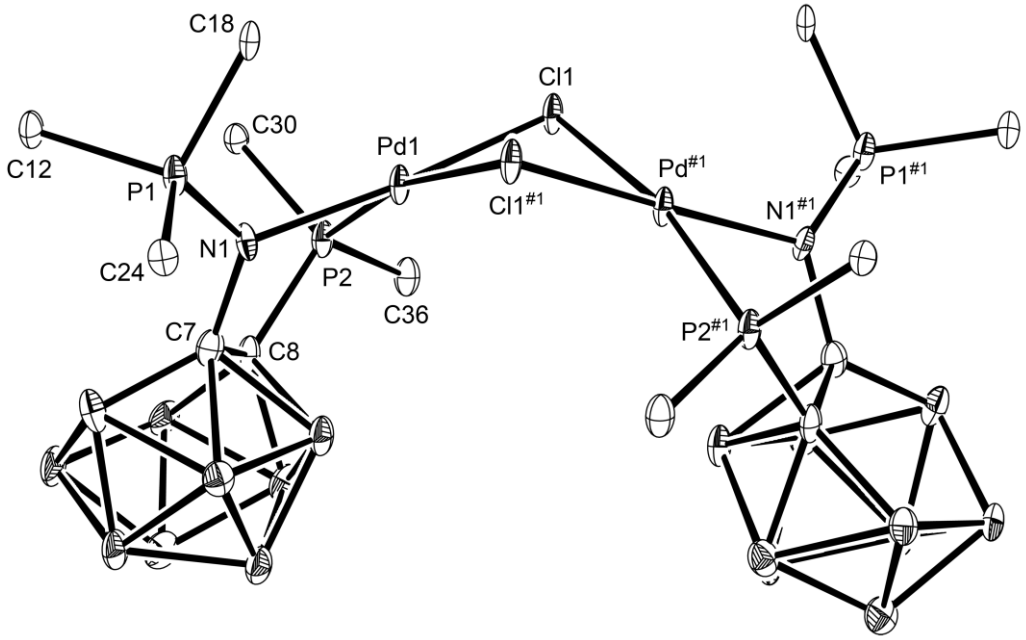


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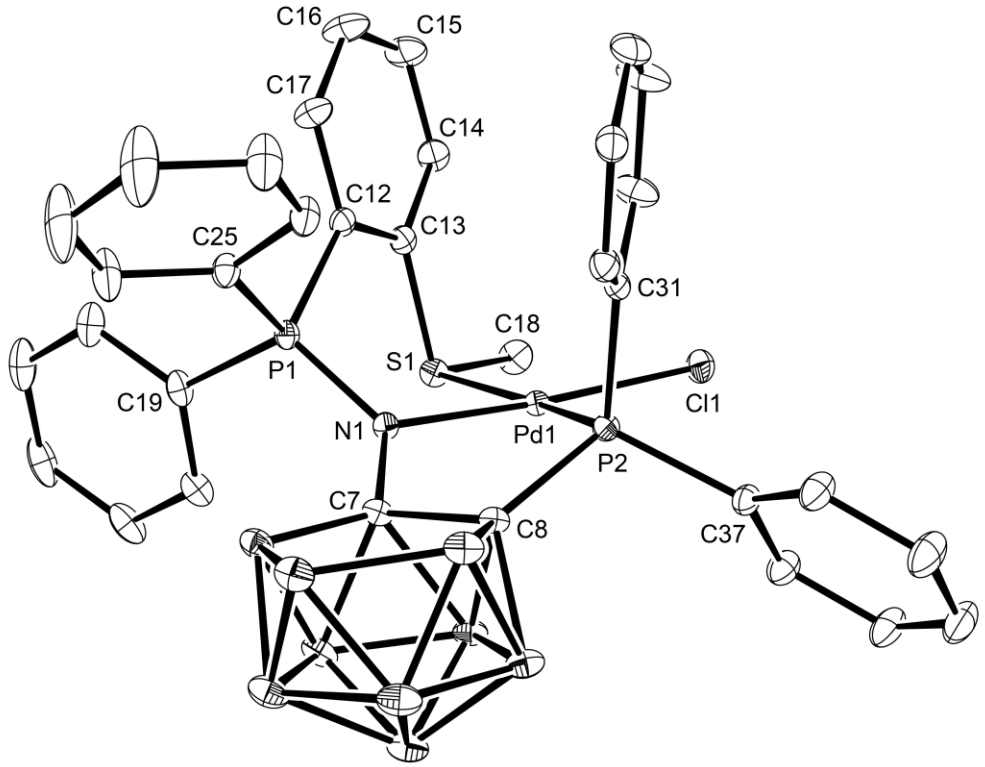
Figure 7. Molecular structure of compound **Pd*nido*IP2**. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms omitted for clarity.



