

## ELECTRONIC SUPPORTING INFORMATION

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

Javier A. Cabeza,<sup>a\*</sup> Pablo García-Álvarez,<sup>a</sup> Carlos J. Laglera-Gándara<sup>a</sup> and Enrique Pérez-Carreño<sup>b</sup>

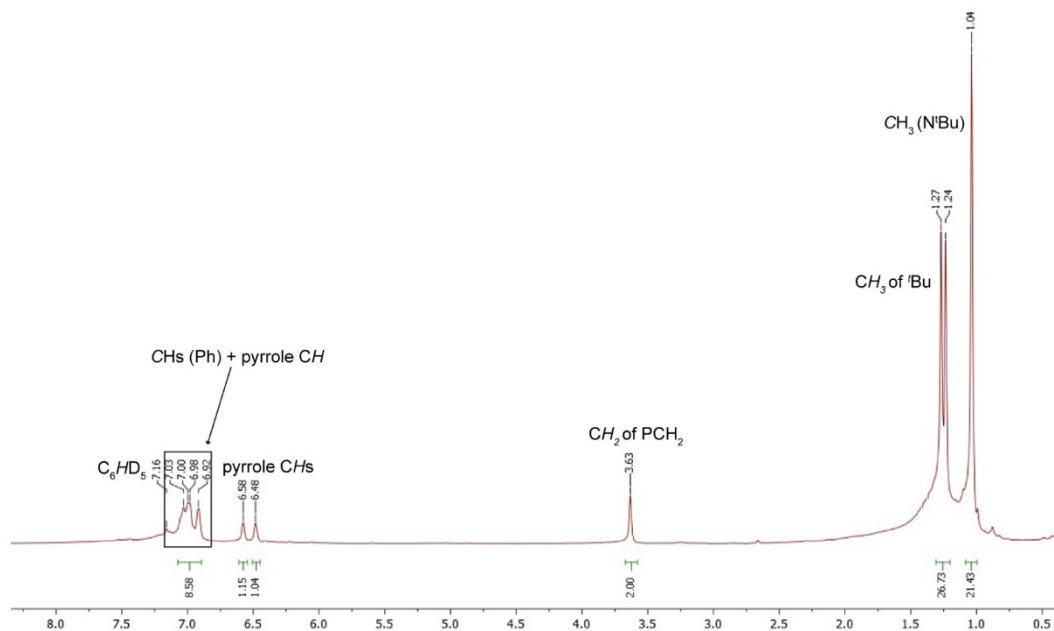
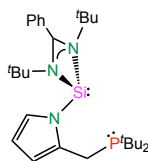
---

<sup>a</sup>*Centro de Innovación en Química Avanzada (ORFEO-CINQA) and Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, 33071 Oviedo, Spain.*

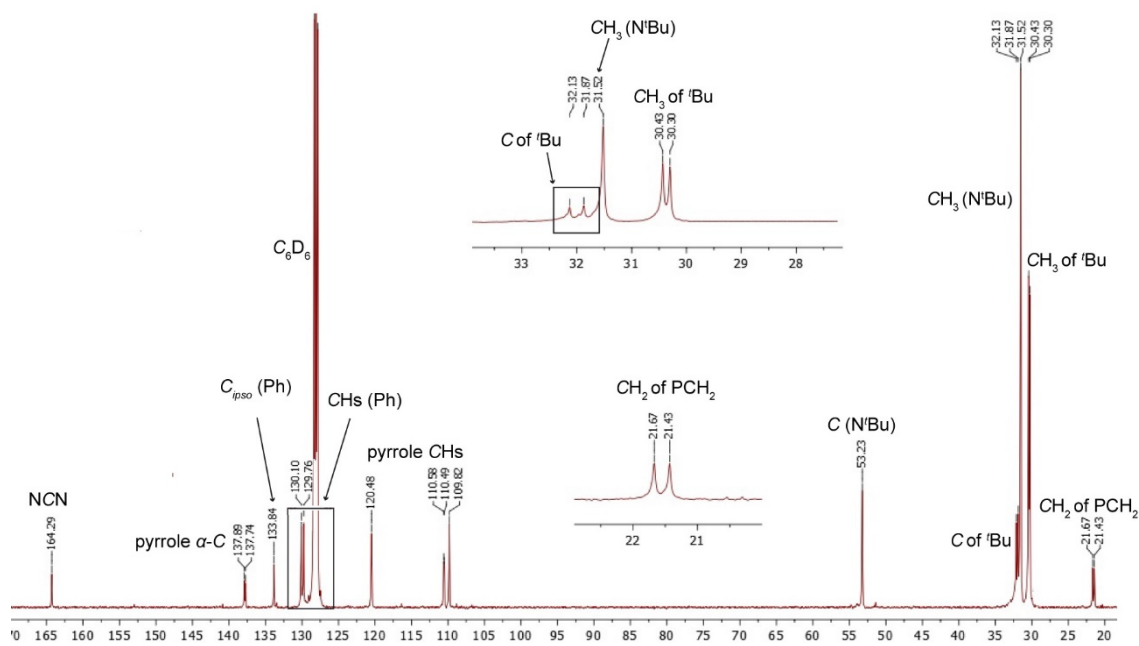
<sup>b</sup>*Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain.*

1. NMR spectra	S2
2. Figures of DFT/NBO calculations	S28
3. XRD data	S30
4. Atomic coordinates of DFT-optimized structures	S31

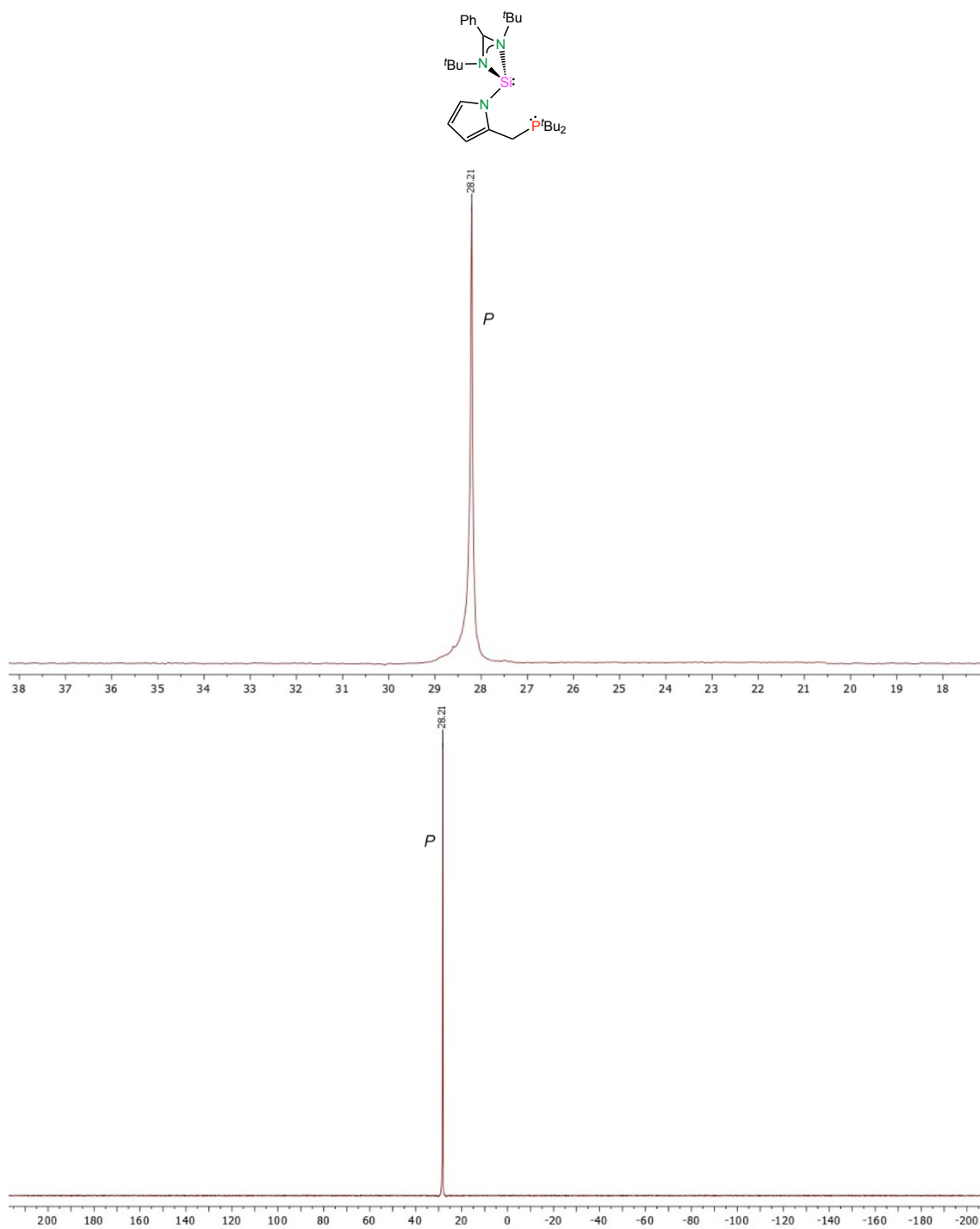
# 1. NMR spectra



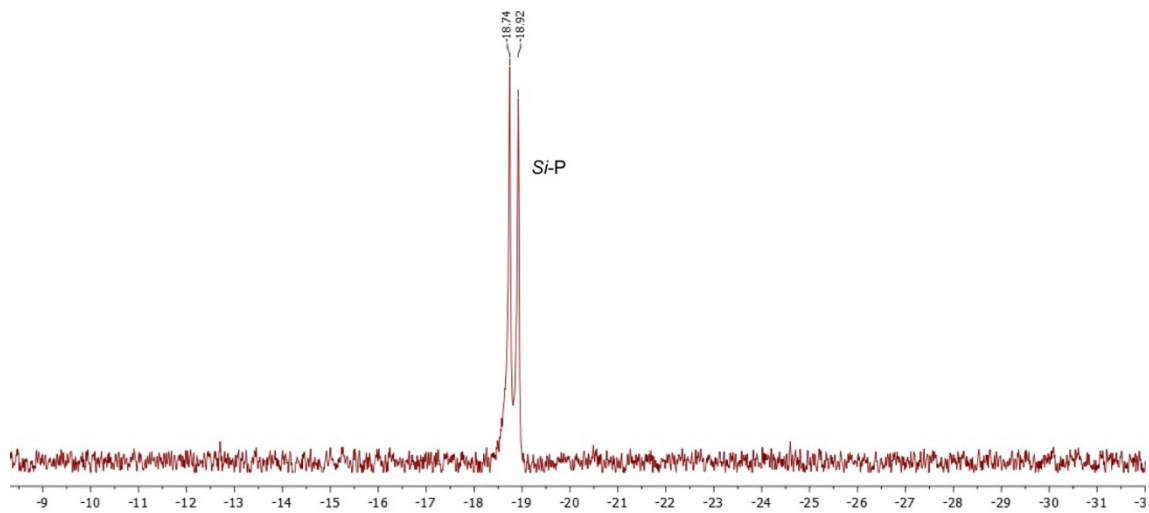
**Fig. S1**  $^1\text{H}$  NMR spectrum (300.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Si}(\text{tBu}_2\text{bzam})\text{pyrmP}^t\text{Bu}_2$  (**1si**).



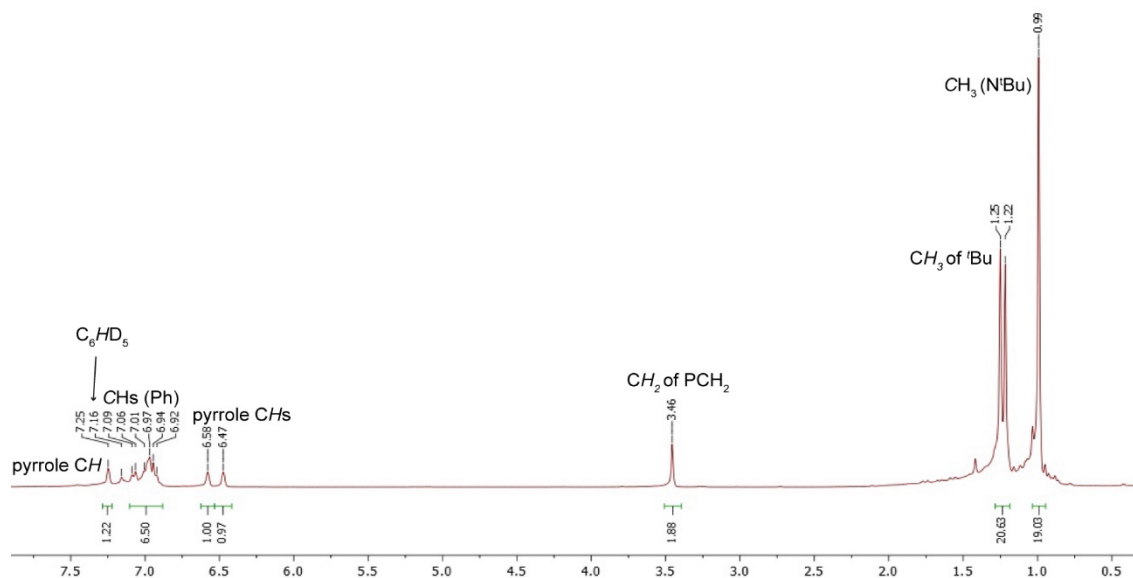
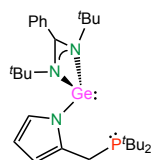
**Fig. S2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Si}(\text{tBu}_2\text{bzam})\text{pyrmP}^t\text{Bu}_2$  (**1si**).



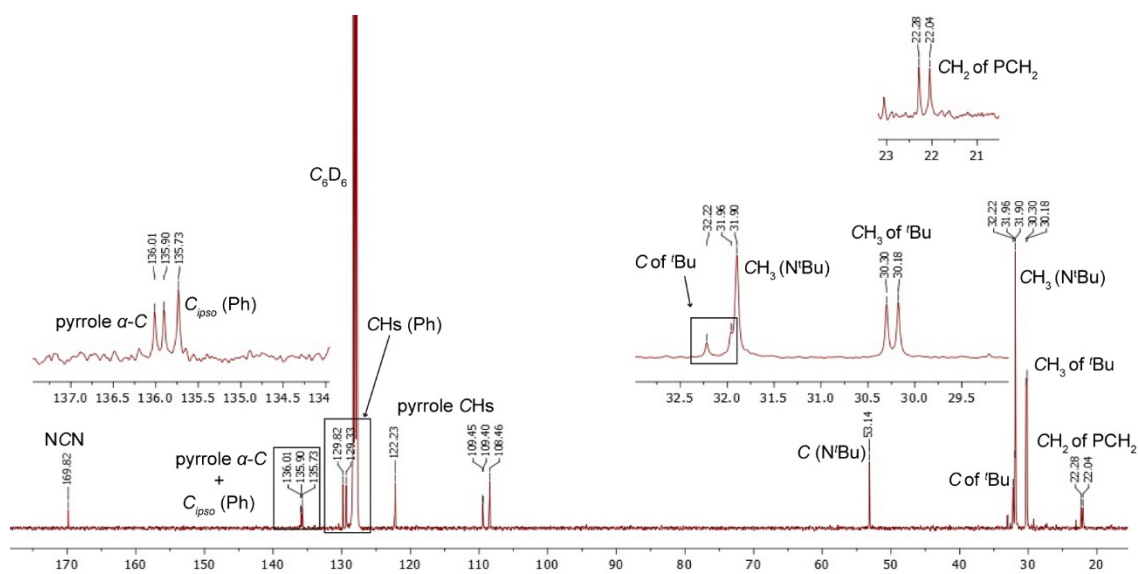
**Fig. S3**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (121.5 MHz,  $\text{C}_6\text{D}_6$  298 K) of  $\text{Si}(\text{tBu}_2\text{bzam})\text{pyrmP}(\text{tBu})_2$  ( $1_{\text{Si}}$ ).



