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ARTICLE

Phosphane-functionalized heavier tetrylenes: Synthesis of silylene- and germylene-decorated phosphanes and their reactions with Group 10 metal complexes†

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The stable phosphane-functionalized heavier tetrylenes E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$ (E = Si (**1**$_{\mathbf{Si}}$), Ge (**1**$_{\mathbf{Ge}}$); ^{t}Bu$_2$bzam = *N,N'*-di*tert*butylbenzamidinate; HpyrmP^{t}Bu$_2$ = di*tert*butyl(2-pyrrolylmethyl)phosphane) have been prepared by reacting the amidinatotetrylenes E(^{t}Bu$_2$bzam)Cl (E = Si, Ge) with LipyrmP^{t}Bu$_2$. The reactions of **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ with selected M^0 and M^{II} (M = Ni, Pd, Pt) metal precursors have allowed the synthesis of square-planar [MCl$_2${κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (M = Ni, Pd, Pt; E = Si, Ge), tetrahedral [Ni(κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$)(cod)] (E = Si, Ge; cod = 1,5-cyclooctadiene) and triangular [M(κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$)(PPh$_3$)] (M = Pd, Pt; E = Si, Ge) complexes, showing that **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ are excellent *Si*,*P*- and *Ge*,*P*-chelating ligands that, due to their large steric bulk, are able to stabilize three-coordinate Pd^0 and Pt^0 complexes.

Introduction

The heavier analogues of carbenes, *i.e.* silylenes, germylenes, stannylenes and plumbylenes, also known as heavier tetrylenes (HTs),[1] have been recognized as very strong electron-donating ligands, particularly if they are stabilized by donor groups,[2] and some of their transition metal (TM) complexes have already demonstrated high efficiency in various catalytic reactions.[3,4]

Stimulated by the above-mentioned facts, the synthesis and coordination chemistry of potentially bidentate ligands containing HTs as donor groups have recently started to be investigated.[4a,5-9] However, despite the excellent coordination and catalytic properties of phosphanes, prior to the start of this work (May 2019), the known stable (isolated) phosphane-functionalized HTs that had proven to lead to bidentate κ^2*P*,*E*-ligands (E = HT tetrel atom) upon reactions with transition metal complexes were restricted to Wesemann's very bulky stannylene compounds **A**–**C** (Fig. 1). **A**[6] and **B**[6,7] have been reported to react with Ni^0 and Pd^0 metal precursors to give products that result from the insertion of the metal atom into the Sn–P bond, while anionic stannylene **C** replaces the nitrile ligands of [PtCl$_2$(MeCN)$_2$] and undergoes transmetalation with [Rh$_2$(μ-Cl)$_2$(CO)$_4$] to give the corresponding square-planar complexes.[8] In some occasions, the reactions of **A**,[7] **B**[7] and other[9] phosphane-functionalized HTs with TM complexes lead to metal products that no longer contain an HT fragment (it has been transformed into a tetryl ligand by insertion of the HT E atom into an M–X bond).

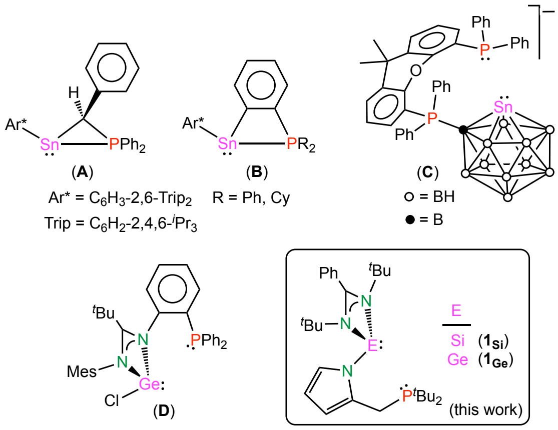

Fig. 1 The currently known stable phosphane-functionalized HTs that have led to bidentate κ^2*P*,*E*-ligands (E = HT tetrel atom) upon reactions with TM complexes.

The absence of phosphane-functionalized silylenes and germylenes having unengaged the lone pairs of their HT and phosphane functionalities and our previous experience on transition metal chemistry of amidinatotetrylenes[1f,2e,4b,4g,10] and PEP pincer (E = HT tetrel atom) compounds,[11,12] including those involving pyrrolylphosphane groups,[12] to led us to investigate the synthesis of such compounds by combining amidinatotetrylenes with pyrrolylphosphanes. As amidinatotetrylenes are donor-stabilized tetrylenes, they are not prone to be transformed into tetryl ligands upon reactions with TM complexes containing polar M–X bonds.[1f]

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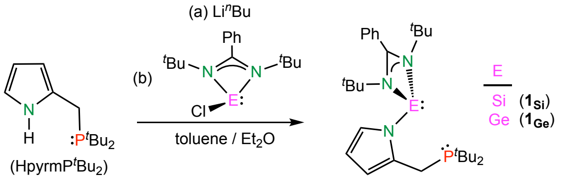
We now report that such a synthetic approach has allowed the preparation of a silylene-phosphane and a germylene-phosphane (**1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$, respectively; Fig. 1) and that both compounds behave as genuine bidentate κ^2*P*,*E*-ligands (E = Si, Ge) in their reactions with Group 10 metal (0 and II) complexes.

When we were finishing the labwork described in this article, Tan, Zhang, Huang et al. reported the synthesis of a germylene-phosphane (**D** in Fig. 1) that can also behave as a bidentate κ^2*P*,*Ge*-ligand.[13]

Results and discussion

The reactions of di*tert*butyl(2-pyrrolylmethyl)phosphane[12a] (HpyrmP^{t}Bu$_2$) first with *n*-butyl lithium and then with E(^{t}Bu$_2$bzam)Cl (E = Si,[14] Ge;[15] ^{t}Bu$_2$bzam = *N,N'*-di*tert*butylbenzamidinate) cleanly led to the silylene- and germylene-decorated phosphanes E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$ (**1**$_{\mathbf{E}}$; E = Si, Ge) (Scheme 1). Both compounds are very air-sensitive and very soluble in organic solvents (including aliphatic hydrocarbons).



Scheme 1 Synthesis of the heavier tetrylene–phosphane compounds **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ are very similar and indicate equivalence of their N^{t}Bu groups, denoting an average C_S symmetry in solution. The chemical shifts of their ^{31}P{^{1}H} NMR signals, 28.2 (**1**$_{\mathbf{Si}}$) and 28.3 (**1**$_{\mathbf{Ge}}$) ppm, which differ from that of HpyrmP^{t}Bu$_2$ (22.8 ppm) by only 5 ppm,[12b] hint to the absence of direct P···E interactions. The X-ray diffraction (XRD) structure of silylene **1**$_{\mathbf{Si}}$ (Fig. 2) shows that the Si atom is in the apex of a trigonal pyramid, attached to both benzamidinate N atoms and to the pyrrolyl fragment of the pyrmP^{t}Bu$_2$ group. The very long Si1···P1 distance, 4.795(1) Å, discards any interaction between these atoms.

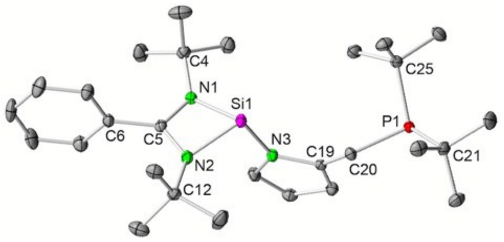


Fig. 2 Molecular structure of compound **1**$_{\mathbf{Si}}$ (50% displacement ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Si1–N1 1.873(1), Si1–N2 1.869(1), Si1–N3 1.809(1), C4–N1 1.483(2), C5–N1 1.341(2), C5–C6 1.492(2), C5–N2 1.337(2), C12–N2 1.480(2), C19–N3 1.397(2), C19–C20 1.505(2), C20–P1 1.868(1), C21–P1 1.895(1), C25–P1 1.892(2), N1–Si1–N2 69.56(5), N1–Si1–N3 100.47(6), N2–Si1–N3 101.52(5), N1–C5–N2 105.7(1).