10.1002/ejic.201700487

Table 1. Summary of crystal data and refinement for the crystal structures.

	IP1	**IP2**	**$SnMe_3I1$**	**$SnClMe_2I1$**	**Pd*nido*IP1·2$CHCl_3$**	**Pd*nido*IP2**
Empirical Formula	$C_{32}H_{35}B_{10}NP_2$	$C_{66}H_{74}B_{20}N_2P_4S_2O_{0.65}$	$C_{23}H_{34}B_{10}NPSn$	$C_{22}H_{31}B_{10}ClNPSn$	$C_{66}H_{72}B_{18}C_{l8}N_2P_4Pd_2$	$C_{33}H_{37}B_9ClNP_2SPd$
Formula weight	603.65	1309.87	582.27	602.69	1708.11	780.77
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	3	0.71073
Crystalline system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	ıombic	Tetragonal
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	Pbca		$I4_1/a$
Cell Constants (Å, °)	a = 13.2882(10)	a = 12.9084(16)	a = 10.4900(5)	a = 19.0871(12)	9428(12)	a = 36.887(5)
	b = 14.8346(10)	b = 17.906(2)	b = 18.7975(7)	b = 14.1331(10)	3807(13)	b = 36.887(5)
	c = 16.5792(12)	c = 29.814(4)	c = 14.3317(7)	c = 20.4385(14)	4292(11)	c = 12.9984(19)
	α = 90	α = 90	α = 90	α = 90		α = 90
	β = 90.567(4)	β = 101.850(8)	β = 98.918(3)	β = 90		β = 90
	γ = 90	γ = 90	γ = 90	γ = 90		γ = 90
Volume ($Å^3$)	3268.0(4)	6744.5(14)	2791.8(2)	5513.5(6)	5(14)	17686(5)
Z	4	4	4	8		16
Absorption coefficient (mm^{-1})	0.159	0.220	0.987	1.096		0.622
F(000)	1256	2725	1172	2416		6336
Theta range for data collection (°)	1.842-28.281	1.620-26.543	1.801-30.580	2.051-30.430	5.350	1.561-30.724
Index ranges	$-17 \le h \le 17$	$-16 \le h \le 16$	$-14 \le h \le 15$	$0 \le h \le 27$	≤ 32	$-36 \le h \le 37$
	$0 \le k \le 19$	$-22 \le k \le 22$	$-26 \le k \le 26$	$0 \le k \le 20$	≤ 34	$0 \le k \le 52$
	$0 \le l \le 22$	$-37 \le l \le 37$	$-20 \le l \le 20$	$0 \le l \le 29$	≤ 25	$0 \le l \le 18$
Size (mm)	0.33 x 0.25 x 0.15	0.38 x 0.21 x 0.18	0.27 x 0.13 x 0.12	0.40 x 0.35 x 0.17	0.10 x 0.04	0.33 x 0.20 x 0.14
Collected reflections	58383	129280	63363	51522		105688
Independent reflections	8105 [R(int) = 0.0641]	13906 [R(int) = 0.0600]	8574 [R(int) = 0.0397]	8320 [R(int) = 0.0408]	R(int) = 0.1178]	13701 [R(int) = 0.0567]
Data/ restraints/ parameters	8105 / 0 / 406	13906 / 0 / 867	8574 / 0 / 328	8320 / 0 / 327	0 / 476	13701 / 0 / 450
Goodness-on-fit (F^2)	1.027	1.034	1.018	1.014		1.010
Final R indices [I>2s(I)][a]	$R_1 = 0.0467$	$R_1 = 0.0458$	$R_1 = 0.0258$	$R_1 = 0.0251$	0460	$R_1 = 0.0318$
	$wR_2 = 0.1073$	$wR_2 = 0.1135$	$wR_2 = 0.0552$	$wR_2 = 0.0553$	0.1018	$wR_2 = 0.0701$
R indices (all data)	$R_1 = 0.0762$	$R_1 = 0.0627$	$R_1 = 0.0405$	$R_1 = 0.0353$	1171	$R_1 = 0.0461$
	$wR_2 = 0.1215$	$wR_2 = 0.1241$	$wR_2 = 0.0608$	$wR_2 = 0.0590$	0.1369	$wR_2 = 0.0760$
Largest diff. peak and hole ($e^- Å^{-3}$)	0.577 and -0.359	1.603 and -0.669	0.445 and -0.474	0.456 and -0.406	nd -0.887	0.524 and -0.439