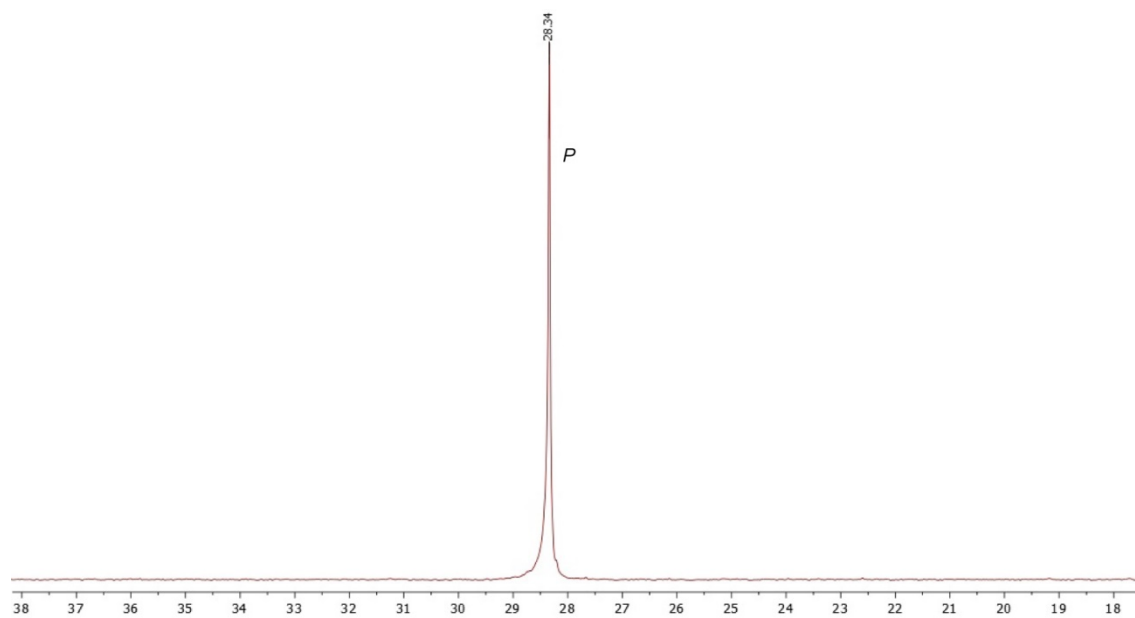
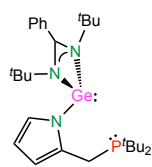
**Fig. S4**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$  298 K) of  $\text{Si}(\text{tBu}_2\text{bzam})\text{pyrmP}^t\text{Bu}_2$  (**1<sub>Si</sub>**).



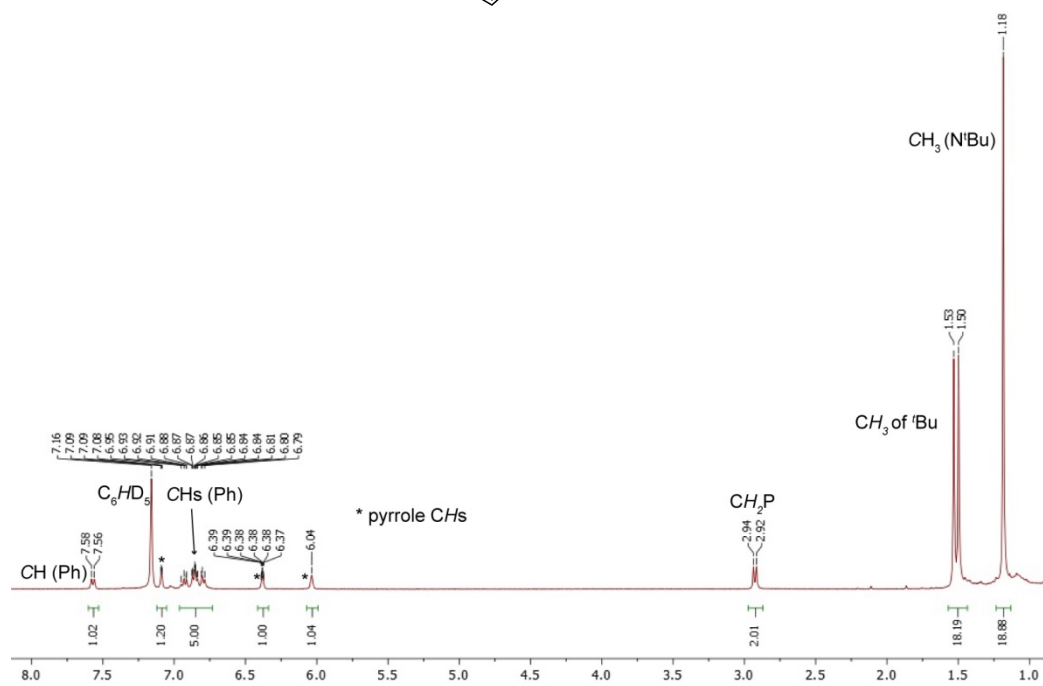
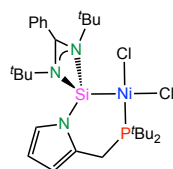
**Fig. S5**  $^1\text{H}$  NMR spectrum (300.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Ge}(\text{tBu}_2\text{bzam})\text{pyrmP}^{\text{tBu}}_2$  (**1Ge**).



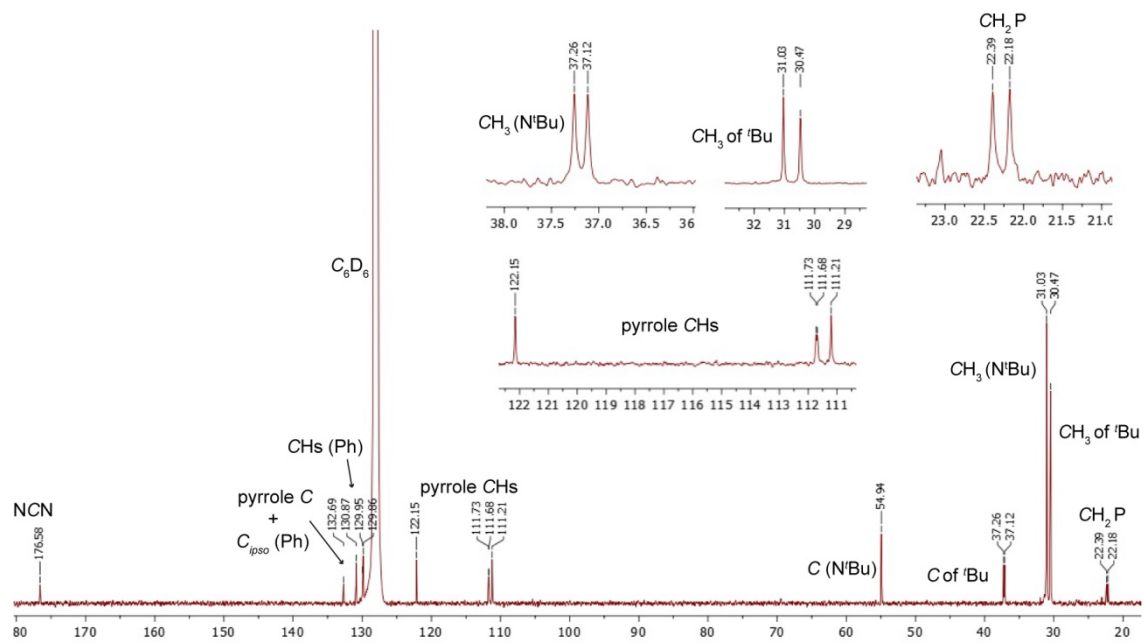
**Fig. S6**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $\text{Ge}(\text{tBu}_2\text{bzam})\text{pyrmP}^{\text{tBu}}_2$  (**1Ge**).



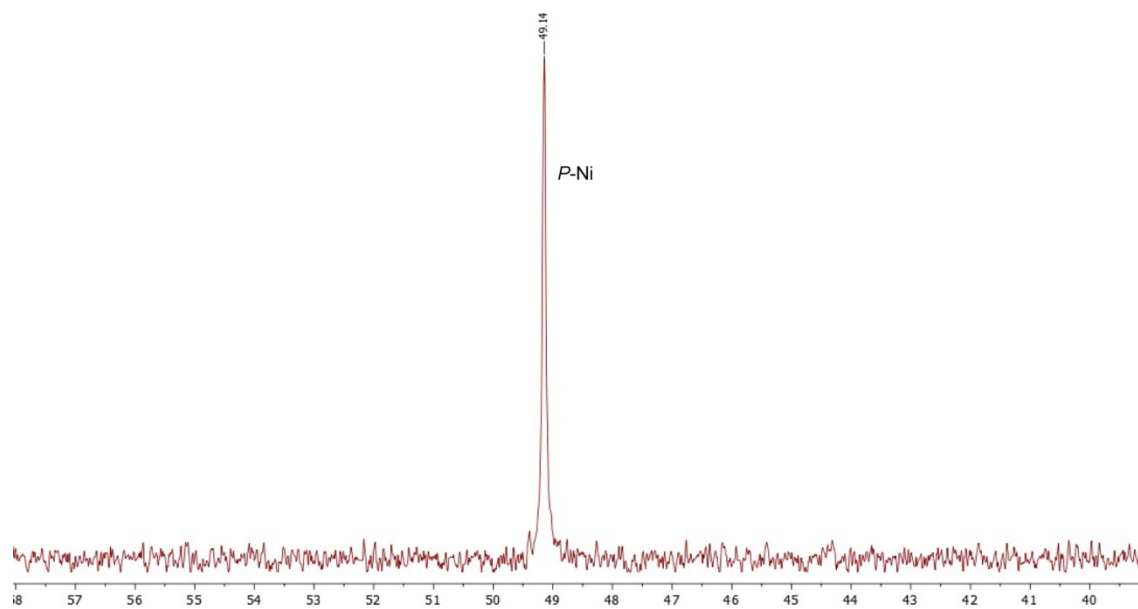
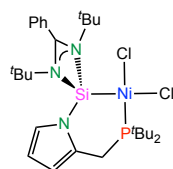
**Fig. S7**  $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.5 MHz,  $\text{C}_6\text{D}_6$  298 K) of  $\text{Ge}(\text{tBu}_2\text{bzam})\text{pyrmP}^{\text{tBu}}_2$  (**1<sub>Ge</sub>**).



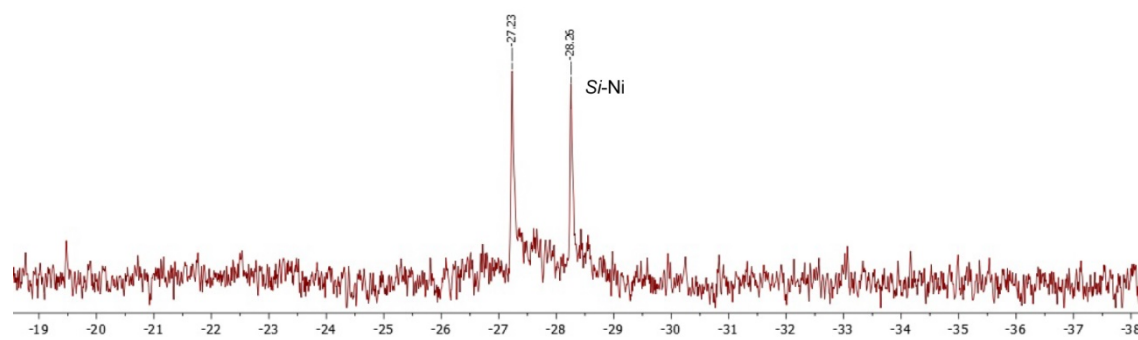
**Fig. S8**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Ni-Si**).



**Fig. S9**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Ni-Si**).

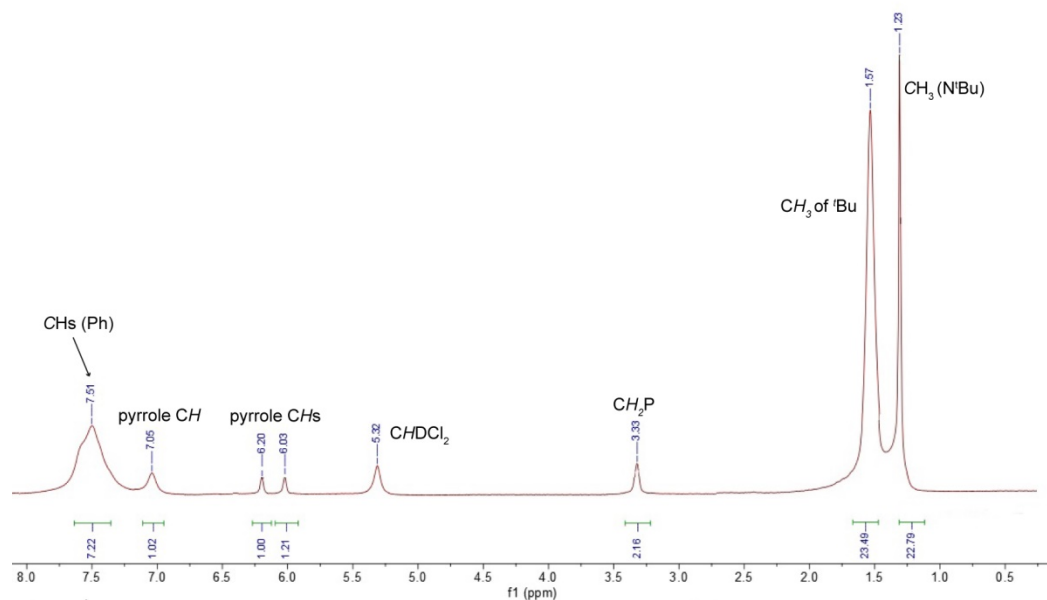
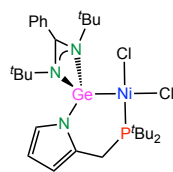