A theoretical DFT/NBO analysis (at the wB97XD/cc-pVDZ level) of **1**$_{\mathbf{Si}}$ (Table 1) showed that the energy of the orbital containing the lone pair (LP) of the silylene fragment lies 42.66 kcal mol^{-1} above the orbital that contains the LP of the phosphane fragment, indicating that the basicity of the amidinatosilylene fragment is considerably higher than that of the trialkylphosphane scaffold.[2c] However, in the case of **1**$_{\mathbf{Ge}}$, the basicity of the amidinatogermylene fragment is slightly smaller than that of the trialkylphosphane scaffold as the germylene LP lies 16.75 kcal mol^{-1} below the phosphane LP (Table 2).[2a] In addition, the silylene LP has a smaller *s* (and a greater *p*) character than the germylene LP (Tables 1 and 2), also pointing to a stronger basicity of the silylene. The filled molecular orbitals (HOMO, HOMO–1, etc.) that are higher in energy than those containing the tetrylene and phosphane LPs are not relevant to the coordination chemistry of these molecules because they are not LPs (they are π-type orbitals of the amidinate or pyrrole fragments; ESI, Fig. S50).

Table 1 Selected orbital properties of silylene-phosphane **1**$_{\mathbf{Si}}$

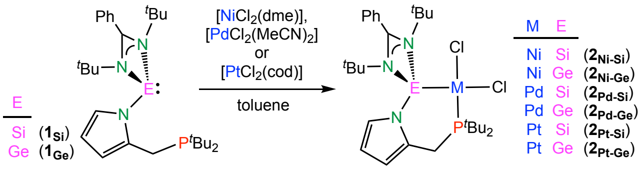
Orbital	*E* (hartree)	ΔE (kcal mol^{-1})	Composition (%)
LP Si (HOMO–7)	–0.36111	42.66	65.46 (*s*), 34,45 (*p*)
LP P (HOMO–11)	–0.42909	0	49.01 (*s*), 50.98 (*p*)

Table 2 Selected orbital properties of germylene-phosphane **1**$_{\mathbf{Ge}}$

Orbital	*E* (hartree)	ΔE (kcal mol^{-1})	Composition (%)
LP P (HOMO–10)	–0.43002	0	49.07 (*s*), 50.92 (*p*)
LP Ge (HOMO–11	–0.45671	–16.75	81,6 (*s*), 18.39 (*p*)

In order to verify and compare the coordination ability of HT-phosphanes **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$, they were reacted with Group 10 metal complexes in +2 and 0 oxidation states.

Both **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ reacted at room temperature with Group 10 metal(II) complexes containing easy displaceable ligands, [NiCl$_2$(dme)] (dme = 1,2-dimethoxyethane), [PdCl$_2$(MeCN)$_2$] and [PtCl$_2$(cod)] (cod = 1,5-cyclooctadiene), to give the corresponding [MCl$_2${κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (**2**$_{\mathbf{M\text{-}E}}$; M = Ni, Pd, Pt; E = Si, Ge) reaction products (Scheme 2).



Scheme 2 Reactions of **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$.with Group 10 metal dichlorido complexes.

All compounds of type **2**$_{\mathbf{M\text{-}E}}$ are diamagnetic species with very similar ^{1}H and ^{13}C{^{1}H} NMR spectra that are compatible with C_S molecular symmetry in solution. In all cases, the ^{31}P resonances appear at higher frequencies than those of the free tetrylenes-phosphanes. Large $J_{\text{Pt-P}}$, 3701.2 (**2**$_{\mathbf{Pt\text{-}Si}}$) and 3553.2 (**2**$_{\mathbf{Pt\text{-}Ge}}$) Hz, and $J_{\text{Pt-Si}}$, 2298.4 (**2**$_{\mathbf{Pt\text{-}Si}}$) Hz, coupling constants were observed in the ^{31}P{^{1}H} and ^{29}Si{^{1}H} spectra of the platinum complexes, corroborating the direct attachment of the Pt atom to the Si and P atoms. The XRD molecular structure of **2**$_{\mathbf{Pd\text{-}Si}}$ (Fig. 3) confirms the square-planar coordination geometry and the chelating ability of the silylene-phosphane ligand. The notably different Pd–Cl1 and Pd–Cl2 bond lengths, 2.361(1) and 2.408(1) Å, respectively, demonstrates that the *trans* influence of the silylene is much greater than that of the phosphane. A strong *trans* influence has been previously observed for monodentate amidinatosilylenes.[16]

Regarding reactions of **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ with Group 10 metals in zero oxidation state, both HT-phosphanes reacted at room temperature with [Ni(cod)$_2$], displacing one of the cod ligands, to give complexes of the type [Ni{κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(cod)] (**3**$_{\mathbf{Ni\text{-}E}}$; E = Si, Ge) as single reaction products (Scheme 3).

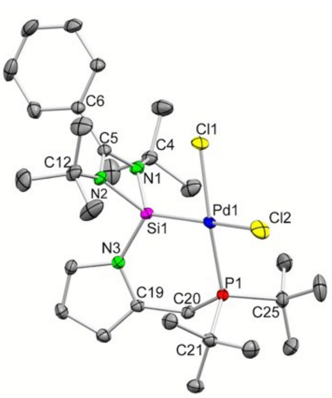
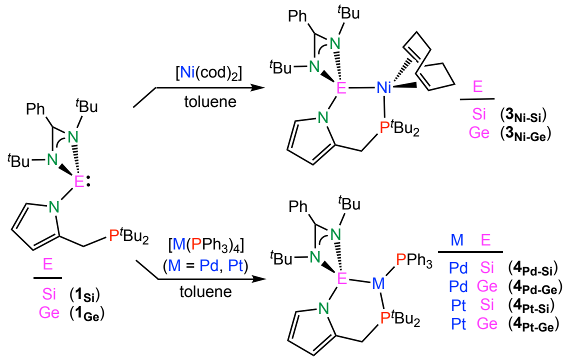


Fig. 3 XRD molecular structure of complex **2**$_{\mathbf{Pd\text{-}Si}}$ (30 % displacement ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pd1–Cl1 2.361(1), Pd1–Cl2 2.408(1), Pd1–P1 2.2654(9), Pd1–Si1 2.228(1), Si1–N1 1.807(3), Si1–N2 1.818(3), Si1–N3 1.760(3), C4–N1 1.488(5), C5–N1 1.338(5), C5–C6 1.483(5), C5–N2 1.335(5), C12–N2 1.494(5), C19–N3 1.400(5), C19–C20 1.489(5), C20–P1 1.837(4), C21–P1 1.885(4), C25–P1 1.899(4), Cl1–Pd1–Cl2 91.20(4), Cl1–Pd1–P1 170.93(4), Cl1–Pd1–Si1 83.42(4), Cl2–Pd1–P1 93.95(4), Cl2–Pd1–Si1 161.67(4), P1–Pd1–Si1 93.86(3), N1–Si1–N2 102.9(2), N1–Si1–N3 106.8(2), N2–Si1–N3 102.9(2), N1–Si1–Pd1 125.8(1), N2–Si1–Pd1 119.2(1), N3–Si1–Pd1 119.1(1), N1–C5–N2 106.7(3).