[a] $R_1 = \sum[|F_o| - |F_c|/\Sigma|F_o|]$; $wR_2 = [|\Sigma(F_o^2 - F_c^2)/\Sigma(F_o^2)]^{1/2}$

Table 2. Selected bond lengths (Å) and angles (º) for the phosphine-iminophosphorane ligands.

	Cc-Cc	Cc-N	Cc-P	P=N	Cc-Cc-N	Cc-Cc-P	Cc-N-P
IP1	1.785(2)	1.369(2)	1.8758(17)	1.5800(15)	115.36(13)	109.97(10)	129.91(13)
IP2*	1.828(3) 1.776(3)	1.355(3) 1.368(3)	1.858(2) 1.867(2)	1.5815(18) 1.5812(18)	115.14(17) 114.34(16)	108.11(12) 113.71(13)	133.18(16) 129.69(15)

Cc: cage carbon atom. *Two molecules per asymmetric unit.

Table 3. Selected bond lengths (Å) for the tin compounds.

	Sn-Cc	Sn-Me	Sn-Cl	Sn-N*	Cc-Cc	P=N	
$SnMe_3I1$	2.1893(16)	C21; 2.1296(19) C22: 2.1199(18) C23: 2.1342(19)	---	[3.3458(14)]	1.701(2)	1.5755(15)	1.
$SnClMe_2I1$	2.1629(15)	C21: 2.1206(18) C22: 2.1134(16)	2.3884(4)	[2.9240(13)]	1.677(2)	1.5918(14)	1.4)

Cc: cage carbon atom; *Values in square brackets correspond to weak interactions.

Table 4. Selected bond angles (º) for the tin compounds.

	Cc-Sn-Me	Cc-Sn-Cl	Me-Sn-Me	Cl-Sn-Me	Cc-Cc-Sn	-N	Cc-N-P
$SnMe_3I1$	C21: 108.13(7) C22: 110.49(6) C23: 101.59(7)	---	C21-Sn-C22: 115.03(8) C21-Sn-C23: 111.30(8) C22-Sn-C23:109.46(8)	---	118.01(10)	(13)	129.82(12)
$SnClMe_2I1$	C21: 114.22(6) C22: 114.64(6)	96.62(4)	C21-Sn-C22: 123.00(7)	C21: 101.76(6) C22: 100.02(5)	107.87(9)	(12)	127.23(11)

Table 5. Selected bond lengths (Å) for the palladium compounds.

	Pd-Cl	**Pd-N**	**Pd-P**	**Pd-S**	**Cc-N**	**Cc-P**	**Cc-Cc**	**P=N**
Pd*nido*IP1	Cl1: 2.3213(13) $Cl1^{\#1}$: 2.4783(13)	2.072(4)	2.2054(14)	---	1.467(7)	1.797(6)	1.566(7)	1.611(5)
Pd*nido*IP2	2.2834(5)	2.0447(13)	2.2317(5)	2.3731(5)	1.448(2)	1.8182(17)	1.569(	.6100(14)

Symmetry transformation used to generate equivalent atoms: #1 -x+3/2, -y, z.