**Fig. S10**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2}]$  ( $\mathbf{2}_{\text{Ni-Si}}$ ).

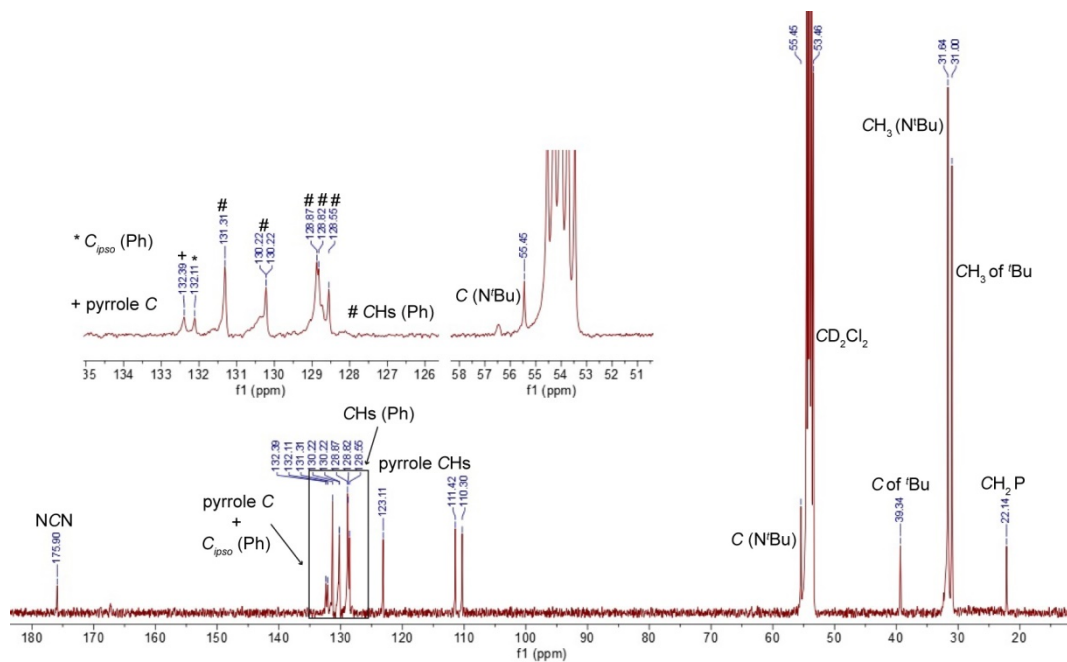


**Fig. S11**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2}]$  ( $\mathbf{2}_{\text{Ni-Si}}$ ).

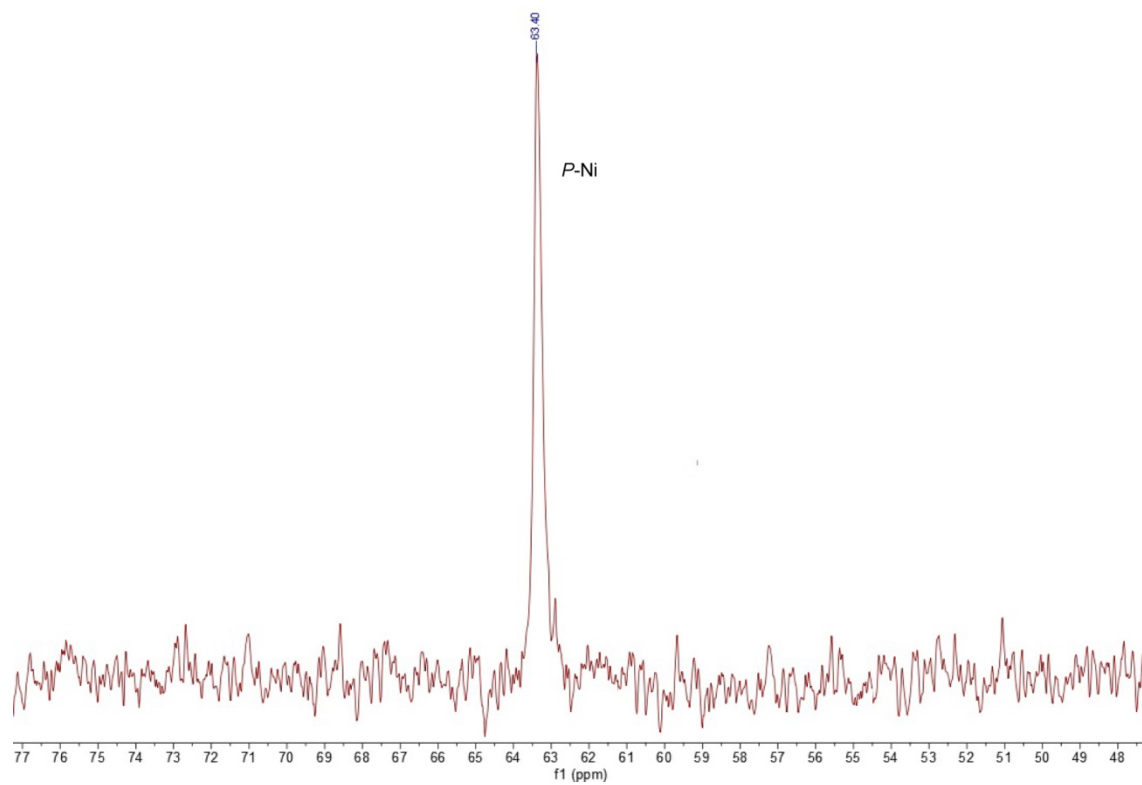
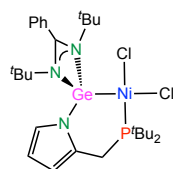




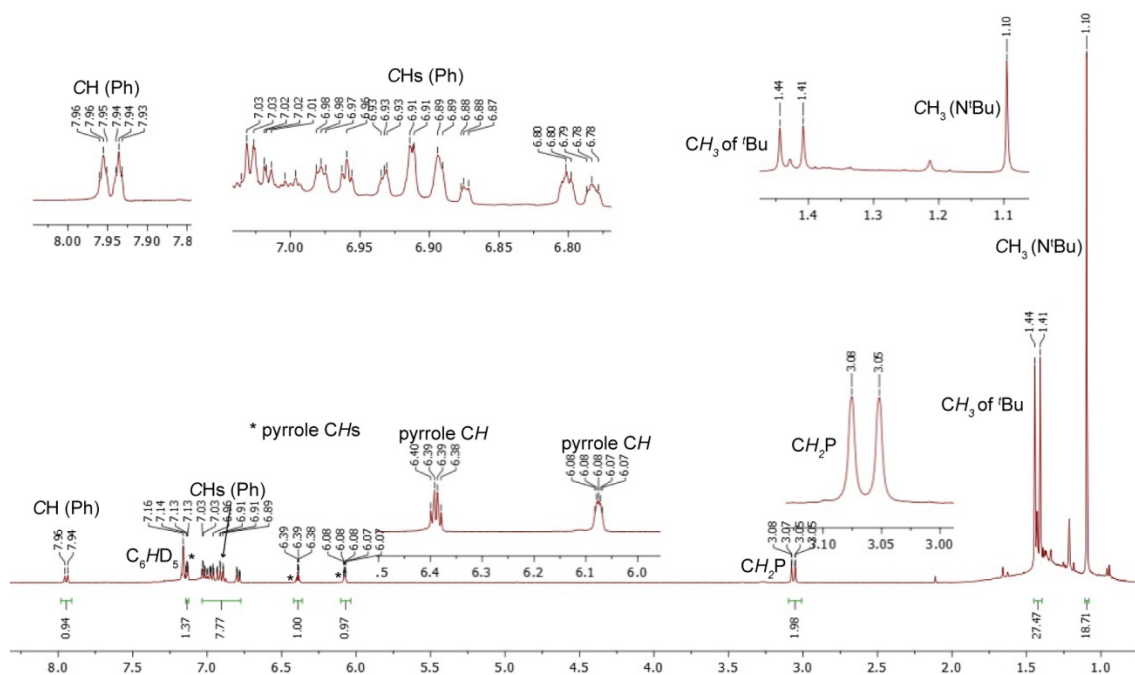
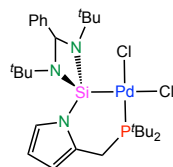
**Fig. S12**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2]$  ( $\mathbf{2}_{\text{Ni-Ge}}$ ).



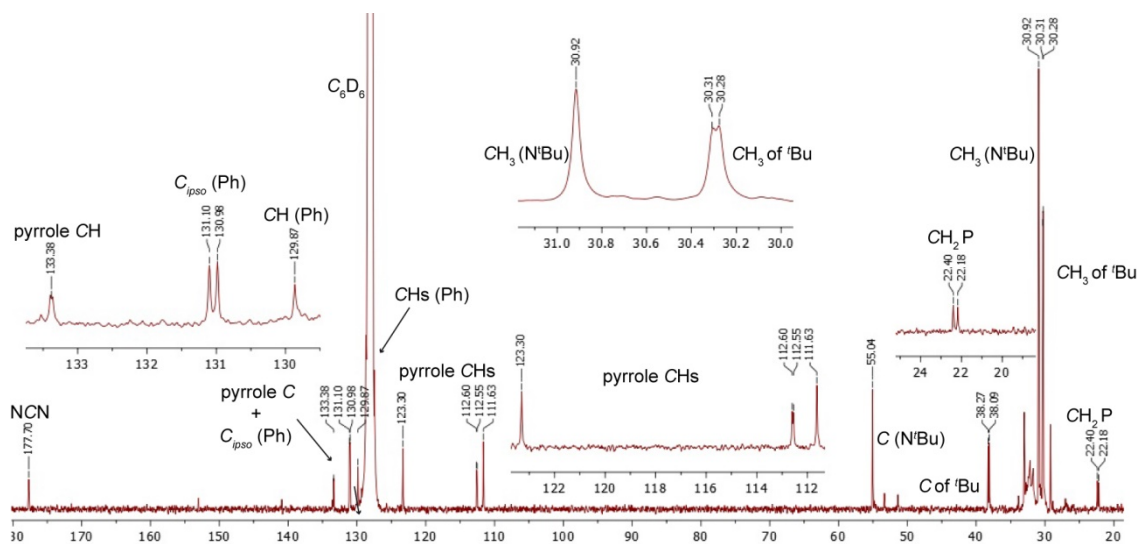
**Fig. S13**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2]$  ( $\mathbf{2}_{\text{Ni-Ge}}$ ).



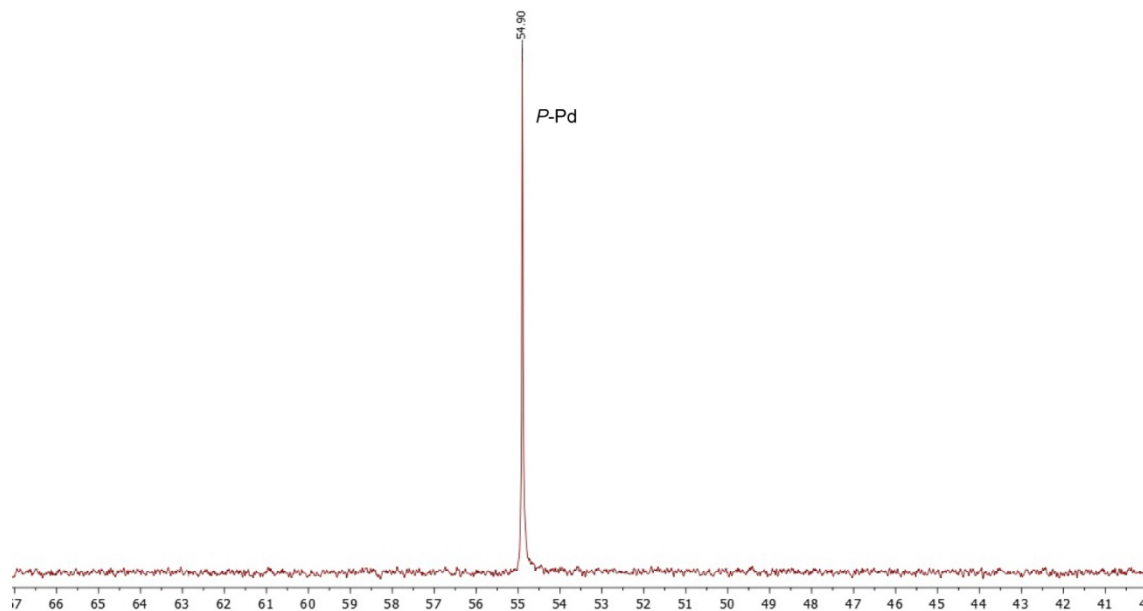
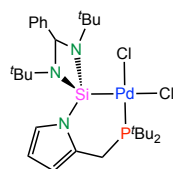
**Fig. S14**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{NiCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2}]$  (**2**<sub>Ni-Ge</sub>).



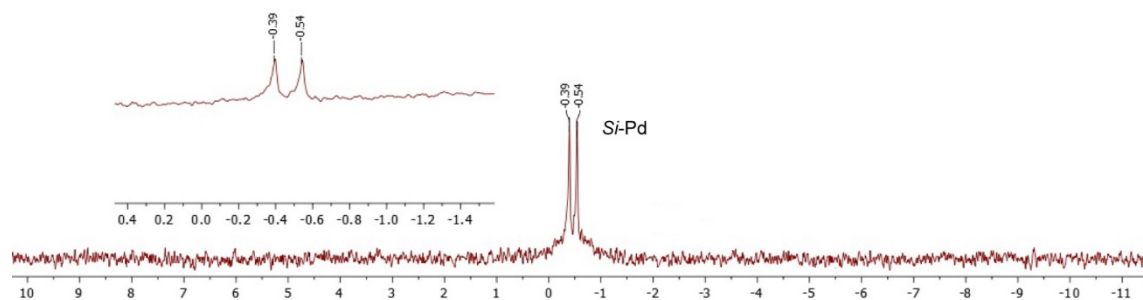
**Fig. S15**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}_2\{\text{k}^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmp}^{\text{tBu}}_2]$  (**2Pd-Si**).



**Fig. S16**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}_2\{\text{k}^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmp}^{\text{tBu}}_2]$  (**2Pd-Si**).



**Fig. S17**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2}]$  (**2Pd-si**).



**Fig. S18**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PdCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2}]$  (**2Pd-si**).

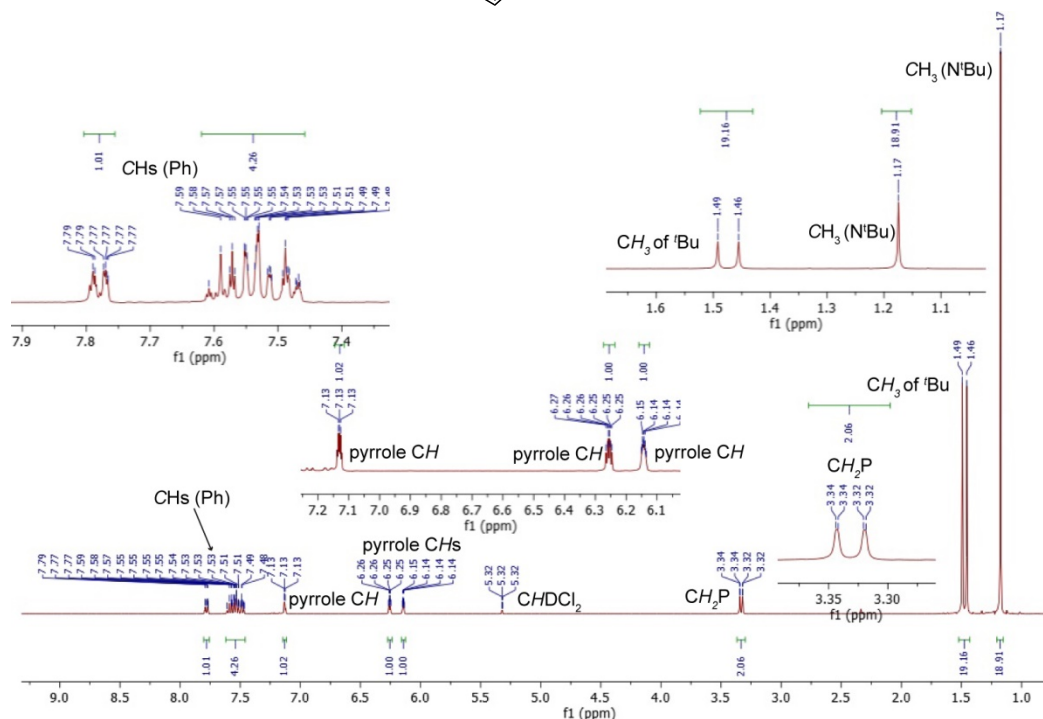
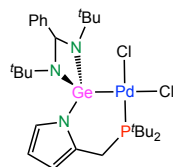


Fig. S19 <sup>1</sup>H NMR spectrum (400.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) of [PdCl<sub>2</sub>{κ<sup>2</sup>P,Ge-Ge(<sup>t</sup>Bu)<sub>2</sub>bzam}pyrmP<sup>t</sup>Bu<sub>2</sub>]} (2Pd-Ge).