Scheme 3 Reactions of **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$.with Group 10 metal(0) complexes.

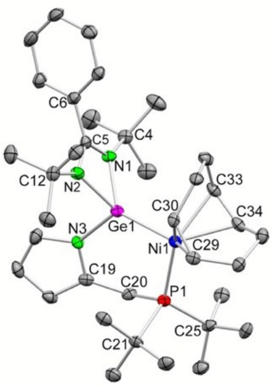


Fig. 4 XRD molecular structure of complex **3**$_{\mathbf{Ni\text{-}Ge}}$ (40% displacement ellipsoids, H atoms omitted for clarity). Ni1–C29 2.126(4), Ni1–C30 2.131(4), Ni1–C33 2.119(4), Ni1–C34 2.145(4), Ni1–P1 2.222(1), Ni1–Ge1 2.2439(7), Ge1–N1 2.013(3), Ge1–N2 2.004(3), Ge1–N3 1.921(3), C4–N1 1.474(5), C5–N1 1.330(5), C5–C6 1.495(5), C5–N2 1.344(4), C12–N2 1.492(5), C19–N3 1.383(4), C19–C20 1.491(5), C20–P1 1.869(4), C21–P1 1.899(4), C25–P1 1.900(4), {C29-C30$_{centroid}$}–Ni1–{C33-C34$_{centroid}$} 90.32(2), {C29-C30$_{centroid}$}–Ni1–Ge1 114.37(3), {C33-C34$_{centroid}$}–Ni1–Ge1 113.79(2), {C29-C30$_{centroid}$}–Ni1–P1 122.28(3), {C33-C34$_{centroid}$}–Ni1–P1 122.72(4), Ge1–Ni1–P1 95.00(4), N1–Ge1–N2 65.50(1), N1–Ge1–N3 97.7(1), N2–Ge1–N3 97.2(1), N1–Ge1–Ni1 130.0(1), N2–Ge1–Ni1 131.9(1), N3–Ge1–Ni1 120.0(1), N1–C5–N2 108.7(3).

NMR spectroscopy confirmed that **3**$_{\mathbf{Ni\text{-}Si}}$ and **3**$_{\mathbf{Ni\text{-}Ge}}$ contain one cod and one HT-phosphane ligand and that they behave as C_S symmetric molecules in solution. The molecular structure of **3**$_{\mathbf{Ni\text{-}Ge}}$ was determined by XRD. Fig. 4 shows that the Ni atom is in a distorted tetrahedral coordination environment. The chelating bite angle of the HT-phosphane ligand is a quite narrow for a tetrahedral complex, Ge1–Ni1–P1 95.00(4)° (ideal angle = 109.5°), being only 1.2° wider than the P1–Pd1–Si1 angle of **2**$_{\mathbf{Pd\text{-}Si}}$, 93.86(3)° (ideal angle = 90.0°).

Both **1**$_{\mathbf{Si}}$ and **1**$_{\mathbf{Ge}}$ reacted cleanly at room temperature with [M(PPh$_3$)$_4$] (M = Pd, Pt) to give the three-coordinated complexes [M{κ^2*E*,*P*-E(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(PPh$_3$)] (**4**$_{\mathbf{M\text{-}E}}$; M = Pd, Pt; E = Si, Ge) (Scheme 3). The use of an excess of HT-phosphane reagent had no effect on the outcome of these reactions. Probably the HT-phosphanes **1**$_{\mathbf{E}}$ ate too large to allow an appropriate fitting of two of them around the metal atom. The isolation of pure products from these reactions required several recrystallizations (in order to get rid of the accompanying PPh$_3$) and this reduced the final yields to 30-40 %. The similar solubility of PPh$_3$ and **4**$_{\mathbf{Pd\text{-}Ge}}$ avoided the isolation of a PPh$_3$-free sample of the metal complex.

NMR spectroscopy confirmed that, in solution, the compounds of type **4**$_{\mathbf{M\text{-}E}}$ behave as symmetric molecules (C_S) and that they contain one PPh$_3$ per HT-phosphane ligand; for example, the ^{31}P{^{1}H} NMR spectrum of **4**$_{\mathbf{Pt\text{-}Si}}$ consists of two doublets ($J_{P\text{-}P}$ = 118.4 Hz) with ^{195}Pt satellites ($J_{P\text{-}Pt}$ = 3521.7 and 4287.0 Hz). An XRD study on a crystal of **4**$_{\mathbf{Pd\text{-}Si}}$ (Fig. 5) established that the Pd atom is in a distorted triangular coordination environment. Again, the chelating bite angle of the HT-phosphane ligand, Si1–Pd1–P1 98.77(2)°, is narrower than expected (ideal angle for a planar triangular complex: 120.0°).

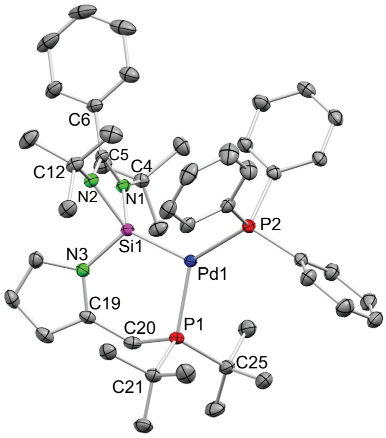


Fig. 5 XRD molecular structure of complex **4**$_{\mathbf{Pd\text{-}Si}}$ (30% displacement ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pd1–P1 2.3108(4), Pd1–P2 2.2881(4), Pd1–Si1 2.2622(4), Si1–N1 1.862(1), Si1–N2 1.858(1), Si1–N3 1.804(1), C4–N1 1.476(2), C5–N1 1.337(2), C5–C6 1.489(2), C5–N2 1.338(2), C12–N2 1.483(2), C19–N3 1.393(2), C19–C20 1.499(2), C20–P1 1.866(2), C21–P1 1.885(2), C25–P1 1.895(2), P1–Pd1–P2 131.06(2), P1–Pd1–Si1 98.77(2), P2–Pd1–Si1 130.18(2), N1–Si1–N2 70.06(6), N1–Si1–N3 101.21(6), N2–Si1–N3 99.70(6), N1–Si1–Pd1 130.31(5), N2–Si1–Pd1 128.86(5), N3–Si1–Pd1 116.06(5), N1–C5–N2 105.9(1).

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Conclusions

In summary, this work describes the syntheses of the first silylene-phosphane ($\mathbf{1_{Si}}$) and the second[13] germylene-phosphane ($\mathbf{1_{Ge}}$) whose coordination abilities have been proven by reactions with transition-metal complexes. The reactivity studies have indicated that both $\mathbf{1_{Si}}$ and $\mathbf{1_{Ge}}$ are excellent chelating ligands for square-planar and octahedral complexes (their bite angle is close to 90^o) and that they can also participate as chelating ligands in tetrahedral and triangular-planar complexes, leading to slightly distorted coordination geometries. No doubt, the offering of $\mathbf{1_{Si}}$ and $\mathbf{1_{Ge}}$ to the chemical community will open up new pathways toward TM complexes for which interesting structural, bonding and catalytic properties can be anticipated.