Table 6. Selected bond angles (º) for the palladium compounds.

	P-Pd-N	**N-Pd-X**	**X-Pd-Cl1**	**Cl1-Pd-P**	**P-Pd-X**	**N-Pd-Cl1**	**Cc-Cc-N**	**-P**	**Cc-N-P**
Pd*nido*IP1	79.15(12)	101.12(12)	84.45(5)	96.17(5)	167.44(6)	173.45(12)	110.8(4)	4)	122.3(3)
Pd*nido*IP2	81.50(4)	86.64(4)	95.328(16)	96.229(16)	167.581(16)	175.24(4)	112.03(13)	11)	121.15(11)

X= $Cl^{\#1}$ (**Pd*nido*IP1**), S (**Pd*nido*IP2**). Symmetry transformation used to generate equivalent atoms: #1 -x+3/2

References

[1] (a) R. N Grimes, Carboranes, 2nd ed.; Academic Press: London, UK, **2011**; (b) M. Scholz, E. Hey-Hawkins, *Chem. Rev.* **2011**, *111*, 7035-7062; (c) V. N. Kalinin, V. A. Ol´shevskaya, *Russ. Chem. Bull., Int. Ed.* **2008**, *57*, 815-836; (d) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209-223.

[2] (a) M. Patel, A. C. Swain, A. R. Skinner, L. G. Mallinson, G. F. Hayes, *Macromol. Symp.* **2003**, *202*, 47-58; (b) E. N. Peters, *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 28-32.

[3] A. Gonzalez-Campo, R. Nuñez, F. Teixidor, B. Boury, *Chem. Mater*. **2006**, *18*, 4344-4353

[4] A. Ferrer-Ugalde, E. J. Juarez-Perez, F. Teixidor, C. Viñas, R. Nuñez, *Chem. Eur. J.* **2013**, *19*, 17021-17030.

[5] O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 12680-12681.

[6] (a) N. Tsuboya, M. Lamrani, R. Hamasaki, M. Ito, M. Mitsuishi, T. Miyashitab, Y. Yamamoto, *J. Mater. Chem.* **2002**, *12*, 2701-2705; (b) B. Fabre, J. C. Clark, M. G. H. Vicente, *Macromolecules* **2006**, *39*, 112-119; (c) D. M. Murphy, D. M. P. Mingos, J. L. Haggitt, H. R. Poell, S. A. Westcott, T. B. Marder, N. J. Taylor, D. R. Kanis, *J. Mater. Chem.* **1993**, *3*, 139-148.

[7] (a) J. Plesek, S. Hermanek, *Collection Czechoslov. Chem. Commun.* **1979**, *44*, 24-33; (b) V. N. Kalinin, V. A. Ol'shevskaya, *Russ. Chem. Bull* **2008**, *57*, 815-836 and references therein; (c) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209-223 and references therein.

[8] A. M. Spokoyny, *Pure Appl. Chem.* **2013**, *85*, 903-919.

[9] D. Olid, R. Nuñez, C. Viñas, F. Teixidor, *Chem. Soc. Rev.* **2013**, *42*, 3318-3336.

[10] Z.-J. Yao, G.-X. Jin, *Coordination Chemistry Reviews* **2013**, *257*, 2522-2535.

[11] P. A. Jelliss in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press **2011**, chapter 13, pages 295-318.

[12] (a) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press **2011**, chapter 26, pages 675-699; (b) C. Viñas, R. Núñez, F. Teixidor, in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press **2011**, chapter 27, pages 701-740.

[13] (a) F. Issa, M. Kassiou, L. M. Rendina, *Chem. Rev.* **2011**, *111*, 5701-5722; (b) J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, K. Stephenson, *Coord. Chem. Rev.* **2002**, *232*, 173-230; (c) V. I. Bregadze, I. B. Sivaev in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press **2011**, chapter 9, pages 181-207; (d) M. Sibrian-Vazquez, M. G. H. Vicente, in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press **2011**, chapter 10, pages 209-241.