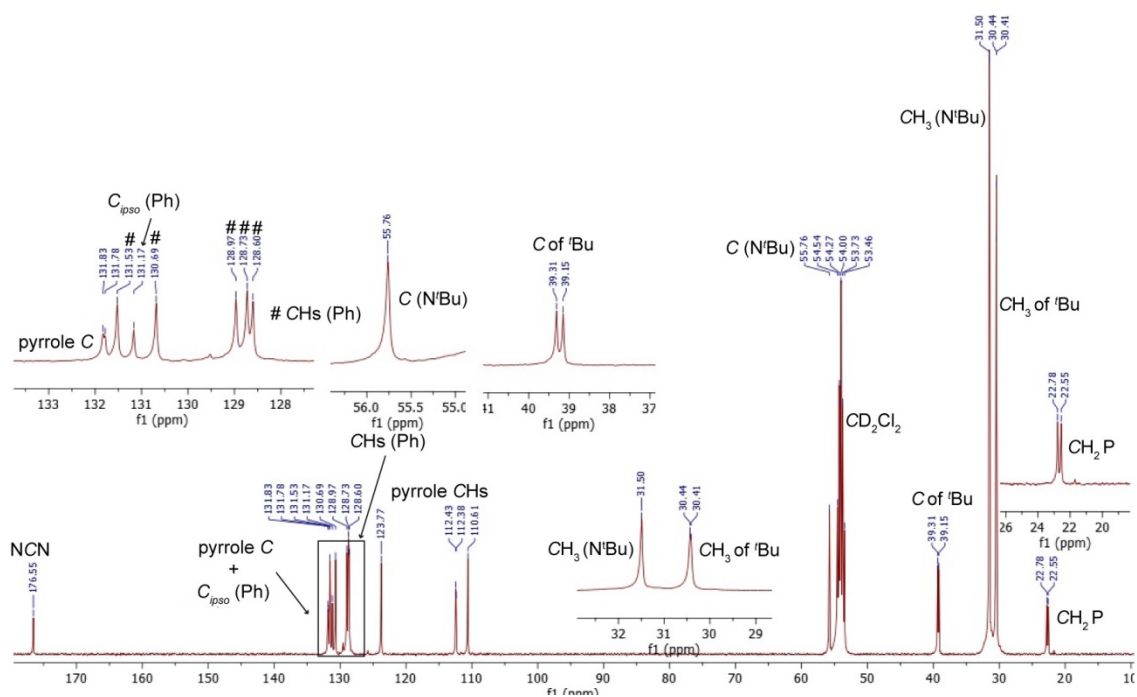
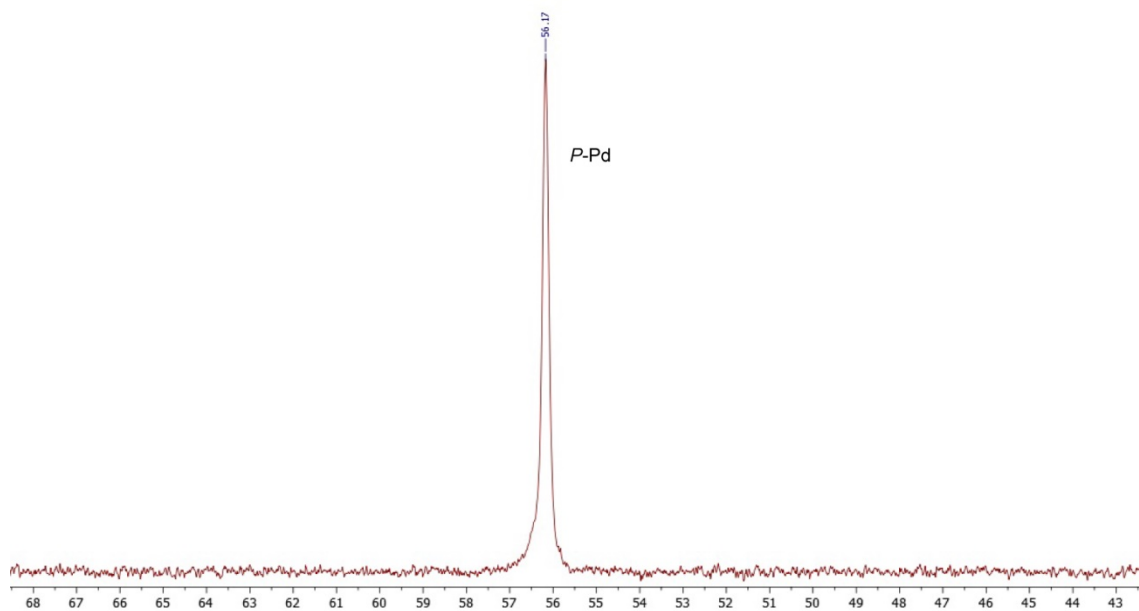
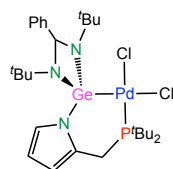
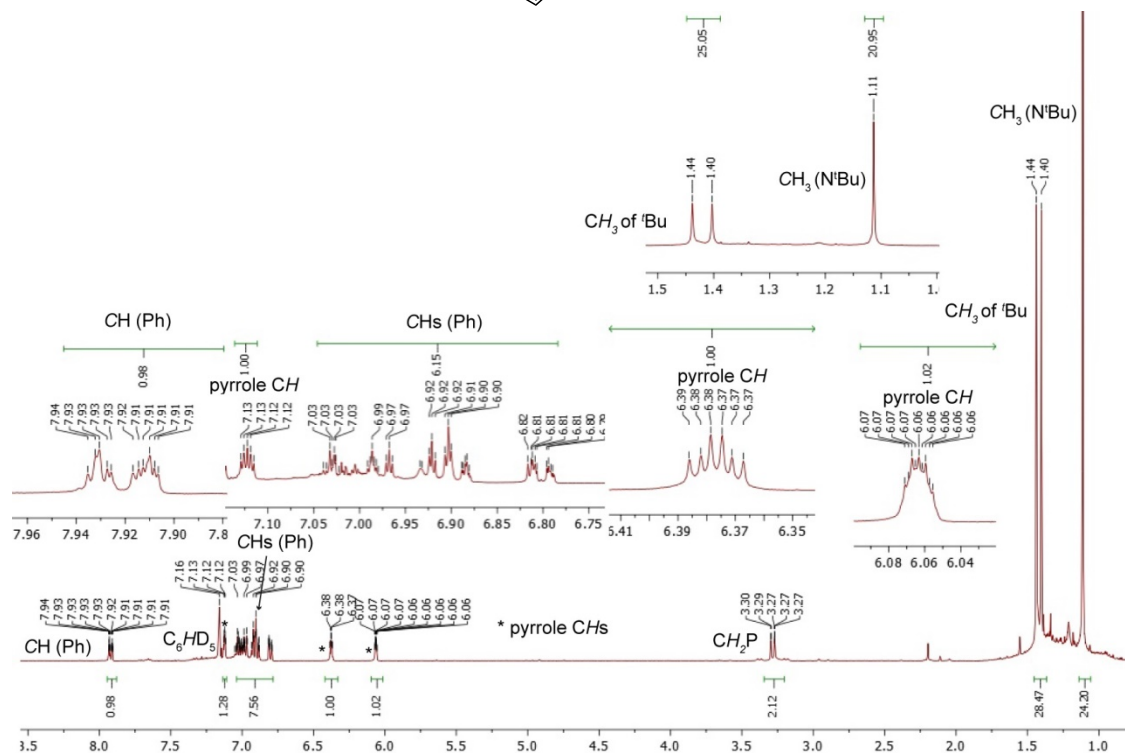
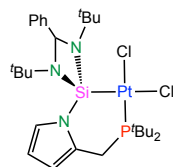


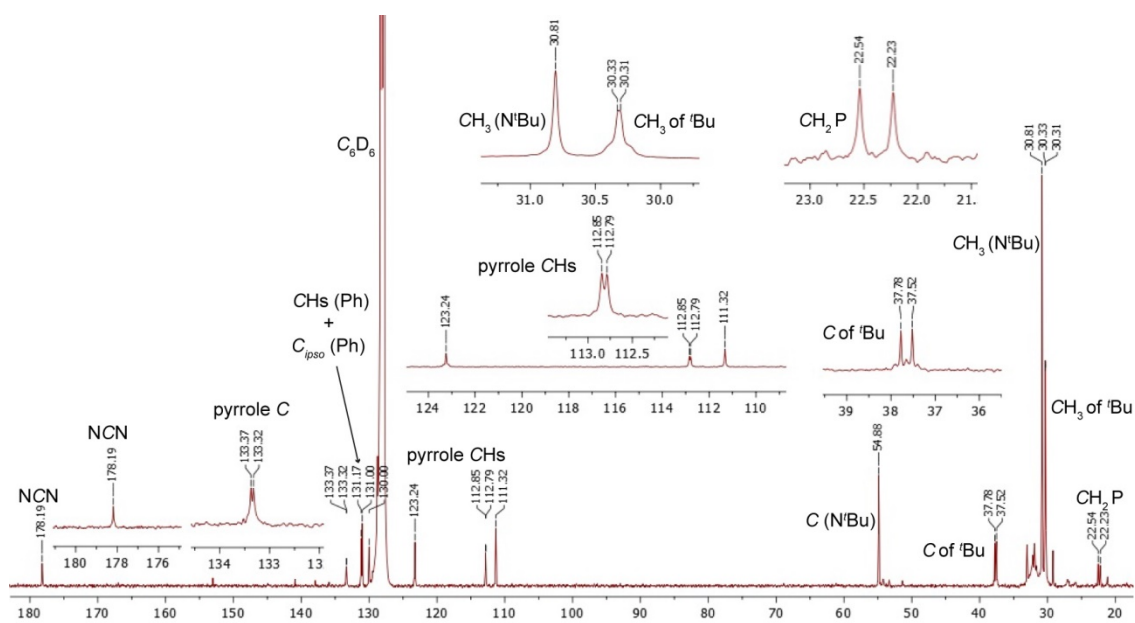
Fig. S20 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) of [PdCl<sub>2</sub>{κ<sup>2</sup>P,Ge-Ge(<sup>t</sup>Bu)<sub>2</sub>bzam}pyrmP<sup>t</sup>Bu<sub>2</sub>]} (2Pd-Ge).



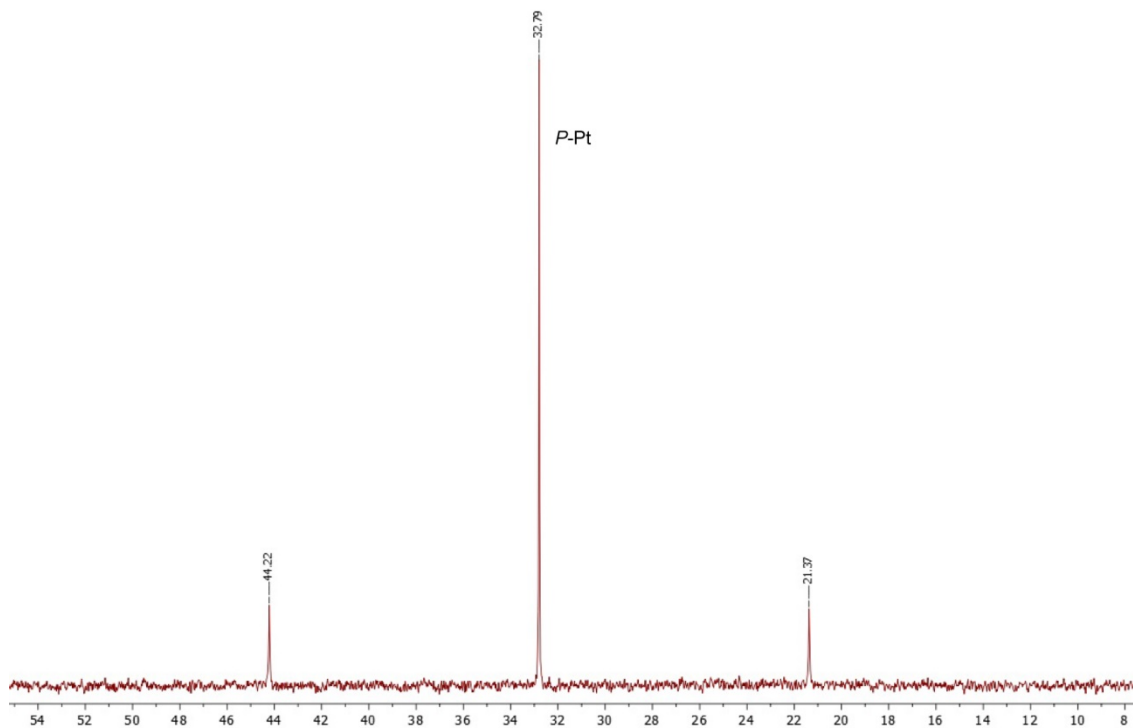
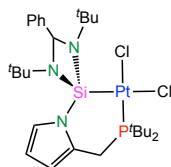
**Fig. S21**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{PdCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2]$  (**2**<sub>Pd-Ge</sub>).



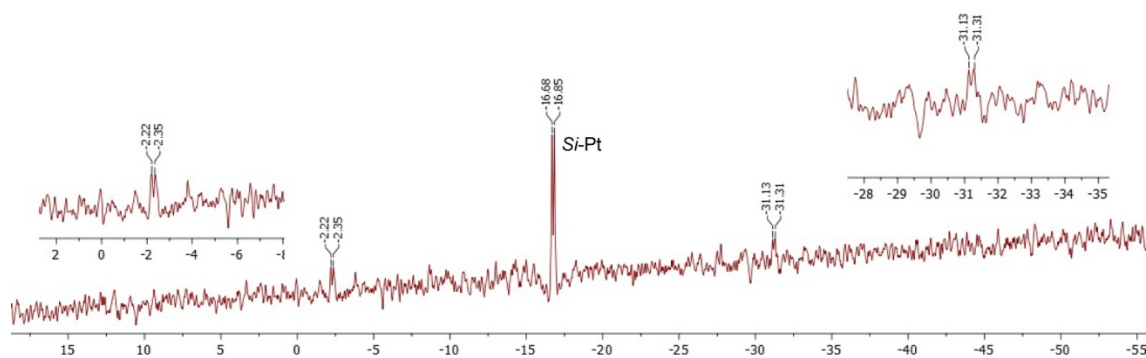
**Fig. S22**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Pt-Si**).