Experimental section

General data

All reactions and product manipulations were carried out under argon in a drybox or using Schlenk-vacuum line techniques. Solvents were dried over appropriate desiccating reagents and were distilled under argon before use. The compounds HpyrmP^{t}Bu$_2$,[12b] E(^{t}Bu$_2$bzam)Cl (E = Si,[14] Ge;[15]) [PdCl$_2$(MeCN)$_2$],[16] [PtCl$_2$(cod)][17] and [Pt(PPh$_3$)$_4$][18] were prepared following published procedures. All remaining reagents were purchased from commercial sources and were stored under argon in a drybox. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. NMR spectra were run on Bruker NAV-400 and AC-300 instruments, using as standards the residual protic solvent resonance for ^{1}H [δ(C*H*Cl$_3$) 7.26 ppm; δ(C$_6$*H*D$_5$) 7.16 ppm; δ(C*H*DCl$_2$) 5.32 ppm], the solvent resonance for ^{13}C [δ(*C*DCl$_3$) 77.16 ppm; δ(*C*$_6$D$_6$) 128.10 ppm; δ(*C*D$_2$Cl$_2$) 54.00 ppm], external 85% H$_3$PO$_4$ for ^{31}P (δ 0.00 ppm) and external SiMe$_4$ in CDCl$_3$ for ^{29}Si (δ = 0.00 ppm). Microanalyses were obtained with a FlashEA112 (Thermo-Finnigan) microanalyzer. High-resolution mass spectra (HRMS) were obtained with a Bruker Impact II mass spectrometer operating in the ESI-Q-ToF positive mode; data given refer to the most abundant isotopomer of the species with the greatest mass. CHN microanalysis and/or mass spectra were not obtained for the products that were very air- and/or moisture-sensitive.

Synthetic procedures and characterization data

Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$ ($\mathbf{1_{Si}}$): Li^{n}Bu (0.75 mL, 1.6 M in hexanes, 1.2 mmol) was dropwise added to a cold (–78 ^{o}C) solution of HpyrmP^{t}Bu$_2$ (2.5 mL, 0.4 M in toluene, 1.0 mmol) in diethyl ether (2 mL). The resulting bright yellow solution was allowed to reach the room temperature, was stirred for 2 h and was added to a suspension of Si(^{t}Bu$_2$bzam)Cl (0.295 g, 1.0 mmol) in diethyl ether (2 mL). The resulting orange suspension was stirred for 18 h. Solvents were removed under vacuum and the residue was extracted into hexane (4 x 5 mL). A white solid was separated by decantation from a clear yellow solution that was evaporated to dryness to give $\mathbf{1_{Si}}$ as a pale yellow solid (0.436 g, 90 %). ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): δ 7.03–6.92 (m, 6 H, C*H*s of Ph and 1 C*H* of pyrrole), 6.58 (s, 1 H, 1 C*H* of pyrrole), 6.48 (s, 1 H, 1 C*H* of pyrrole), 3.63 (s, 2 H, 1 C*H*$_2$ of PCH$_2$), 1.26 (d, $J_{\text{H-P}}$ = 10.2 Hz, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.04 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 164.3 (s, N*C*N), 137.8 (d, $J_{\text{C-P}}$ = 15.4 Hz, pyrrole *C*^{2}), 133.8 (s, *C$_{ipso}$* of Ph), 130.1–128.0 (m, *C*Hs of Ph),120.5 (s, pyrrole *C*H), 110.5 (d, $J_{\text{C-P}}$ = 9.1 Hz, pyrrole *C*H), 109.8 (s, 1 pyrrole *C*H), 53.2 (s, 2 *C* of 2 N^{t}Bu), 32.0 (d, $J_{\text{C-P}}$ = 25.8 Hz, 2 *C* of P^{t}Bu$_2$), 31.5 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.4 (d, $J_{\text{C-P}}$ = 13.1 Hz, 6 *C*H$_3$ of P^{t}Bu$_2$), 21.6 (d, $J_{\text{C-P}}$ = 24.1 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz, 298 K): δ 28.2 (s) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz, 298 K): δ –18.8 (d, $J_{\text{Si-P}}$ = 14.2 Hz) ppm.

Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$ ($\mathbf{1_{Ge}}$): This compound was prepared as a pale orange solid following the procedure described above for $\mathbf{1_{Si}}$. Reagents: HpyrmP^{t}Bu$_2$ (2.5 mL, 0.4 *M* in toluene, 1.0 mmol), BuLi (0.75 mL, 1.6 M in hexanes, 1.2 mmol), Ge(^{t}Bu$_2$bzam)Cl (0.340 g, 1.0 mmol). Yield: 0.286 g, 54 %. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): δ 7.25 (s, 1 H, pyrrole C*H*), 7.09–6.92 (m, 5 H, C*H*s of Ph), 6.58 (s, 1 H, pyrrole C*H*), 6.47 (s, 1 H, pyrrole C*H*), 3.46 (s, 2 H, PC*H*$_2$),1.24 (d, $J_{\text{H-P}}$ = 9.0 Hz, 18 H, 6 C*H$_3$* de P^{t}Bu$_2$), 0.99 (s, 18 H, 6 C*H$_3$* de 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 169.8 (s, N*C*N), 136.0 (d, $J_{\text{C-P}}$ = 11.1 Hz, pyrrole *C*^{2}), 135.7 (*C*$_{\text{ipso}}$ of Ph), 129.8–127.7 (m, *C*Hs of Ph), 122.2 (s, pyrrole *C*H), 109.4 (d, $J_{\text{C-P}}$ = 5.0 Hz, pyrrole *C*H), 108.5 (s, pyrrole *C*H), 53.1 (s, 2 *C* of 2 N^{t}Bu), 32.1 (d, $J_{\text{C-P}}$ = 26.2 Hz, 2 *C* of P^{t}Bu$_2$), 31.9 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.2 (d, $J_{\text{C-P}}$ = 12.1 Hz, 6 *C*H$_3$ de P^{t}Bu$_2$), 22.2 (d, $J_{\text{C-P}}$ = 24.2 Hz, P*C*H$_2$) ppm.^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz, 298 K): δ 28.3 (s) ppm.

[NiCl$_2${κ^2*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] ($\mathbf{2_{Ni\text{-}Si}}$): Silylene $\mathbf{1_{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of [NiCl$_2$(dme)] (0.013 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give $\mathbf{2_{Ni\text{-}Si}}$ as a pale brown solid (0.025 g, 69 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$N$_3$NiPSi (M$_W$ = 613.34 amu): C, 54.83; H, 7.56; N, 6.85; found: C, 54.92; H,7.65; N, 6.82. (+)-ESI HRMS: *m/z* 576.1960, calcd. for C$_{28}$H$_{46}$ClN$_3$NiPSi [*M* – Cl]$^+$: 576.2241. ^{1}H NMR (C$_6$D$_6$, 400.5 MHz, 298 K): δ 7.57 (d, $J_{\text{H-P}}$ = 9.0 Hz, 1 C*H* of Ph), 7.09 (s, 1 H, pyrrole C*H*), 6.93–6.79 (m, 4 H, 4 C*H* of Ph), 6.38 (s, 1 H, pyrrole C*H*), 6.04 (s, 1 H, pyrrole C*H*), 2.93 (d, $J_{\text{H-P}}$ = 9.0 Hz, 2 H, C*H$_2$*P), 1.52 (d, $J_{\text{H-P}}$ = 15.0 Hz, 18 H, 6 C*H$_3$* of P^{t}Bu$_2$), 1.18 (s, 18 H, 6 C*H$_3$* of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 176.6 (s, N*C*N), 132.7 (s, pyrrole *C*^{2}), 130.9–127.6 (m, *C*Hs + *C*$_{\text{ipso}}$ of Ph), 122.2 (s, pyrrole *C*H), 111.7 (d, $J_{\text{C-P}}$ = 5.0 Hz, pyrrole *C*H), 111.2 (s, pyrrole *C*H), 54.9 (s, 2 *C* of 2 N^{t}Bu),37.2 (d, $J_{\text{C-P}}$ = 14.1 Hz, 2 *C* of P^{t}Bu$_2$), 31.0 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.5 (s, 6 Me of P^{t}Bu$_2$), 22.3 (d, $J_{\text{C-P}}$ = 21.8 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.1 MHz, 298 K): δ 49.1 (s) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz, 298 K): δ –27.7 (d, $J_{\text{Si-P}}$ = 81.3 Hz) ppm.