[14] (a) I. T. Chizhevsky, *Coord. Chem. Rev.* **2007**, *251*, 1590-1619; (b) Z. Qiu, S. Ren, Z. Xie, *Acc. Chem. Res.* **2011**, *44*, 299-309; (c) J. D. Lee, Y. J. Lee, K. C. Son, M. Cheong, J. Ko, S. O. Kang, *Organometallics* **2007**, *26*, 3374-3384; (d) H. Shen, Z. Xie in "Boron Science New Technologies and Applications" (Ed: Narayan S. Hosmane), CRC Press 2011, chapter 21, pages 517-528; (e) S. Bauer, E. Hey-Hawkins in "Boron Science New Technologies

and Applications" (Ed: Narayan S. Hosmane), CRC Press 2011, chapter 22, pages 529-577.

[15] C. A. Lugo, C. E. Moore, A. L. Rheingold, V. Lavallo, *Inorg. Chem.* **2015**, *54*, 2094-2096.

[16] A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant, C. A. Mirkin, *Nature Chem.* **2011**, *3*, 590-596.

[17] A. M. Spokoyny, C. D. Lewis, G. Teverovskiy, S. L. Buchwald, *Organometallics* **2012**, *31*, 8478-8481 and references therein.

[18] P. Crujeiras, J. L. Rodríguez-Rey, A. Sousa-Pedrares, *Dalton Trans.* **2017**, *46*, 2572-2593.

[19] M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, I. S. Neretin, K. Wade, *Chem. Commun.* **1999**, 1649-1650.

[20] R. D. Kennedy, *Chem. Commun.* **2010**, *46*, 4782-4784.

[21] J. García-Álvarez, S. E. García-Garrido, V. Cadierno, *J. Organomet. Chem.* **2014**, *751*, 792-808, and references therein.

[22] (a) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233-350; (b) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680-699; (c) Z. Weng, S. Teo, T. S. Hor, *Acc. Chem. Res.* **2007**, *40*, 676-684.

[23] W.-H.Zhang, S. W. Chien, T.S. A. Hor, *Coordination Chemistry Reviews* **2011**, *255*, 1991-2024.

[24] H.-S. Lee, J.-Y. Bae, J. Ko, Y. S. Kang, H. S. Kim, S.-J. Kim, J.-H. Chung, S. O. Kang, *J. Organomet. Chem.* **2000**, *614-615*, 83-91.

[25] J. D. Lee, T. T. Co, T.-J. Kim, S. O. Kang, *Synlett* **2009**, 771-774.

[26] P. Coburger, J. Schulz, J. Klose, B. Schwarze, M. B. Sárosi, E. Hey-Hawkins, *Inorg. Chem.* **2017**, *56*, 292-304.

[27] T. L. Chan, Z. Xie, *Chem. Commun.* **2016**, *52*, 7280-7283.

[28] A. R. Popescu, A. Laromaine, F. Teixidor, R. Sillanpää, R. Kivekäs, J. I. Llambias, C. Viñas, *Chem. Eur. J.* **2011**, *17*, 4429‑4443.

[29] W. E. Hill, L. M. Silva-Trivino, *Inorg. Chem.* **1979**, *18*, 361-364.

[30] A. R. Popescu, I. Rojo, F. Teixidor, R. Sillanpää, C. Viñas, Chem. Eur. J. 2015, 21, 8613-8625.

[31] L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. McKinnon, R. J. Peace, K. Wade, *Dalton Trans.* **2004**, 2786-2799.

[32] The crystal structure of the unsubstituted compound **I1**, reported in the literature, presents cluster disorder, so the Cc-Cc distance is artificially long and will not be used for comparison (see reference [14]).

[33] R. Kivekäs, R.Sillanpää, F. Teixidor, C. Viñas, R. Nuñez, Acta Cryst. 1994, C50, 2027-2030.

[34] F. Teixidor, C. Viñas, R. Benakki, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **1997**, *36*, 1719-1723.