**Fig. S23**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Pt-Si**).

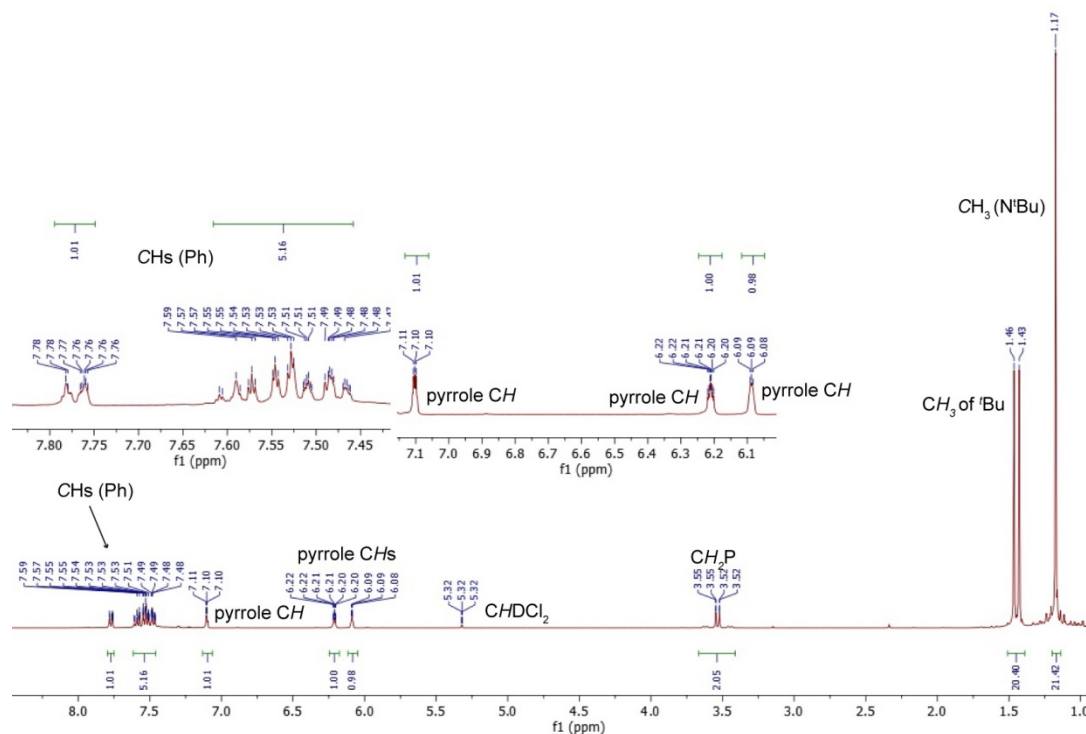
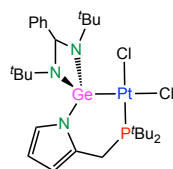


**Fig. S24**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2]$  (**2Pt-Si**).

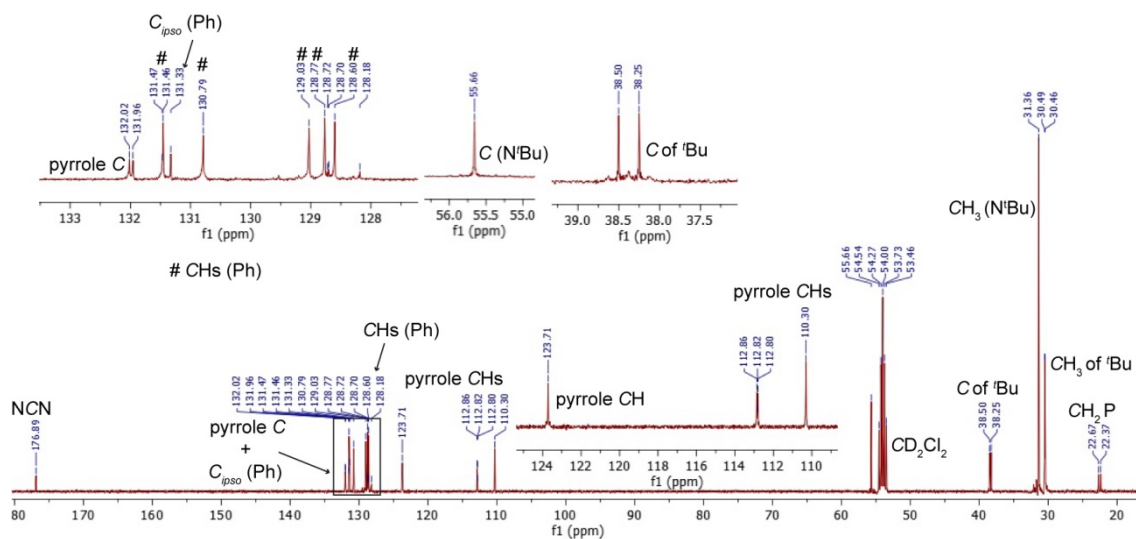


**Fig. S25**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2]$  (**2Pt-Si**).

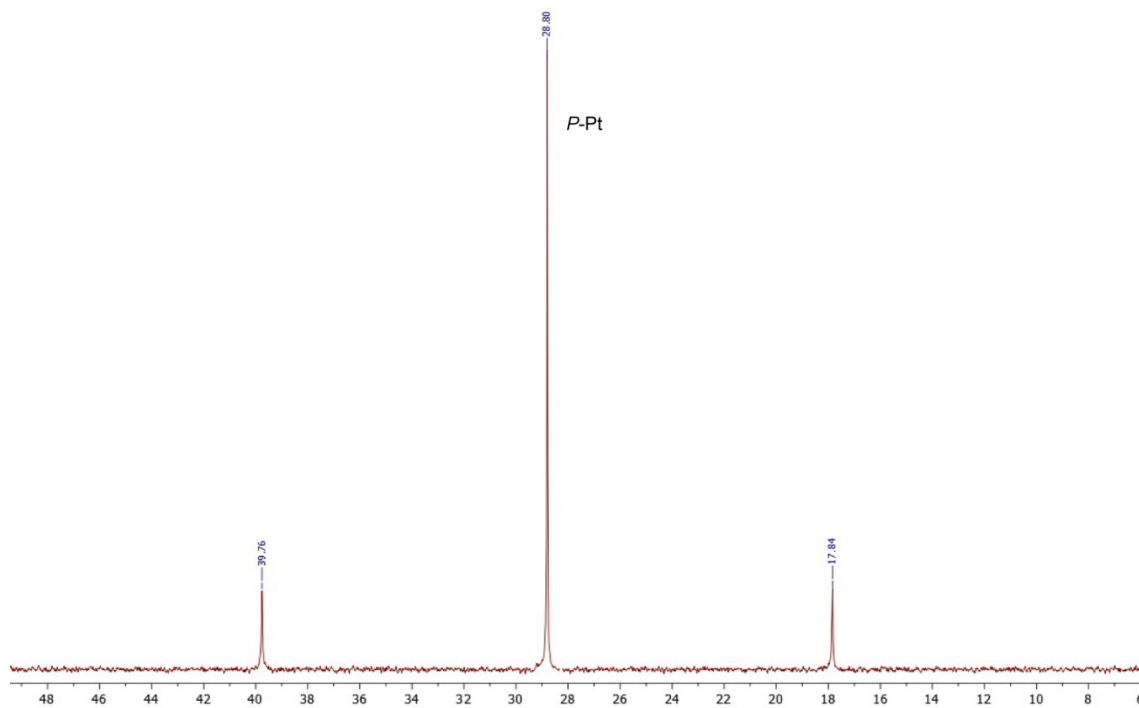
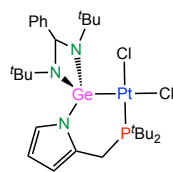




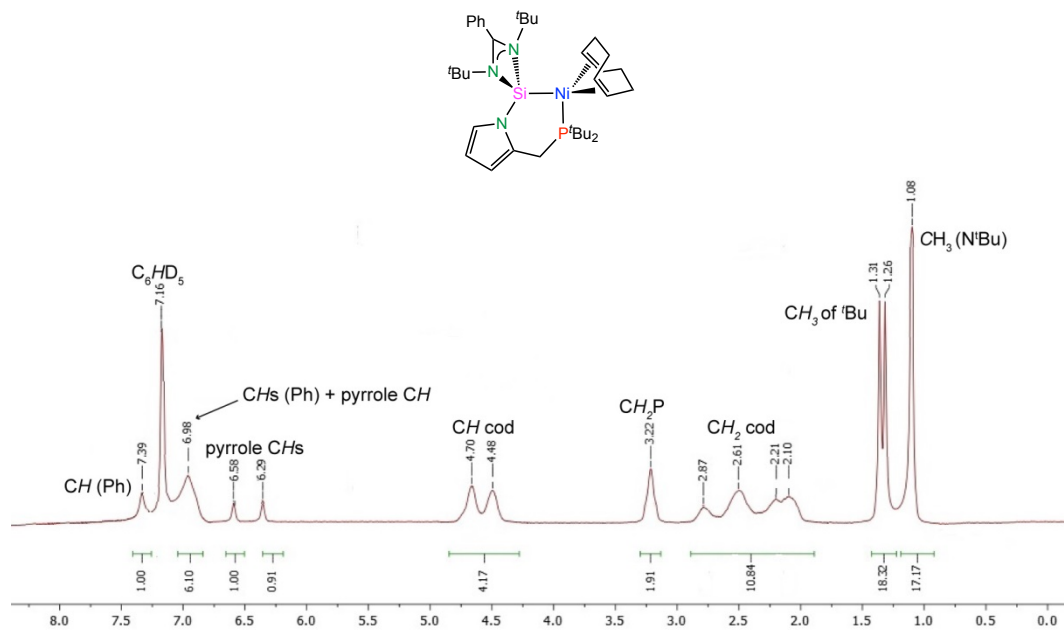
**Fig. S26**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Pt-Ge**).



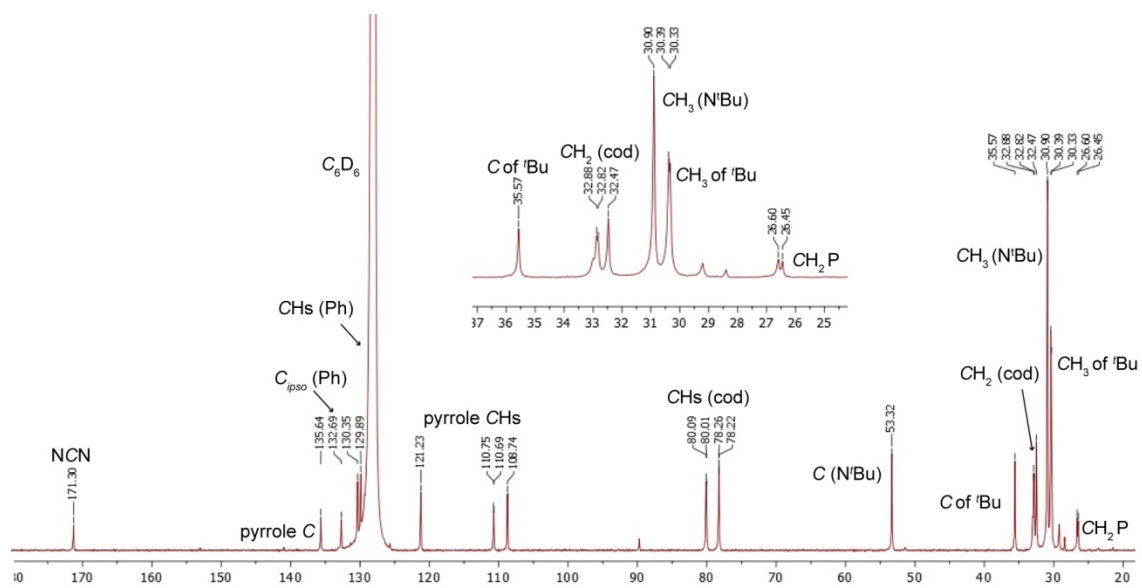
**Fig. S27**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Pt-Ge**).



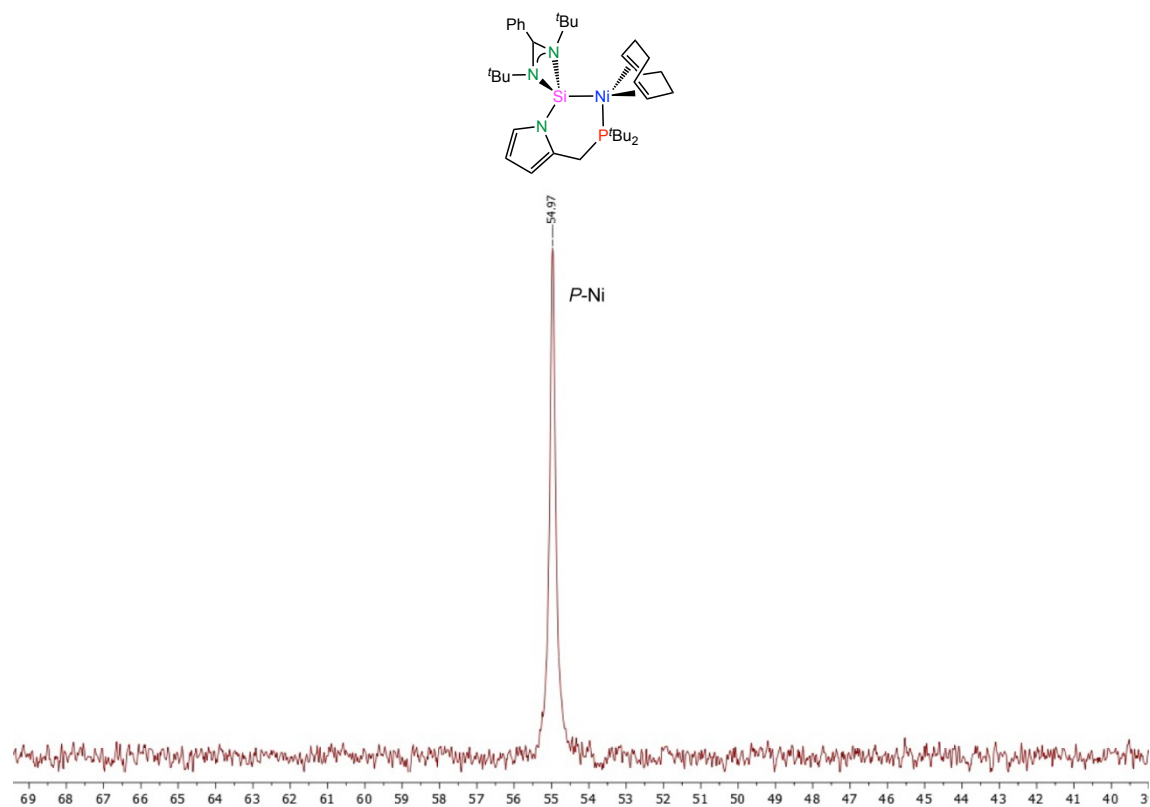
**Fig. S28**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of  $[\text{PtCl}_2\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^{\text{tBu}}_2]$  (**2Pt-Ge**).



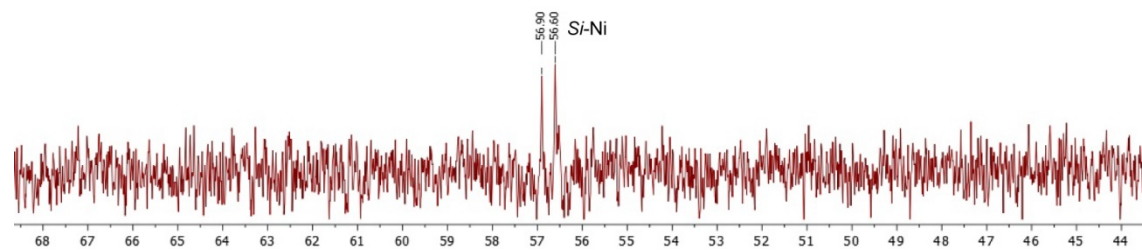
**Fig. S29**  $^1H$  NMR spectrum (300.1 MHz,  $C_6D_6$ , 298 K) of  $[Ni\{k^2P,Si-Si(tBu)_2bzam\}pyrmP^tBu_2\}(cod)]$  ( $3_{Ni-Si}$ ).