[NiCl$_2${κ^2*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] ($\mathbf{2_{Ni\text{-}Ge}}$): Germylene $\mathbf{1_{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of [NiCl$_2$(dme)] (0.013 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give $\mathbf{2_{Ni\text{-}Ge}}$ as a purple solid (0.025 g, 63 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$NiP (M$_W$ = 657.88 amu): C, 51.12; H, 7.05; N, 6.39; found: C, 51.20; H, 7.13; N, 6.37. (+)-ESI HRMS: *m/z* 680.1135, calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$NaNiP [*M* + Na]$^+$: 680.1269. ^{1}H NMR (CD$_2$Cl$_2$, 400.5 MHz, 298 K): δ 7.59–7.49 (m, 5 H, 5 C*H* of Ph), 7.05 (s, 1 H, pyrrole C*H*), 6.20 (s, 1 H, pyrrole C*H*), 6.03 (s, 1 H, pyrrole

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C*H*), 3.33 (s, br, 2 H, *C*H$_2$P), 1.57 (s, br, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.23 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz, 298 K): δ 175.9 (s, N*C*N), 132.4 (s, pyrrole *C*^{2}), 132.1 (s, *C*$_{\text{ipso}}$ of Ph), 131.3–128.6 (m, *C*Hs of Ph), 123.1 (s, pyrrole *C*H), 111.4 (s, pyrrole *C*H), 110.3 (s, pyrrole *C*H), 55.5 (s, 2 *C* of 2 N^{t}Bu), 39.3 (s, 2 *C* of P^{t}Bu$_2$), 31.8 (s, 6 *C*H$_3$ of N^{t}Bu), 30.0 (s, 6 *C*H$_3$ of P^{t}Bu$_2$), 22.1 (d, $J_{\text{C-P}}$ = 22.1 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162.1 MHz, 298 K): δ 63.4 (s) ppm.

[PdCl$_2${κ^2*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (2$_{\text{Pd-Si}}$): Silylene **1**$_{\text{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of [PdCl$_2$(MeCN)$_2$] (0.016 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give **2**$_{\text{Pd-Si}}$ as a pale brown solid (0.034 g, 86 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$N$_3$PPdSi (M$_{\text{W}}$ = 661.07 amu): C, 50.87; H, 7.01; N, 6.36; found: C, 50.95; H, 7.08; N, 6.29. (+)-ESI HRMS: *m/z* 626.1644, calcd. for C$_{28}$H$_{46}$ClN$_3$PPdSi [*M* – Cl]$^+$: 626.1921. ^{1}H NMR (C$_6$D$_6$, 400.5 MHz, 298 K): δ 7.95 (d, $J_{\text{H-P}}$ = 7.8 Hz, 1 C*H* of Ph),7.13 (dt, $J_{\text{H-H}}$= 2.9 Hz; 1.4 Hz, 1 H, pyrrole C*H*), 7.03–6.89 (m, 4 H, 4 C*H* of Ph), 6.39 (q, $J_{\text{H-H}}$= 2.9 Hz ,1 H, pyrrole C*H*), 6.08 (m, 1 H, pyrrole C*H*), 3.06 (d, $J_{\text{H-P}}$ = 9.4 Hz, 2 H, *C*H$_2$P), 1.43 (d, $J_{\text{H-P}}$ = 14.4 Hz, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.10 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 177.7 (s, N*C*N), 133.4 (s, pyrrole *C*^{2}), 131.1–127.2 (m, *C*Hs of Ph), 123.3 (s, pyrrole *C*H), 112.6 (d, $J_{\text{C-P}}$ = 5.4 Hz, pyrrole *C*H), 111.2 (s, pyrrole *C*H), 55.0 (s, 2 *C* of 2 N^{t}Bu), 38.1 (d, $J_{\text{C-P}}$ = 17.5 Hz, 2 *C* of P^{t}Bu$_2$), 31.0 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.3 (s, 6 *C*H$_3$ of P^{t}Bu$_2$), 22.3 (d, $J_{\text{C-P}}$ = 22.1 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.1 MHz, 298 K): δ 54.9 (s) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz, 298 K): δ –0.46 (d, $J_{\text{Si-P}}$ = 11.7 Hz) ppm.

[PdCl$_2${κ^2*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (2$_{\text{Pd-Ge}}$): Germylene **1**$_{\text{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of [PdCl$_2$(MeCN)$_2$] (0.016 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h a solid was precipitated. The solution was removed and the solid was dried under vacuum to give **2**$_{\text{Pd-Ge}}$ as a yellow solid (0.026 g, 62 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$PPd (M$_{\text{W}}$ = 705.62 amu): C, 47.66; H, 6.57; N, 5.96; found: C, 47.74; H, 6.65; N, 5.89. (+)-ESI HRMS: *m/z* 728.0630, calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$NaPPd [*M* + Na]$^+$: 728.0960. ^{1}H NMR (CD$_2$Cl$_2$, 400.5 MHz, 298 K): δ 7.78 (m, 1 C*H* of Ph), 7.59–7.49 (m, 4 H, 4 C*H* of Ph), 7.13 (td, $J_{\text{H-H}}$ = 3.0, 1.7 Hz, 1 H, pyrrole C*H*), 6.26 (td, $J_{\text{H-H}}$ = 3.0, 1.7 Hz ,1 H, pyrrole C*H*), 6.08 (m, 1 H, pyrrole C*H*), 3.33 (d, $J_{\text{H-P}}$ = 9.4 Hz, 2 H, *C*H$_2$P), 1.47 (d, $J_{\text{H-P}}$ = 14.7 Hz, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.17 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz, 298 K): δ 176.6 (s, N*C*N), 131.8 (s, pyrrole *C*^{2}), 131.5 (s, *C*H of Ph), 131.2 (s, *C*$_{\text{ipso}}$ of Ph), 130.7 (s, *C*H of Ph), 129.0 (s, *C*H of Ph), 128.7 (s, *C*H of Ph), 128.65 (s, *C*H of Ph), 123.8 (s, pyrrole *C*H), 112.4 (d, $J_{\text{C-P}}$ = 5.1 Hz, pyrrole *C*H), 110.6 (s, pyrrole *C*H), 55.8 (s, 2 *C* of 2 N^{t}Bu), 39.23 (d, $J_{\text{C-P}}$ = 16.4 Hz, 2 *C* of P^{t}Bu$_2$), 31.5 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.4 (s, 6 *C*H$_3$ of P^{t}Bu$_2$), 22.7 (d, $J_{\text{C-P}}$ = 22.1 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162.1 MHz, 298 K): δ 56.2 (s) ppm.