[35] J.-D. Lee, S.-J. Kim, D. Yoo, J. Ko, S. Cho, S. O. Kang, *Organometallics* **2000**, *19*, 1695-1703

[36] E. I. Matrosov, V. A. Gilyarov, V. Yu. Kovtun, M. I. Kabachnik, *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1971**, *6*, 1162-1168.

[37] (a) E. W. Abel, S. A. Mucklejohn, *Phosphorus Sulfur Relat. Elem.* **1981**, *9*, 235-266; (b) R. Bielsa, A. Larrea, R. Navarro, T. Soler, E. P. Urriolabeitia, *Eur. J. Inorg. Chem.* **2005**, 1724-1736; (c) C. J. Wallis, I. L. Kraft, J. N. Murphy, B. O. Patrick, P. Mhrkhodavandi, *Organometallics* **2009**,

28, 3889-3895; (d) S. D. J. Brown, W. Henderson, K. J. Kilpin, B. K. Nicholson, *Inorg. Chim. Acta* **2007**, *360*, 1310-1315.

[38] See for example: (a): S. Ramírez-Rave, F. Estudiante-Negrete, R. A. Toscano, S. Hernández-Ortega, D. Morales-Morales, J.-M. Grévy, *J. Organomet. Chem.* **2014**, *749*, 287-295; (b) C. J. Wallis, I. L. Kraft, J. N. Murphy, B. O. Patrick, P. Mhrkhodavandi, *Organometallics* **2009**, *28*, 3889-3895; (c) S. D. J. Brown, W. Henderson, K. J. Kilpin, B. K. Nicholson, *Inorg. Chim. Acta* **2007**, *360*, 1310-1315; (d) R. Bielsa, A. Larrea, R. Navarro, T. Soler, E. P. Urriolabeitia, *Eur. J. Inorg. Chem.* **2005**, 1724-1736.

[39] T. P. Lockhart, W. F. Manders, *Inorg. Chem.*, **1986**, *25*, 892-895.

[40] A. S. Batsanov, M. A. Fox, T. G. Hibbert, J. A. K. Howard, R. Kivekäs, A. Laromaine, R. Sillanpää, C. Viñas, K. Wade, *Dalton Trans.* **2004**, 3822-3828;

[41] J.-D. Lee, H.-S. Kim, W.-S. Han, S. O. Kang, *J. Organomet. Chem.* **2010**, *695*, 463-468.

[42] T. Lee, S. W. Lee, H. G. Jang, S. O. Kang, J. Ko, *Organometallics* **2001**, *20*, 741-748.

[43] J. Holeček, M. Nádvorník. K. Handlíř, *Journal of Organometallic Chemistry* **1986**, *3*, 299-308.

[44] (a) A. R. Popescu,F. Teixidor,C. Viñas, *Coordination Chemistry Reviews* **2014**, *269*, 54-84. (b) A. L. Chan, J. Estrada, C. E. Kefalidis, V. Lavallo, *Organometallics* **2016**, *35*, 3257-3260.

[45] G. K. Anderson, L. Minren, *Inorg. Synth.* **1990**, *28*, 60-63.

[46] I. Maulana, P. Lönnecke, E. Hey-Hawkins, *Inorg. Chem.* **2009**, *48*, 8638-8645.

[47] S. Paavola, R. Kivekäs, F. Teixidor, C. Viñas, *J. Organomet. Chem.* **2000**, *606*, 183-187.

[48] (a) S. Paavola, F. Teixidor, C. Viñas, R. Kivekäs, *Journal of Organometallic Chemistry* **2002**, *645*, 39-46; (b) S. Paavola, F. Teixidor, C. Viñas, R. Kivekäs, *Journal of Organometallic Chemistry* **2002**, *657*, 187-193.

[49] C. Viñas, M. M. Abad, F. Teixidor, R. Sillanpää, R. Kivekäs, *Journal of Organometallic Chemistry* **1998**, *555*, 17-23.