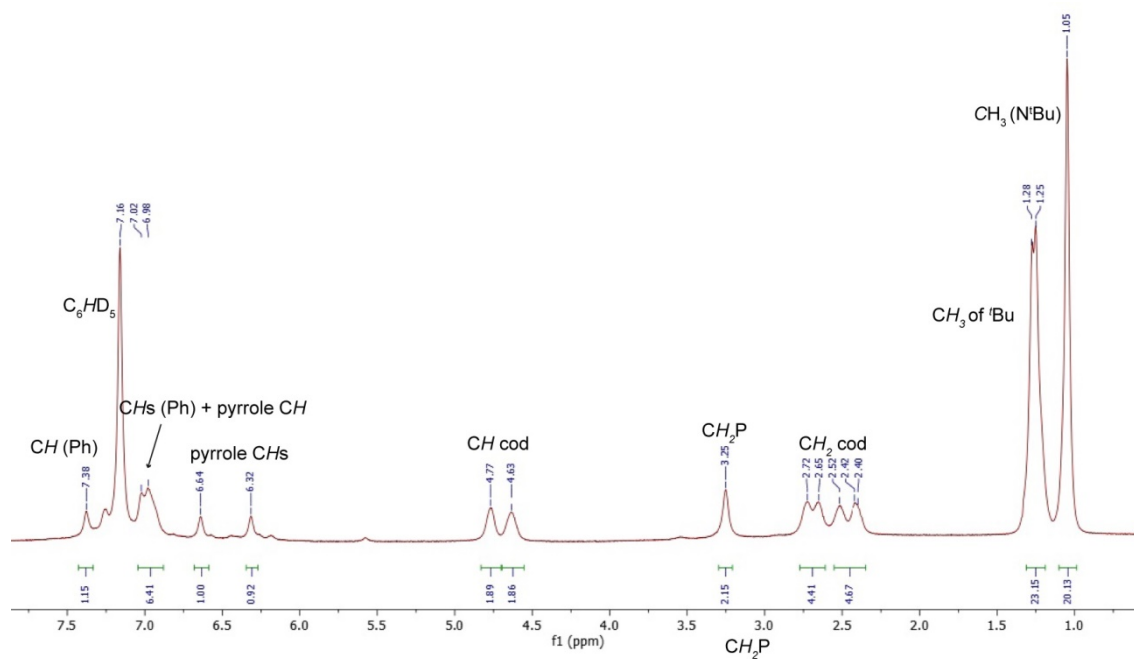
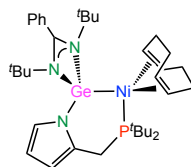
**Fig. S30**  $^{13}C\{^1H\}$  NMR spectrum (100.6 MHz,  $C_6D_6$ , 298 K) of  $[Ni\{k^2P,Si-Si(tBu)_2bzam\}pyrmP^tBu_2\}(cod)]$  ( $3_{Ni-Si}$ ).



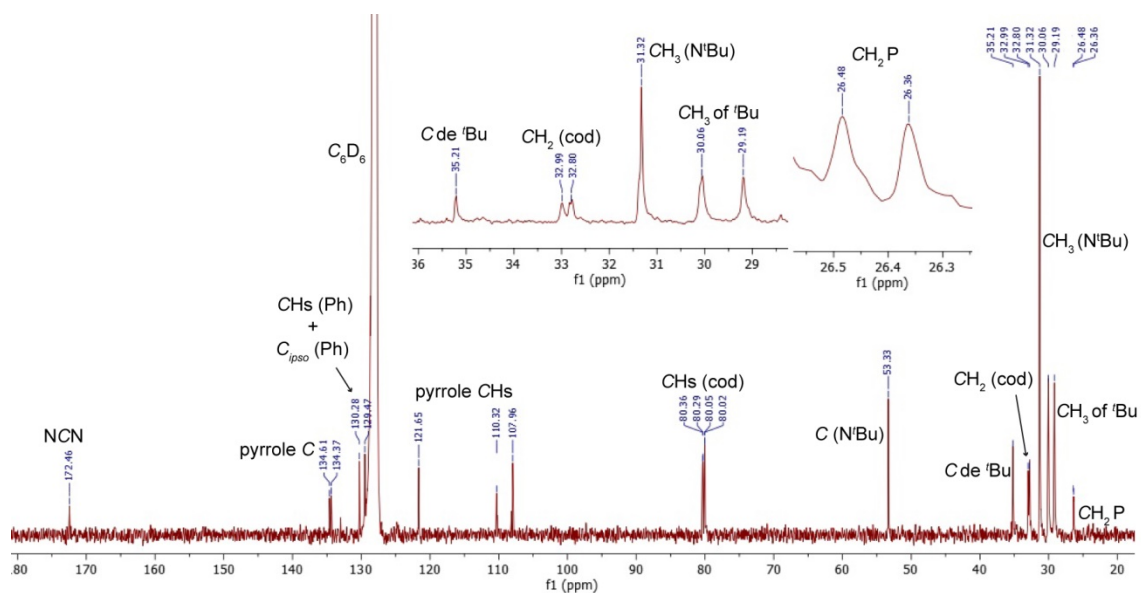
**Fig. S31**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (121.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Ni}\{\kappa^2\text{P}, \text{Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{cod}\}]$  ( $\mathbf{3}_{\text{Ni-Si}}$ ).



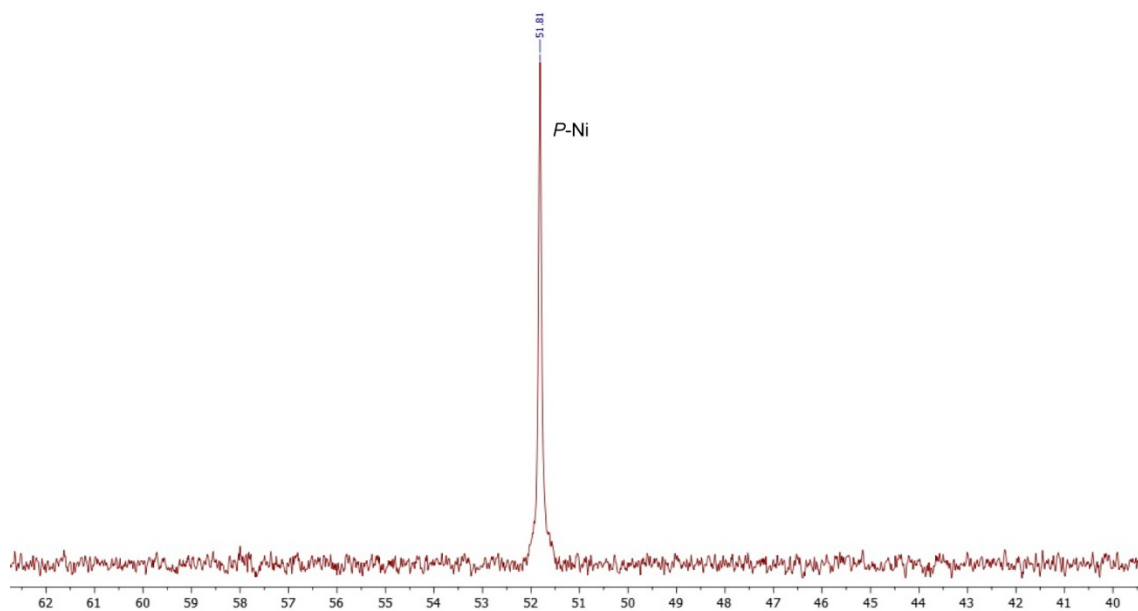
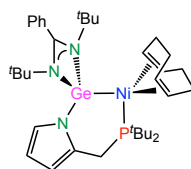
**Fig. S32**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Ni}\{\kappa^2\text{P}, \text{Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{cod}\}]$  ( $\mathbf{3}_{\text{Ni-Si}}$ ).



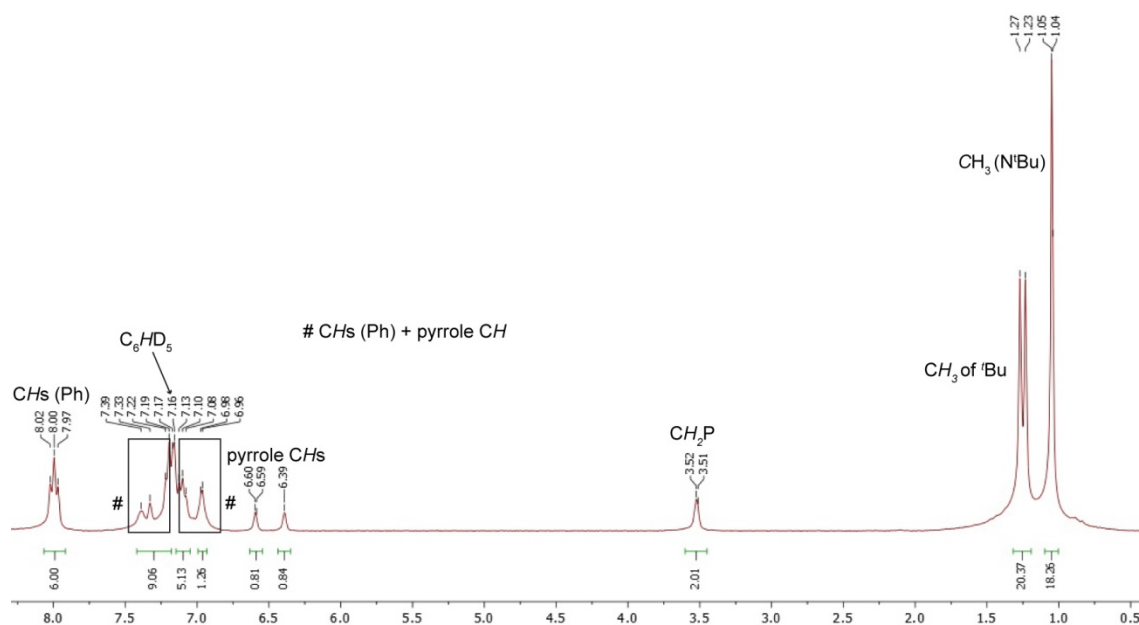
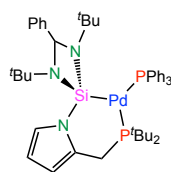
**Fig. S33**  $^1\text{H}$  NMR spectrum (400.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Ni}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{cod}\}]$  (**3**<sub>Ni-Ge</sub>).



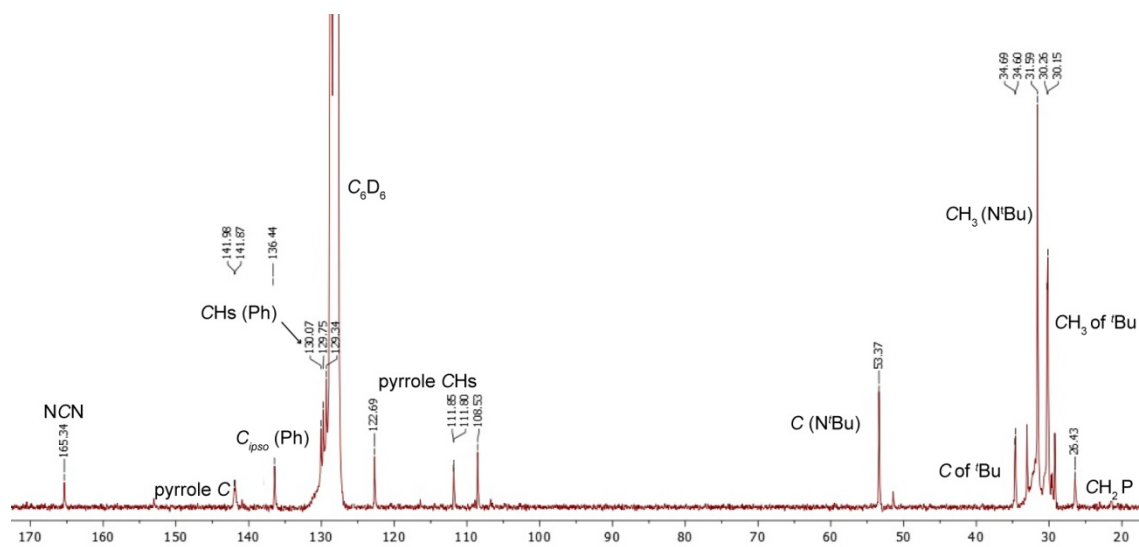
**Fig. S34**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Ni}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{cod}\}]$  (**3**<sub>Ni-Ge</sub>).



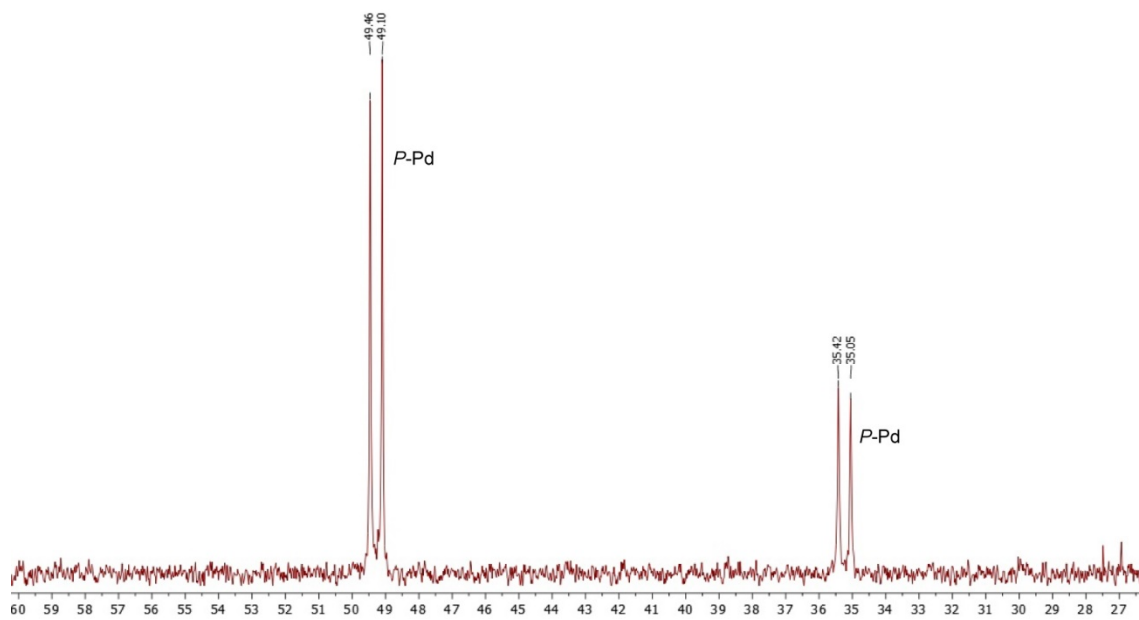
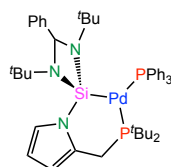
**Fig. S35**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Ni}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{cod}\}]$  (**3<sub>Ni-Ge</sub>**).



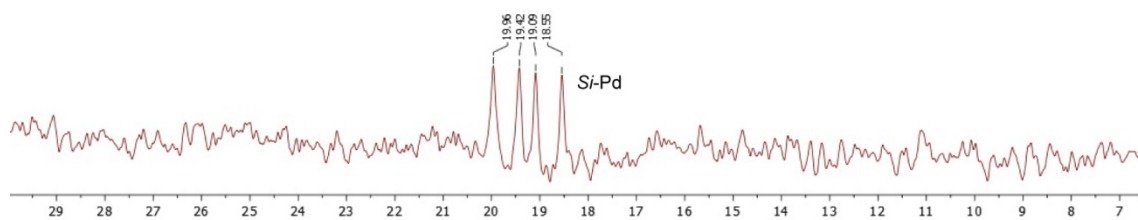
**Fig. S36**  $^1\text{H}$  NMR spectrum (300.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pd-si**).