[PtCl$_2${κ^2*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (2$_{\text{Pt-Si}}$): Silylene **1**$_{\text{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of [PtCl$_2$(cod)] (0.022 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give **2**$_{\text{Pt-Si}}$ as a brown solid (0.042 g, 90 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$N$_3$PPtSi (M$_{\text{W}}$ = 749.73 amu): C, 44.86; H, 6.18; N, 5.61; found: C, 44.93; H, 6.23; N 5.57. (+)-ESI HRMS: *m/z* 715.2221, calcd. for C$_{28}$H$_{47}$ClN$_3$PPtSi [*M* – Cl + H]$^+$: 715.2611. ^{1}H NMR (C$_6$D$_6$, 400.5 MHz, 298 K): δ 7.92 (m, 1 C*H* of Ph), 7.12 (dt, $J_{\text{H-H}}$= 2.9, 1.5 Hz, 1 H, pyrrole C*H*), 7.03–6.90 (m, 4 H, 4 C*H* of Ph), 6.38 (td, $J_{\text{H-H}}$= 2.9, 1.5 Hz, 1 H, pyrrole C*H*), 6.06 (m, 1 H, pyrrole C*H*), 3.28 (dd, $J_{\text{H-P}}$ = 10.3 Hz, $J_{\text{H-H}}$ = 1.0 Hz, 2 H, *C*H$_2$P), 1.42 (d, $J_{\text{H-P}}$ = 14.2 Hz, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.18 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 178.2 (s, N*C*N), 133.4 (d, $J_{\text{C-P}}$ = 5.4 Hz, pyrrole *C*^{2}), 131.2–127.5 (m, *C*$_{\text{ipso}}$ + *C*Hs of Ph), 123.2 (s, pyrrole *C*H), 112.8 (d, $J_{\text{C-P}}$ = 6.1 Hz, pyrrole *C*H), 111.3 (s, pyrrole *C*H), 54.9 (s, 2 *C* of 2 N^{t}Bu), 37.7 (d, $J_{\text{C-P}}$ = 26.2 Hz, 2 *C* of P^{t}Bu$_2$), 30.8 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.3 (s, 6 *CH$_3$* of P^{t}Bu$_2$), 22.4 (d, $J_{\text{C-P}}$ = 31.3 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.1 MHz, 298 K): δ 32.8 (s, sat, $J_{\text{P-Pt}}$ = 3701.2 Hz) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz, 298 K): δ –16.8 (d, sat, $J_{\text{Si-P}}$ = 13.1 Hz, $J_{\text{Si-Pt}}$ = 2298.3 Hz) ppm.

[PtCl$_2${κ^2*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}] (2$_{\text{Pt-Ge}}$): Germylene **1**$_{\text{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of [PtCl$_2$(cod)] (0.022 g, 0.06 mmol) in toluene (3 mL). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (2 mL) to give **2**$_{\text{Pt-Ge}}$ as a pale pink solid (0.038 g, 90 %). Anal. (%) Calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$PPt (M$_{\text{W}}$ = 794.28 amu): C, 42.34; H, 5.84; N, 5.29; found: C, 42.46; H, 5.93; N 5.24. (+)-ESI HRMS: *m/z* 816.1184, calcd. for C$_{28}$H$_{46}$Cl$_2$GeN$_3$NaPPt [*M* + Na]$^+$: 816.1562. ^{1}H NMR (CD$_2$Cl$_2$, 400.5 MHz, 298 K): δ 7.77 (m, 1 C*H* of Ph), 7.65–7.34 (m, 4 H, 4 C*H* of Ph),7.10 (m, 1 H, pyrrole C*H*), 6.21 (m, 1 H, pyrrole C*H*), 6.09 (m, 1 H, pyrrole C*H*), 3.53 (d, $J_{\text{H-P}}$ = 10.0 Hz, 2 H, *C*H$_2$P), 1.45 (d, $J_{\text{H-P}}$ = 14.4 Hz, 18 H, 6 CH$_3$ of P^{t}Bu$_2$), 1.17 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz, 298 K): δ 176.9 (s, N*C*N), 132.0 (d, $J_{\text{C-P}}$ = 6.0.Hz, pyrrole *C*^{2}), 131.5 (s, *C*H of Ph), 131.3 (s, *C*$_{\text{ipso}}$ of Ph), 130.8 (s, *C*H of Ph), 129.0 (s, *C*H of Ph), 128.8(s, *C*H of Ph), 128.6 (s, *C*H of Ph), 123.7 (s, pyrrole *C*H), 112.8 (d, $J_{\text{C-P}}$ = 6.0 Hz, pyrrole *C*H), 110.3 (s, pyrrole *C*H), 55.7 (s, 2 *C* of 2 N^{t}Bu), 38.4 (d, $J_{\text{C-P}}$ = 25.2 Hz, 2 *C* of P^{t}Bu$_2$), 31.4 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.5 (d, $J_{\text{C-P}}$ = 2.2 Hz, 6 CH$_3$ of P^{t}Bu$_2$), 22.5 (d, $J_{\text{C-P}}$ = 30.8 Hz, P*C*H$_2$) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162.1 MHz, 298 K): δ 28.80 (s, sat, $J_{\text{P-Pt}}$ = 3553.2 Hz) ppm.

[Ni{κ^2*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(cod)] (3$_{\text{Ni-Si}}$): Silylene **1**$_{\text{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of [Ni(cod)$_2$] (0.017 g, 0.06mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue was washed with hexane (1 mL) to give **3**$_{\text{Ni-Si}}$ as an orange solid (0.014 g, 40 %). Anal. (%) Calcd. for C$_{36}$H$_{58}$N$_3$NiPSi (M$_{\text{W}}$ = 650.62 amu): C, 66.46; H, 8.98; N, 6.46; found: C, 66.53; H, 9.04; N, 6.43. (+)-ESI HRMS: *m/z* 649.3510, calcd. for C$_{36}$H$_{58}$N$_3$NiPSi [*M*]$^+$: 649.3491. ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 298 K): δ 7.39 (s, 1 H, C*H* of Ph), 6.98 (m, 5 H, 4 C*H* of Ph and 1 pyrrole C*H*), 6.58 (s, 1 H, pyrrole C*H*), 6.29 (s, 1 H, pyrrole CH), 4.70 (m, 2 H, 2 C*H* of cod), 4.48 (m, 2 H, 2 C*H* of cod), 3.22 (s, 2 H, *C*H$_2$P), 2.87–2.10 (m, 8 H, 4 C*H*$_2$ of cod), 1.29 (d, $J_{\text{H-P}}$ = 15.0 Hz, 18 H, 6 C*H*$_3$ of P^{t}Bu$_2$), 1.08 (s, 18 H, 6 C*H*$_3$ of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): δ 171.3 (s, N*C*N), 135.6 (s, pyrrole *C*^{2}), 132.7 (s, *C*$_{\text{ipso}}$ of Ph), 130.4–127.6 (m, 5 *C*Hs of Ph), 121.2 (s, pyrrole *C*H), 110.7 (d, $J_{\text{C-P}}$ = 5.3 Hz, pyrrole *C*H), 108.7 (s, pyrrole *C*H), 80.1 (d, $J_{\text{C-P}}$ = 8.0 Hz, 2 *C*H of cod), 78.2 (d, $J_{\text{C-P}}$ = 4.1 Hz, 2 *C*H of cod), 53.3 (s, 2 *C* of 2 N^{t}Bu), 35.6 (s, 2 *C* of P^{t}Bu$_2$), 32.9 (d, $J_{\text{C-P}}$ = 6.0 Hz, 2 *C*H$_2$ of cod), 32.5 (s, 2 *C*H$_2$ of cod), 30.9 (s, 6 *C*H$_3$ of 2 N^{t}Bu), 30.4 (s, 6 *C*H$_3$ of P^{t}Bu$_2$), 26.5 (d, $J_{\text{C-P}}$ = 14.8 Hz, P*C*H$_2$) ppm.^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz, 298 K): δ 55.0 (s) ppm. ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 79.5 MHz, 298 K): δ 56.8 (d, $J_{\text{Si-P}}$ = 26.3 Hz) ppm.