[50] C. A. Sanz, M. J. Ferguson, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem.Commun.* **2014**, *50*, 11676-11678, and references therein.

[51] F. Teixidor, C. Viñas, M. M. Abad, M. Lopez, J. Casabó, *Organometallics* **1993**, *12*, 3766-3768.

[52] A. R. Popescu, F. Teixidor, C. Viñas, *Coordination Chemistry Reviews* **2014**, 269, 54-84.

[53] Z.-J. Yao, G.-X. Jin, *Coordination Chemistry Reviews* **2013**, *257*, 2522-2535.

[54] J. Dou, D. Zhang, D. Li, D. Wang, Eur. J. Inorg. Chem. 2007, 53-59.

[55] F. Teixidor, C. Viñas, M. M. Abad, R. Nuñez, R. Kivekäs, R. Sillanpää, *Journal of Organometallic Chemistry* **1995**, *503*, 193-203.

[56] F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, J. Casabó, *Inorg. Chem.* **1994**, *33*, 2645-2650.

[57] F. Teixidor, R. Benakki, C. Viñas, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **1999**, *38*, 5916-5919.

[58] F. Teixidor, R. Benakki, C. Viñas, R. Kivekäs, R. Sillanpää, *Organometallics* **1998**, *17*, 4630-4633.

[59] (a) S. V. Timofeev, O. B. Zhidkova, E. M. Mosolova, I. B. Sivaev, I. A. Godovikov, K. Yu. Suponitsky, Z. A. Starikova, V. I. Bregadze, *Dalton Trans.* **2015**, *44*, 6449-6456; (b) C. Viñas, M. R. Cirera, F. Teixidor, R. Kivekäs, R. Sillanpää, J. Llibre, *Journal of Organometallic Chemistry* **1998**, *568*, 149-155.

[60] (a) R. Bielsa, R. Navarro, T. Solerb, E. P. Urriolabeitia, *Dalton Trans.* **2008**, 1203-1214; (b) D. Aguilar, R. Bielsa, M. Contel, A. Lledós, R. Navarro, T. Soler, E. P. Urriolabeitia, *Organometallics* **2008**, *27*, 2929–2936; (c) D. Aguilar, M. A. Aragüés, R. Bielsa, E. Serrano, R. Navarro, E. P. Urriolabeitia, *Organometallics* **2007**, *26*, 3541–3551; (d) P. Wei, K. T. K. Chana, D. W. Stephan, *Dalton Trans.* **2003**, 3804-3810;

[61] (a) D.-P. Zhang, J.-M. Dou, D.-C. Li, D.-Q. Wang, *Acta Cryst.* **2006**, *E62*, o418-o419; (b) M. R. Sundberg, R. Uggla, C. Viñas, F. Teixidor, S. Paavola, R. Kivekäs, *Inorganic Chemistry Communications* **2007**, *10*, 713-716.

[62] (a) J.-M. Dou, D.-P. Zhang, D.-C. Li, D.-Q. Wang, Polyhedron 2007, 26, 719-724; (b) X.-Q. Xiao, G.-X. Jin, Journal of Organometallic Chemistry 2011, 696, 504-511.

[63] (a) L. Boubekeur, L. Ricard, N. Mézailles, P. Le Floch, *Organometallics* **2005**, *24*, 1065-1074; (b) P. Molina, A. Arques, A. García, M. C. Ramírez de Arellano, *Eur. J. Inorg. Chem.* **1998**, 1359-1368; (c) R. S. Pandurangi, K. V. Katti, L. Stillwell, C. L. Barnes, *J. Am. Chem. Soc.* **1998**, *120*, 11364-11373; (d) P. Molina, A. Arques, A. García, *Tetrahedron Letters* **1997**, *38*, 7613-7616.

[64] Sheldrick, G.M. SADABS: Program for absorption correction using area detector data. University of Göttingen, Germany, **1996**.

[65] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.

[66] A. L. Spek, *Acta Cryst.* **2015**, *C71*, 9-18.

[67] (a) A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *A46*, C34; (b) A. L. Spek, PLATON, A Multiporpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **1998**.

[68] ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.