**Fig. S37**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pd-si**).

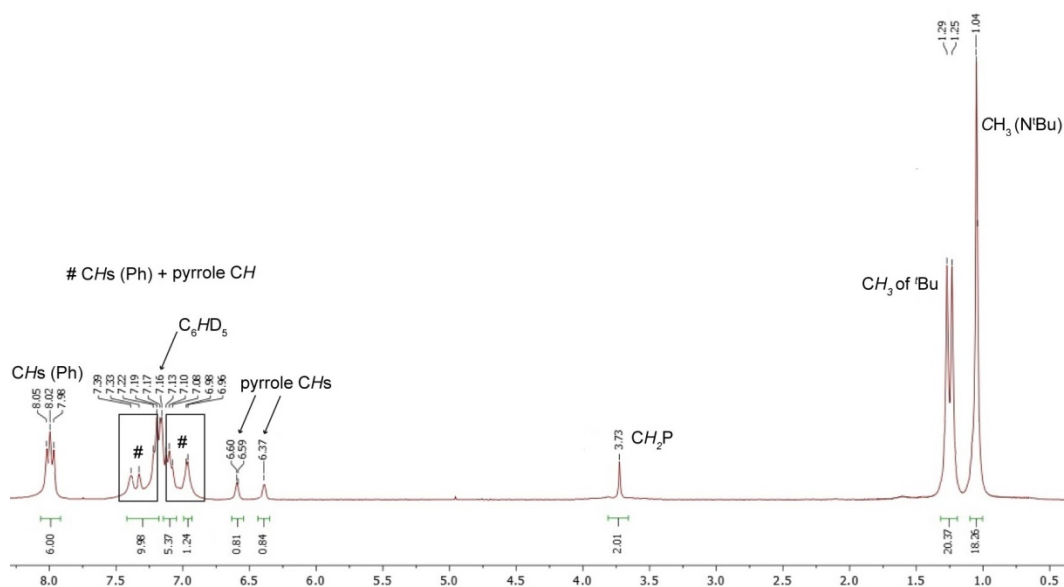
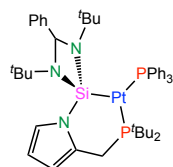


**Fig. S38**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pd-Si**).

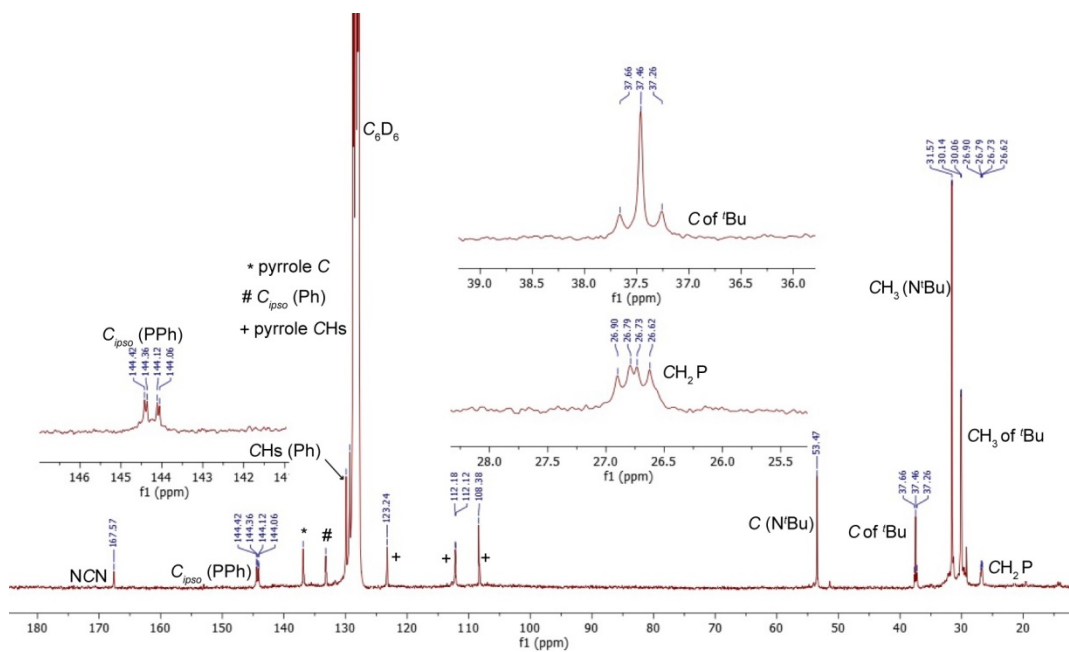


**Fig. S39**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pd}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pd-Si**).

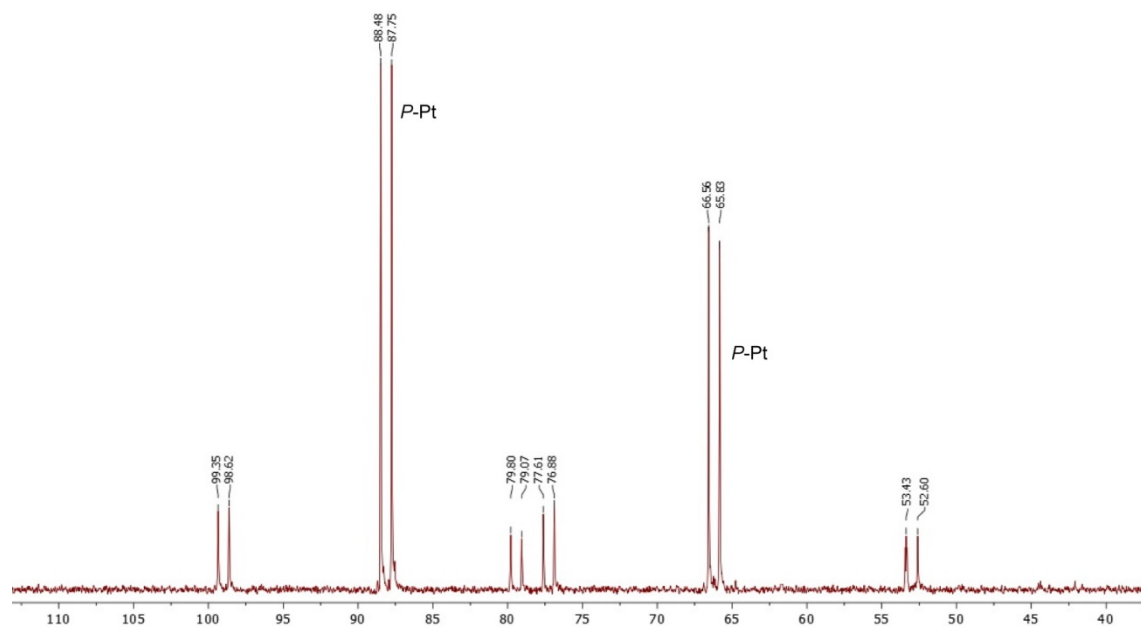
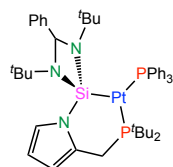




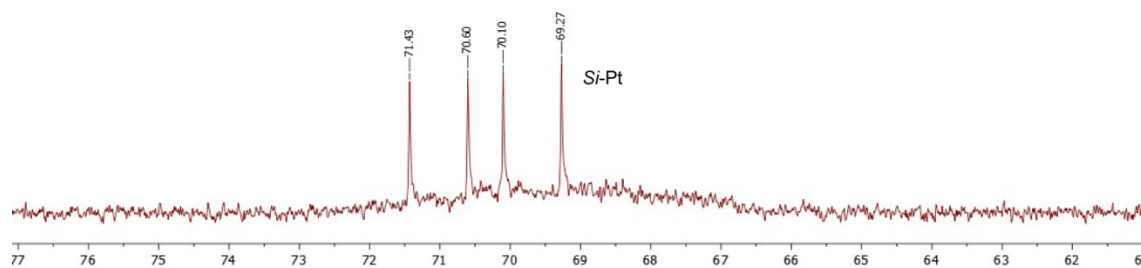
**Fig. S40**  $^1\text{H}$  NMR spectrum (300.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Si**).



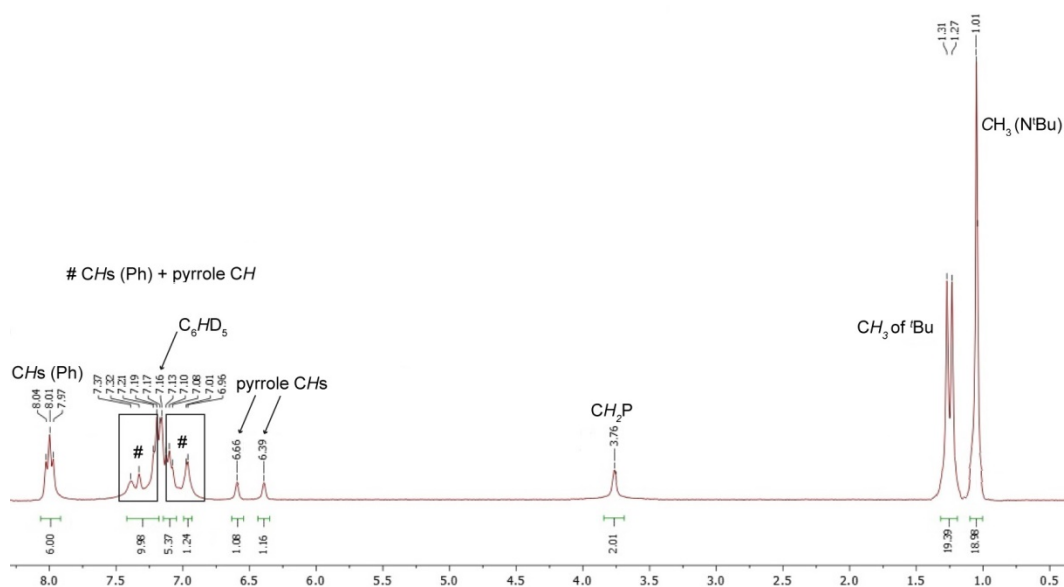
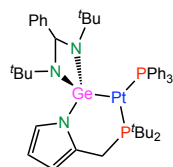
**Fig. S41**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Si**).



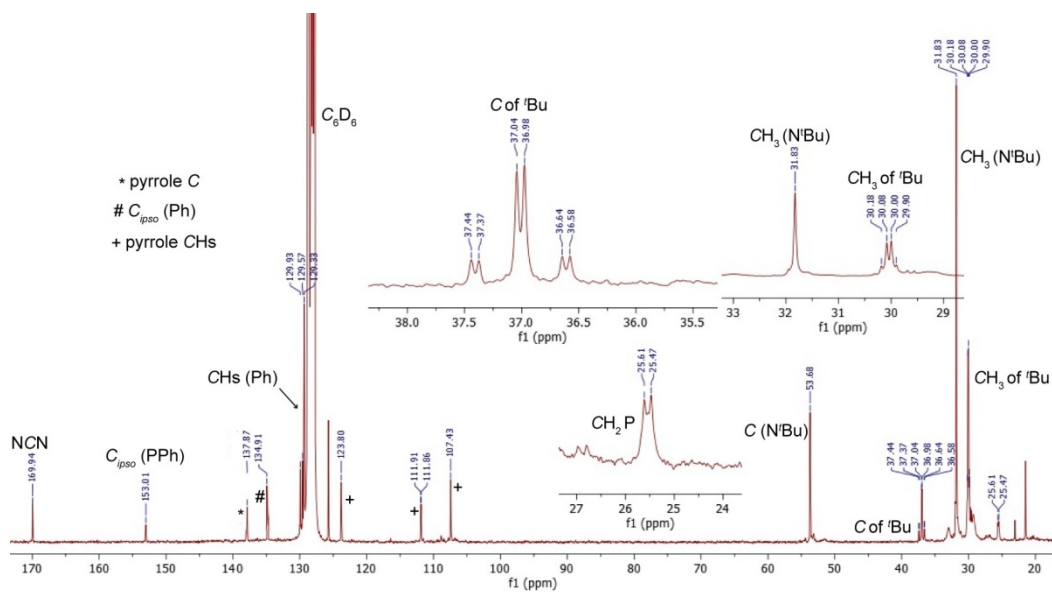
**Fig. S42**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Si**).



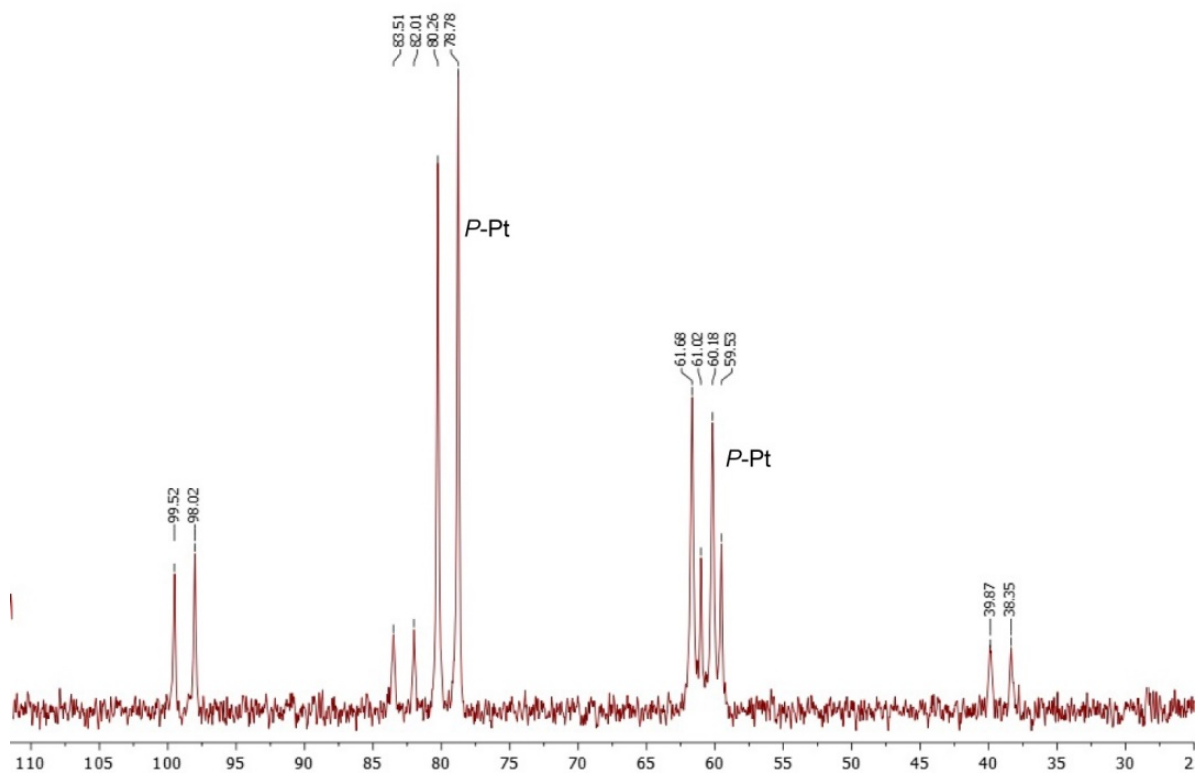
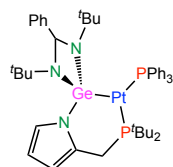
**Fig. S43**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (79.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Si-Si}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Si**).



**Fig. S44**  $^1\text{H}$  NMR spectrum (300.1 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Ge**).

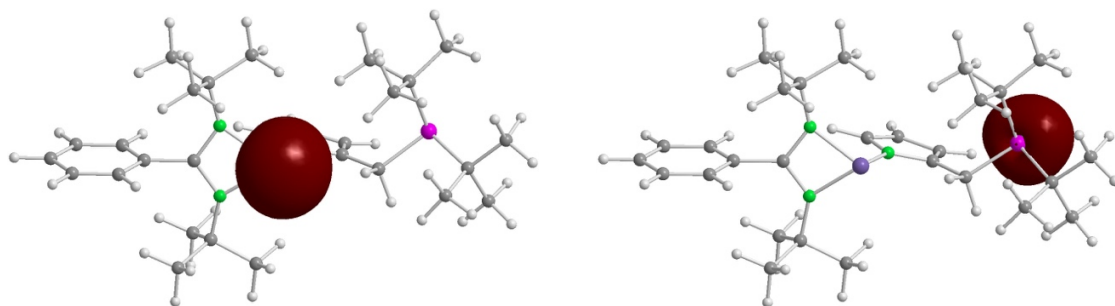


**Fig. S45**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (100.6 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Ge**).