[Ni{κ^2*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(cod)] (3$_{\text{Ni-Ge}}$): Germylene **1**$_{\text{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of [Ni(cod)$_2$] (0.017 g, 0.06 mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue was washed with

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hexane (1 mL) to give **5**$_{\mathbf{Ge}}$ as a pale red solid (0.025 g, 59 %). Anal. (%) Calcd. for $C_{36}H_{58}GeN_3NiP$ (M_W = 695.16 amu): C, 62.20; H, 8.41; N, 6.05; found: C, 62.38; H, 8.48; N 6.01. (+)-ESI HRMS: *m/z* 696.2691, calcd. for $C_{36}H_{59}GeN_3NiP$ $[M + H]^+$: 696.3011. ^{1}H NMR (C_6D_6, 400.5 MHz, 298 K): δ 7.38–6.94 (m, 6 H, 5 C*H* of Ph + pyrrole C*H*), 6.64 (s, 1 H, pyrrole C*H*), 6.32 (s, 1 H, pyrrole C*H*), 4.77 (m, 2 H, 2 C*H* of cod), 4.63 (m, 2 H, 2 C*H* of cod), 3.25 (s, 2 H, CH_2P), 2.72–2.40 (m, 8 H, 4 CH_2 of cod),1.27 (d, $J_{\text{H-P}}$ = 12.0 Hz, 6 CH_3 of P^{t}Bu$_2$), 1.05 (s, 18 H, 6 CH_3 of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 172.5 (s, N*C*N), 134.6 (s, pyrrole C^2), 134.4 (s, C_{ipso} of Ph), 130.3–127.6 (m, *C*Hs of Ph), 121.7 (s, pyrrole *C*H), 110.3 (d, $J_{\text{C-P}}$ = 4.2 Hz, pyrrole *C*H), 108.0 (s, pyrrole *C*H), 80.3 (d, $J_{\text{C-P}}$ = 7.2 Hz, 2 *C*H of cod), 80.0 (d, $J_{\text{C-P}}$ = 3.4 Hz, 2 *C*H of cod), 53.3 (s, 2 *C* of 2 N^{t}Bu), 35.2 (s, 2 *C* of P^{t}Bu$_2$), 33.0 (s, 2 CH_2 of cod), 32.8 (d, $J_{\text{C-P}}$ = 5.2 Hz, 2 CH_2 of cod), 31.3 (s, 6 CH_3 of 2 N^{t}Bu), 30.1 (s, 3 CH_3 of P^{t}Bu$_2$), 29.2 (s, 3 CH_3 of P^{t}Bu), 26.4 (d, $J_{\text{C-P}}$ = 12.3 Hz, PCH_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 162.1 MHz, 298 K): δ 51.8 (s) ppm.

[Pd{κ²*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(PPh$_3$)] (4$_{\text{Pd-Si}}$): Silylene **1**$_{\mathbf{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of $[Pd(PPh_3)_4]$ (0.069 g, 0.06 mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue was recrystallized from to give **4**$_{\mathbf{Pd\text{-}Si}}$ as a pale orange solid (0.014 g, 40 %). Anal. (%) Calcd. for $C_{46}H_{61}N_3P_2PdSi$ (M_W = 852.45 amu): C, 64.81; H, 7.21; N, 4.93; found: C, 64.87; H, 7.29; N 4.89. (+)-ESI HRMS: *m/z* 923.2355, calcd. for $C_{49}H_{67}N_4OP_2PdSi$ $[M + CH_3CN + CH_3OH - H]^+$: 923.3611. ^{1}H NMR ($C_6D_6$, 300.1 MHz, 298 K): δ 8.00 (t, $J_{\text{H-P}}$ = 8.3 Hz, 6 H, 6 C*H* of 3 Ph), 7.39–6.96 (m, 15 H, 14 C*H* of 4 Ph + 1 pyrrole C*H*), 6.60 (s, 1 H, pyrrole C*H*), 6.39 (s, 1 H, pyrrole C*H*), 3.52 (s, 2 H, CH_2P), 1.25 (d, $J_{\text{H-P}}$ = 11.6 Hz, 18 H, 6 CH_3 of P^{t}Bu$_2$), 1.05 (s, 18 H, 6 CH_3 of 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 165.3 (s, N*C*N), 141.9 (m, pyrrole C^2), 131.0–127.8 (m, C_{ipso}s + *C*Hs of Phs), 122.7 (s, pyrrole *C*H), 111.8 (d, $J_{\text{C-P}}$ = 5.5 Hz, pyrrole *C*H), 108.5 (s, pyrrole *C*H), 53.4 (s, 2 *C* of 2 N^{t}Bu), 34.7 (d, $J_{\text{C-P}}$ = 9.1 Hz, 2 *C* of P^{t}Bu$_2$), 31.6 (6 CH_3 of 2 N^{t}Bu), 30.2 (d, $J_{\text{C-P}}$ = 10.9 Hz, 6 CH_3 of P^{t}Bu$_2$), 26.4 (s, PCH_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 162.1 MHz, 298 K): δ 49.3 (d, $J_{\text{P-P}}$= 59.2 Hz), 35.2 (d, $J_{\text{P-P}}$ = 59.2 Hz) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 79.5 MHz, 298 K): δ 19.3 (dd, $J_{\text{Si-P}}$ = 69.7, 42.9 Hz) ppm.

Attempted synthesis of [Pd{κ²*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(PPh$_3$)] (4$_{\text{Pd-Ge}}$): Germylene **1**$_{\mathbf{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of $[Pd(PPh_3)_4]$ (0.069 g, 0.06mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue, which contained a mixture of **4**$_{\mathbf{Pd\text{-}Ge}}$ and PPh_3 (NMR analysis), was recrystallized several times from hexane, but **4**$_{\mathbf{Pd\text{-}Ge}}$ could not be obtained free of PPh_3. ^{31}P{^{1}H} NMR (C_6D_6, 162.1 MHz, 298 K): δ 54.0 (s) ppm.

[Pt{κ²*P*,*Si*-Si(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(PPh$_3$)] (4$_{\text{Pt-Si}}$): Silyene **1**$_{\mathbf{Si}}$ (0.030 g, 0.06 mmol) was added to a solution of $[Pt(PPh_3)_4]$ (0.075 g, 0.06 mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue was recrystallized several times from hexane to give **4**$_{\mathbf{Pt\text{-}Si}}$ as an orange solid (0.018 g, 32 %). Anal. (%) Calcd. for $C_{46}H_{61}N_3P_2PtSi$ (M_W = 941.12 amu): C, 58.71; H, 6.53; N, 4.46; found C, 58.76; H, 6.60; N, 4.38. (+)-ESI HRMS: *m/z* 941.3685, calcd. for $C_{46}H_{62}N_3P_2PtSi$ $[M + H]^+$: 941.3839. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 8.01 (t, $J_{\text{H-P}}$ = 8.9 Hz, 6 H of 3 Ph), 7.39–6.98 (m, 15 H, 14 C*H* of 4 Ph + pyrrole C*H*), 6.60 (s, 1 H, pyrrole C*H*), 6.37 (s, 1 H, pyrrole C*H*), 3.73 (s, 2 H, CH_2 de PCH_2), 1.27 (d, $J_{\text{H-P}}$ = 12.0 Hz, 18 H, 6 CH_3 de P^{t}Bu$_2$), 1.04 (s, 18 H, 6 CH_3 de 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 167.6 (s, N*C*N), 144.2 (m, 3 C_{ipso} of PPh$_3$), 136.9 (s, pyrrole C^2), 133.2 (s, C_{ipso} of Ph), 130.5–127.8 (m, *C*Hs of Phs), 123.2 (s, pyrrole *C*H), 112.2 (d, $J_{\text{C-P}}$ = 6.0 Hz, pyrrole *C*H), 108.4 (s, pyrrole *C*H), 53.5 (s, 2 *C* de 2 N^{t}Bu), 37.5 (s, sat, $J_{\text{C-Pt}}$ = 40.3 Hz, 2 *C* de P^{t}Bu$_2$), 31.6 (s, 6 CH_3 de 2 N^{t}Bu), 30.2 (d, $J_{\text{C-P}}$ = 8.5 Hz, 6 CH_3 de P^{t}Bu$_2$), 26.4 (d, sat, $J_{\text{C-Pt}}$ = 16.7 Hz, $J_{\text{C-P}}$ = 11.0 Hz, CH_2 de PCH_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 162.1 MHz, 298 K): δ 88.1 (d, sat, $J_{\text{P-P}}$ = 118.4 Hz, $J_{\text{P-Pt}}$ = 3521.7), 66.2 (d, sat, $J_{\text{P-P}}$ = 118.4 Hz, $J_{\text{P-Pt}}$ = 4287.0 Hz) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 79.5 MHz, 298 K): δ 70.3 (dd, $J_{\text{Si-P}}$ = 105.7, 65.9 Hz) ppm.

[Pt{κ²*P*,*Ge*-Ge(^{t}Bu$_2$bzam)pyrmP^{t}Bu$_2$}(PPh$_3$)] (4$_{\text{Pt-Ge}}$): Germylene **1**$_{\mathbf{Ge}}$ (0.032 g, 0.06 mmol) was added to a solution of $[Pt(PPh_3)_4]$ (0.075 g, 0.06 mmol) in toluene (3 mL). After stirring for 4 h, the solvent was removed under reduced pressure and the residue was recrystallized several times from hexane to give **4**$_{\mathbf{Pt\text{-}Ge}}$ as an orange solid (0.021 g, 36 %). Anal. (%) Calcd. for $C_{46}H_{61}GeN_3P_2Pt$ (M_W = 985.66 amu): C, 56.05; H, 6.24; N, 4.26; found C, 56.17; H, 6.33; N 4.21. (+)-ESI HRMS: *m/z* 963.3692, calcd. for $C_{41}H_{60}GeN_3NaOP_2Pt$ $[M - Ph + MeOH + Na]^+$: 963.2979. ^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ 8.01 (t, $J_{\text{H-P}}$ = 8.3 Hz, 6 H of 3 Ph), 7.39–6.96 (m, 15 H, 14 C*H* of 4 Ph + pyrrole C*H*), 6.66 (s, 1 H, pyrrole C*H*), 6.39 (s, 1 H, pyrrole C*H*), 3.76 (s, 2 H, CH_2 de PCH_2), 1.29 (d, $J_{\text{H-P}}$ = 12.0 Hz, 18 H, 6 CH_3 de P^{t}Bu$_2$), 1.01 (s, 18 H, 6 CH_3 de 2 N^{t}Bu) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 169.9(s, N*C*N), 153.0 (m, 3 C_{ipso} of PPh$_3$), 137.9 (s, pyrrole C^2), 134.9 (s, C_{ipso} of Ph), 129.9–127.8 (m, *C*Hs of Phs), 123.8 (s, pyrrole *C*H), 111.9 (d, $J_{\text{C-P}}$ = 5.4 Hz, pyrrole *C*H), 107.5 (s, pyrrole *C*H), 53.7 (s, 2 *C* de 2 N^{t}Bu), 36.8 (m, 2 *C* de P^{t}Bu$_2$), 31.8 (s, 6 CH_3 de 2 N^{t}Bu), 30.0 (d, $J_{\text{C-P}}$ = 8.3 Hz, 6 CH_3 de P^{t}Bu$_2$), 25.5 (d, $J_{\text{C-P}}$ = 14.2 Hz, CH_2 de PCH_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 298 K): δ 79.5 (d, sat, $J_{\text{P-P}}$ = 181.3 Hz, $J_{\text{P-Pt}}$ = 4677.0 Hz), 60.9 (d, sat, $J_{\text{P-P}}$ = 181.3 Hz), $J_{\text{P-Pt}}$ = 5788.5 Hz) ppm.

X-Ray diffraction analyses

Crystals of **1**$_{\mathbf{Si}}$, **2**$_{\mathbf{Pd\text{-}Si}}$·THF, **3**$_{\mathbf{Ni\text{-}Ge}}$ and **4**$_{\mathbf{Pd\text{-}Si}}$ were analyzed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table S1. Diffraction data were collected on a Bruker D8 Venture (for **1**$_{\mathbf{Si}}$; MoKα radiation), an Oxford Diffraction Xcalibur Rubi Geminy (for **3**$_{\mathbf{Ni\text{-}Ge}}$; MoKα radiation) and an Oxford Diffraction Xcalibur Onyx Nova (for **2**$_{\mathbf{Pd\text{-}Si}}$·THF and **4**$_{\mathbf{Pd\text{-}Si}}$; CuKα radiation) single crystal diffractometers. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in SADABS-2016/2[19] (for **1**$_{\mathbf{Si}}$) and CrysAlisPro RED[20] (for **2**$_{\mathbf{Pd\text{-}Si}}$·THF, **3**$_{\mathbf{Ni\text{-}Ge}}$ and **4**$_{\mathbf{Pd\text{-}Si}}$). The structures were solved using SIR-97.[221] Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.[22] All non-H atoms were refined anisotropically. H atoms were set in calculated positions and were refined riding on their parent atoms. The WINGX program system[23] was used throughout the structure determinations. The molecular plots were made with MERCURY.[24] CCDC deposition numbers: 2001500 (**1**$_{\mathbf{Si}}$), 2001501 (**2**$_{\mathbf{Pd\text{-}Si}}$·THF), 2001502 (**3**$_{\mathbf{Ni\text{-}Ge}}$) and 2001503 (**4**$_{\mathbf{Pd\text{-}Si}}$).

Computational details

Structure optimizations were performed with the Gaussian09[25] suite of programs, using the wB97XD6[26] functional, which includes the second generation of Grimme's dispersion interaction correction,[27] and the cc-pVDZ[28] basis set (for all atoms). Frequency calculations confirmed the optimized structures as energy minima (zero imaginary eigenvalues). Orbital calculations were performed with the NBO[29] package.

Conflicts of interest

There are no conflicts to declare.

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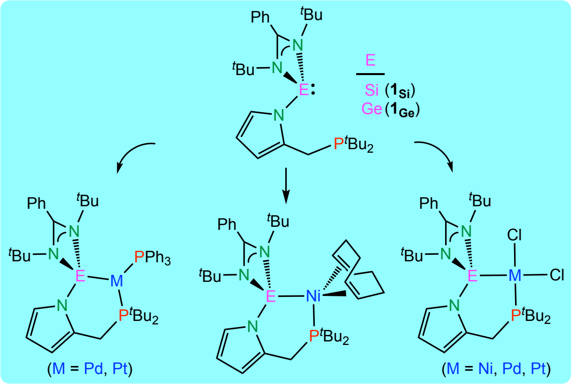
Figure and Text for the Table of Contents



The silylene- and germylene-decorated phosphanes $\mathbf{1}_{\mathbf{Si}}$ and $\mathbf{2}_{\mathbf{Ge}}$ have been prepared and their coordination abilities have been proven by reactions with transition-metal complexes.