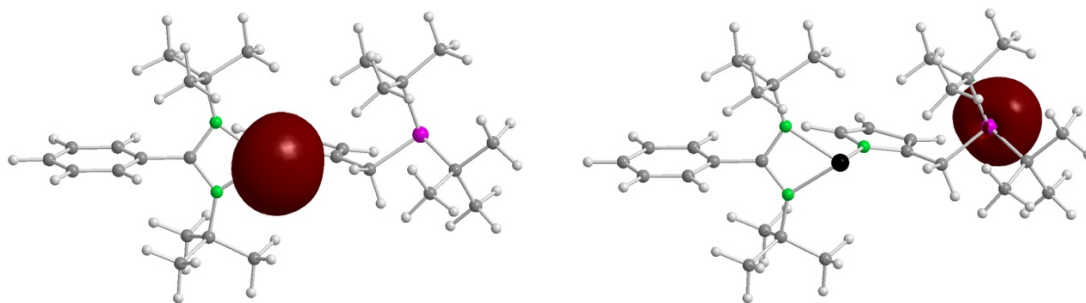


**Fig. S46**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (121.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of  $[\text{Pt}\{\kappa^2\text{P,Ge-Ge}(\text{tBu})_2\text{bzam}\}\text{pyrmP}^t\text{Bu}_2\}\{\text{PPh}_3\}]$  (**4Pt-Ge**).

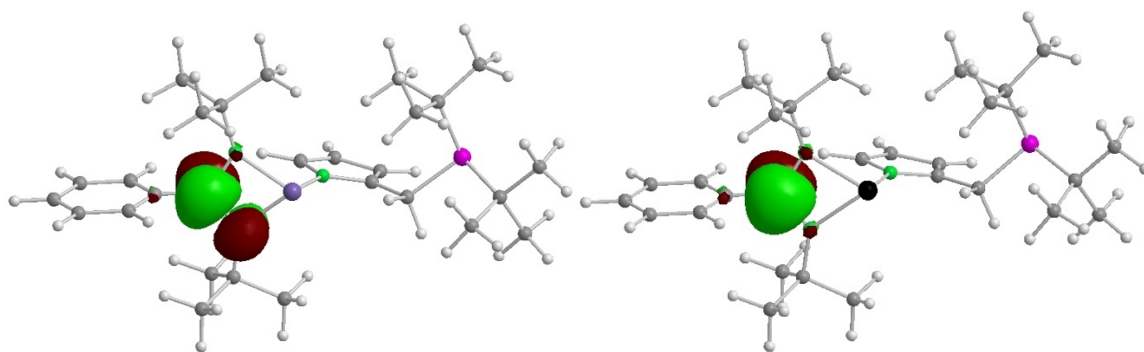
## 2. Figures of DFT/NBO calculations



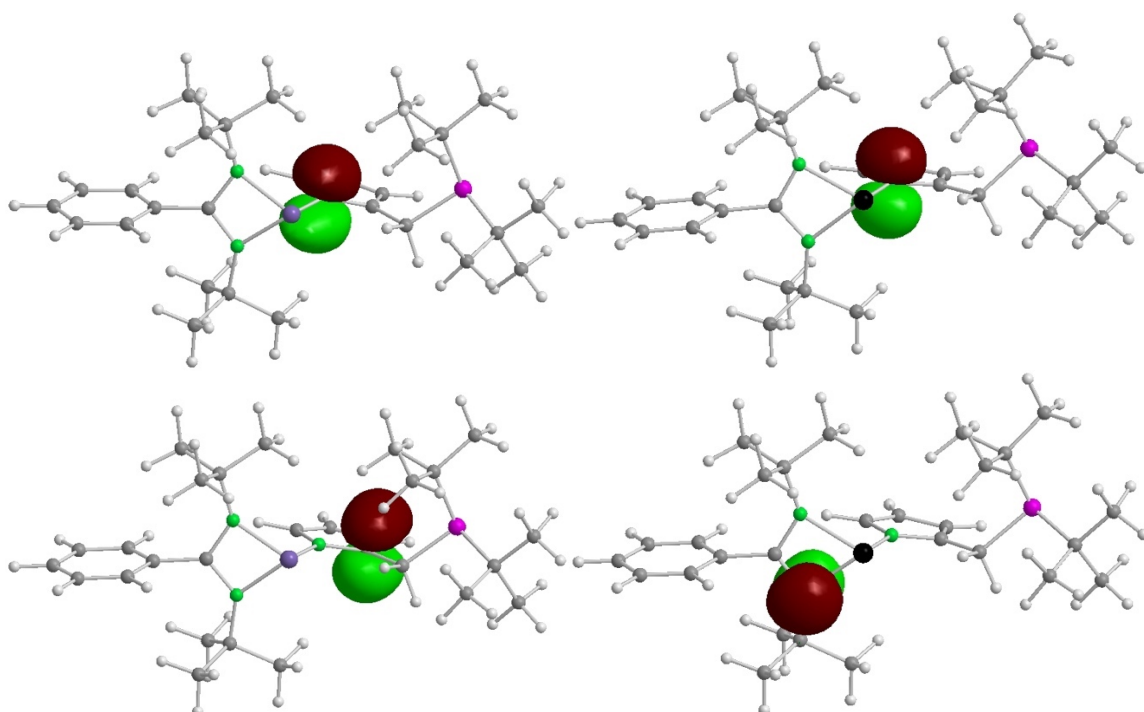
**Fig. S47** HOMO-7 (left) and HOMO-11 (right) orbitals of silylene-phosphane **1<sub>Si</sub>**, corresponding to the lone pairs of the Si and P atoms, respectively.



**Fig. S48** HOMO-11 (left) and HOMO-10 (right) orbitals of germylene-phosphane **1<sub>Ge</sub>**, corresponding to the lone pairs of the Ge and P atoms, respectively.



**Fig. S49** LUMOs of tetrylene-phosphanes **1<sub>Si</sub>** (left) and **1<sub>Ge</sub>** (right).



**Fig. S50** HOMOs (top) and HOMOs-1 (bottom) of tetrylene-phosphanes **1<sub>Si</sub>** (left) and **1<sub>Ge</sub>** (right).

### 3. XRD data

**Table S1.** Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

	<b>1<sub>Si</sub></b>	<b>2<sub>Pd-Si</sub>·(C<sub>4</sub>H<sub>8</sub>O)</b>	<b>3<sub>Ni-Ge</sub></b>	<b>4<sub>Pd-Si</sub></b>
formula	C <sub>28</sub> H <sub>46</sub> N <sub>3</sub> PSi	C <sub>28</sub> H <sub>46</sub> Cl <sub>2</sub> N <sub>3</sub> PPdSi·(C <sub>4</sub> H <sub>8</sub> O)	C <sub>36</sub> H <sub>58</sub> GeN <sub>3</sub> NiP	C <sub>46</sub> H <sub>61</sub> N <sub>3</sub> P <sub>2</sub> PdSi
fw	483.74	733.14	695.12	852.40
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>c</i>	<i>P</i> bca
<i>a</i> , Å	8.833(5)	18.2783(4)	20.592(1)	18.1593(2)
<i>b</i> , Å	18.065(5)	10.5426(2)	8.8479(3)	20.9946(2)
<i>c</i> , Å	18.265(5)	18.3984(4)	20.8528(8)	23.5554(2)
$\alpha$ , deg	90	90	90	90
$\beta$ , deg	94.564(5)	94.109(2)	109.118(5)	90
$\gamma$ , deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	2905(2)	3536.3(3)	3589.7(3)	8980.4(2)
<i>Z</i>	4	4	4	8
<i>F</i> (000)	1056	1536	1480	3584
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.106	1.377	1.286	1.261
$\mu$ , mm <sup>-1</sup> (Mo K $\alpha$ )	0.156	6.591	1.434	4.510
cryst size, mm	0.18 x 0.18 x 0.09	0.39 x 0.14 x 0.10	0.22 x 0.14 x 0.09	0.31 x 0.25 x 0.13
<i>T</i> , K	100(2)	150(2)	150(2)	150(2)
$\theta$ range, deg	2.24 to 28.35	4.82 to 69.60	2.41 to 31.44	3.73 to 69.53
min./max. <i>h, k, l</i>	-11/11, -24/24, -23/24	-22/20, -12/9, -22/21	-28/29, -12/12, -30/28	-22/14, -24/20, -28/23
no. collected reflns	59980	15937	51967	26822
no. unique reflns	7251	6536	11120	8279
no. reflns with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	6123	6069	5388	7706
no. params/restraints	310/0	382/0	391/0	490/0
GOF (on <i>F</i> <sup>2</sup> )	1.056	1.079	1.011	1.027
<i>R</i> <sub>1</sub> (on <i>F</i> , <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.038	0.043	0.075	0.026
<i>wR</i> <sub>2</sub> (on <i>F</i> <sup>2</sup> , all data)	0.099	0.121	0.108	0.068
min./max. $\Delta\rho$ , e Å <sup>-3</sup>	-0.320/0.346	-1.014/0.787	-0.622/0.766	-0.574/0.268
CCDC dep. no.	2001500	2001500	2001500	2001500

#### 4. Atomic coordinates of DFT-optimized structures

1<sub>Si</sub>

E = -1889.52071712 hartree

C	0.628182	3.052166	0.116815
H	-0.148683	2.702633	-0.582144
H	0.671813	4.149402	0.051841
H	0.323854	2.769920	1.135739
C	2.389866	2.833471	-1.658060
H	3.378668	2.428216	-1.918647
H	2.437864	3.929130	-1.757984
H	1.651531	2.451543	-2.379619
C	3.031210	2.955466	0.777550
H	2.803560	2.586197	1.789089
H	3.006680	4.055582	0.800598
H	4.052320	2.649704	0.513204
C	1.992482	2.442376	-0.227994
C	2.689521	-0.016627	-0.217173
C	4.174066	0.103329	-0.246330
C	4.842816	0.167413	-1.471048
H	4.272600	0.117878	-2.400560
C	6.230304	0.290000	-1.502934
H	6.747089	0.344565	-2.462327
C	6.954449	0.340214	-0.312641
H	8.041239	0.435578	-0.338572
C	6.289096	0.268425	0.910755
H	6.852091	0.305420	1.844645
C	4.901583	0.153066	0.945197
H	4.376229	0.104992	1.900636
C	2.364189	-2.552705	-0.301162
C	3.248547	-2.936933	-1.494676
H	2.757031	-2.661271	-2.440131
H	3.423677	-4.023949	-1.500293
H	4.227142	-2.438340	-1.449036
C	3.071566	-2.862590	1.024854
H	4.051144	-2.367784	1.086142
H	3.238203	-3.946807	1.117564
H	2.449447	-2.532594	1.870609
C	1.048749	-3.339896	-0.359184
H	0.400263	-3.077271	0.490796
H	1.251424	-4.420229	-0.322013
H	0.504931	-3.125693	-1.292932
C	0.276451	-0.347438	2.241819
H	1.308188	-0.009783	2.288363
C	-0.574439	-0.739984	3.243892
H	-0.339642	-0.779941	4.305189
C	-1.819293	-1.064439	2.627775
H	-2.734047	-1.388596	3.118363



C	-1.675614	-0.855001	1.274777
C	-2.686475	-1.017054	0.180057
H	-2.928569	-2.085376	0.055374
H	-2.263107	-0.685818	-0.780031
C	-5.330866	-0.935992	-0.937756
C	-4.559228	-1.190760	-2.240754
H	-5.248572	-1.598361	-3.000803
H	-3.753778	-1.927471	-2.108069
H	-4.113598	-0.276115	-2.653891
C	-5.816573	-2.288578	-0.382406
H	-6.400035	-2.822461	-1.152308
H	-6.457023	-2.151608	0.501867
H	-4.980279	-2.944108	-0.091391
C	-6.569827	-0.085699	-1.248976
H	-6.311626	0.831559	-1.798066
H	-7.113706	0.198894	-0.334379
H	-7.262480	-0.663726	-1.884513
C	-3.937029	1.662558	0.114015
C	-2.867885	2.100255	1.132778
H	-1.891958	1.636553	0.942704
H	-3.156912	1.847787	2.164616
H	-2.738540	3.194962	1.070844
C	-3.427363	1.961228	-1.299140
H	-3.128344	3.022244	-1.369963
H	-4.201695	1.792065	-2.062197
H	-2.544805	1.355342	-1.560581
C	-5.198192	2.495091	0.401618
H	-4.947225	3.568982	0.357864
H	-5.594545	2.283013	1.406855
H	-6.001210	2.317923	-0.325136
N	1.808149	0.987024	-0.116812
N	1.983648	-1.135149	-0.352673
N	-0.381374	-0.413580	1.025710
P	-4.329099	-0.167307	0.504939
Si	0.362511	-0.161386	-0.633214

**1<sub>Ge</sub>**

E = -3677.07755888 hartree

C	0.648631	3.076745	0.030413
H	-0.112751	2.741745	-0.693116
H	0.700547	4.174266	-0.023030
H	0.313061	2.786251	1.037147
C	2.455792	2.850205	-1.698231
H	3.443808	2.428675	-1.935510
H	2.524076	3.945293	-1.793394
H	1.730872	2.484100	-2.441715
C	3.031087	2.967988	0.752408

H	2.782835	2.590217	1.755812
H	2.999151	4.067848	0.782702
H	4.059653	2.670033	0.509897
C	2.017358	2.456760	-0.280385
C	2.684375	-0.006109	-0.251004
C	4.166298	0.121123	-0.136640
C	4.950824	0.211196	-1.288811
H	4.474542	0.167228	-2.269923
C	6.333326	0.349117	-1.183409
H	6.940505	0.422566	-2.087099
C	6.937494	0.388351	0.072361
H	8.020264	0.495865	0.155083
C	6.156584	0.289838	1.223827
H	6.625969	0.319198	2.208263
C	4.774045	0.159630	1.120531
H	4.158599	0.094380	2.019534
C	2.423836	-2.543736	-0.340791
C	3.468169	-2.919001	-1.400863
H	3.107684	-2.653179	-2.406692
H	3.655395	-4.003841	-1.376897
H	4.425809	-2.408874	-1.225810
C	2.950433	-2.841263	1.070672
H	3.907743	-2.334343	1.257907
H	3.117917	-3.922953	1.190253
H	2.218461	-2.515858	1.825380
C	1.144666	-3.358671	-0.573284
H	0.380609	-3.100417	0.176905
H	1.356480	-4.434814	-0.492557
H	0.732672	-3.166382	-1.577065
C	0.262243	-0.382772	2.189387
H	1.293821	-0.041529	2.197071
C	-0.551911	-0.769921	3.227141
H	-0.278900	-0.803077	4.279372
C	-1.816602	-1.098853	2.659229
H	-2.713579	-1.419356	3.184224
C	-1.718866	-0.897464	1.298770
C	-2.770942	-1.048246	0.241582
H	-3.047206	-2.110256	0.135583
H	-2.378209	-0.736767	-0.738202
C	-5.444864	-0.885824	-0.851600
C	-4.720340	-1.157561	-2.126987
H	-5.441690	-1.549256	-2.865401
H	-3.928073	-1.912630	-2.019200
H	-4.267776	-0.252969	-2.554681
C	-5.951508	-2.226280	-0.234619
H	-6.578446	-2.737865	-0.985124
H	-6.554955	-2.074638	0.672972

H	-5.126012	-2.908653	0.023405
C	-6.667915	0.450000	-1.071562
H	-6.438400	0.912929	-1.623477
H	-7.177013	0.294229	-0.140235
H	-7.394611	-0.554676	-1.689609
C	-3.948776	1.669466	0.214094
C	-2.835492	2.079857	1.196468
H	-1.875980	1.597499	0.971957
H	-3.093053	1.828241	2.236706
H	-2.687122	3.172118	1.134638
C	-3.479914	1.957685	-1.215145
H	-3.147388	3.799300	-1.294030
H	-4.284545	1.815950	-1.951840
H	-2.628223	1.323330	-1.509452
C	-5.178202	2.533692	0.543851
H	-4.902250	3.686800	0.488848
H	-5.543059	2.332854	1.563118
H	-6.011047	2.375570	-0.153049
N	1.812486	1.443600	-0.186997
N	2.018212	-1.136380	-0.454462
N	-0.438074	-0.459641	1.263600
P	-4.378038	-0.151600	0.613757
Ge	0.268879	-0.170522	-0.785168