

## *Supporting Information*

### **Trapping of Two Mononuclear Silyl Platinum(II)/Palladium(II) and a Unique Dinuclear bis( $\mu_2$ -Disilene)(silyl) Nickel(II) Complexes**

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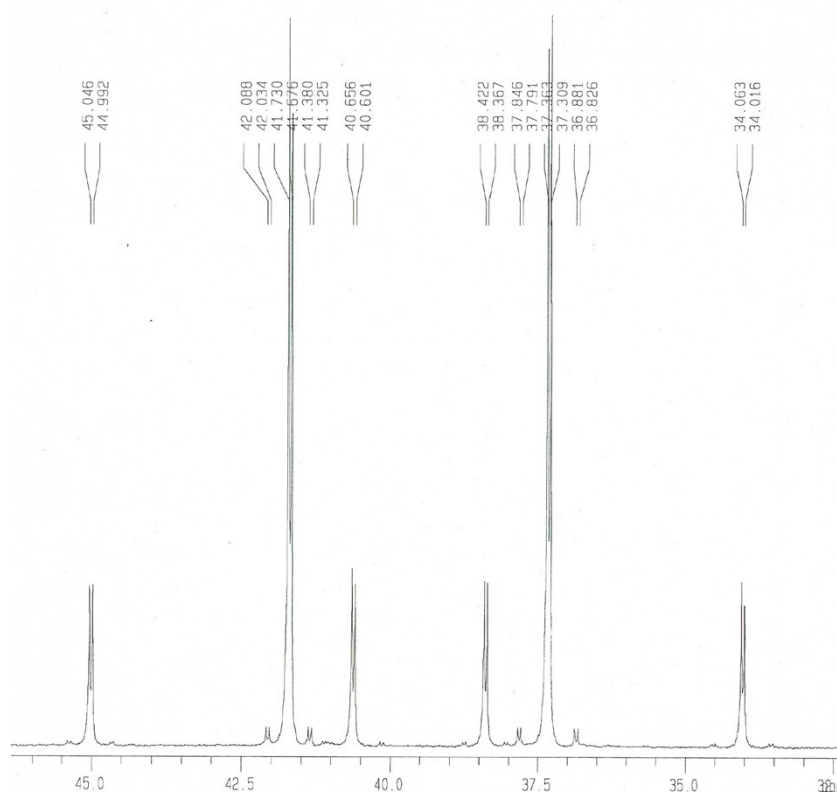
#### **SI. X-ray crystallography**

Single crystals for **4** and **5** were obtained upon slowly evaporation of the mixed solvent of ethyl acetate and hexane. Crystalline **6** is virtually insoluble in most of organic solvents and single crystals were obtained luckily upon cooling a hot tetrahydrofuran solution under nitrogen atmosphere. X-ray diffraction data were collected at 293K and on a Bruker Apex CCD area detector diffractometer using a graphite monochromator with  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections.

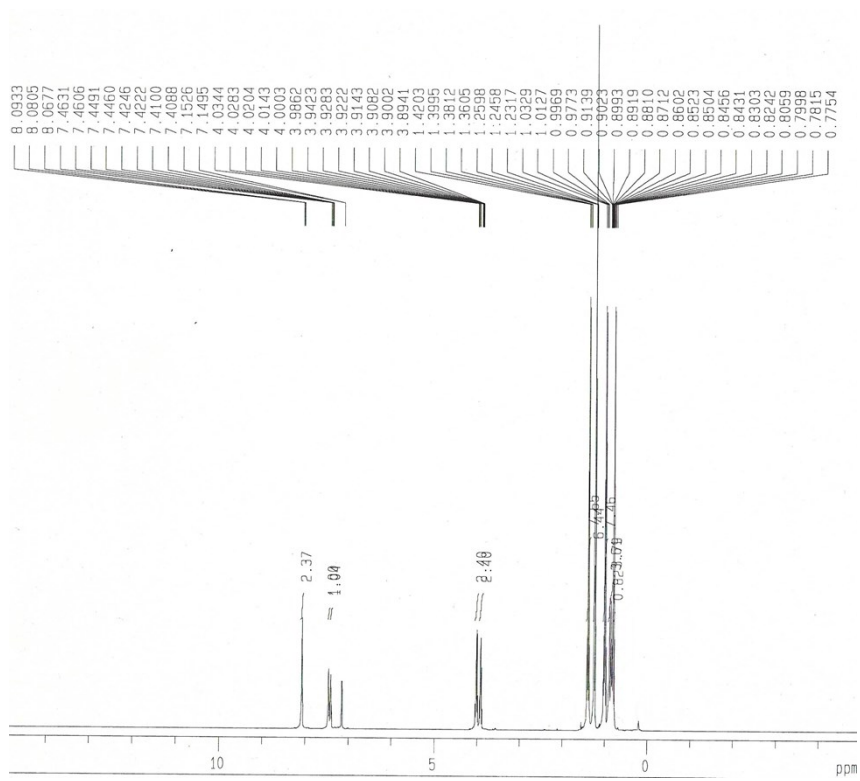
Data reductions were performed using the SAINT software, and absorption corrections were applied using SADABS supplied by Bruker.<sup>[1]</sup> The structures were solved by direct methods and refined to convergence by full-matrix least squares on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms using *SHELX* package.<sup>[2]</sup> As for compound **4**, we performed isotropic refinements on all the non-metallic atoms due to the presence of NPD which was aroused by Pt heavy atom, resulting in relatively high  $R_1$  and  $wR_2$  values. The hydrogen atoms were placed in idealized positions using a riding model. Solvent molecules in structure **6** are highly disordered and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE routine of PLATON.<sup>[3]</sup> Crystal data and structure refinement results were summarized in Table S1. The selected bond lengths and bond angles are listed in Table S2. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition no. CCDC 1972435 for **4**, 1972439 for **5**, 1972446 for **6**. These data can be obtained free of charge ([http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)).

1. (a) SAINT-plus, Version 6.02, Bruker Analytical X-ray System, Madison, WI, 1999; (b) Sheldrick, G. M. *SADABS, an Empirical Absorption Correction Program*, Bruker Analytical X-ray Systems, Madison, WI, 1996
2. Sheldrick, G. M. A short history of SHELX. *Acta. Crystallogr. Sect. A: Found Crystallogr.* **2008**, *64*, 112-122.
3. Spek A. L. J. *Appl. Crystallogr.* **2003**, *36*, 7-13.

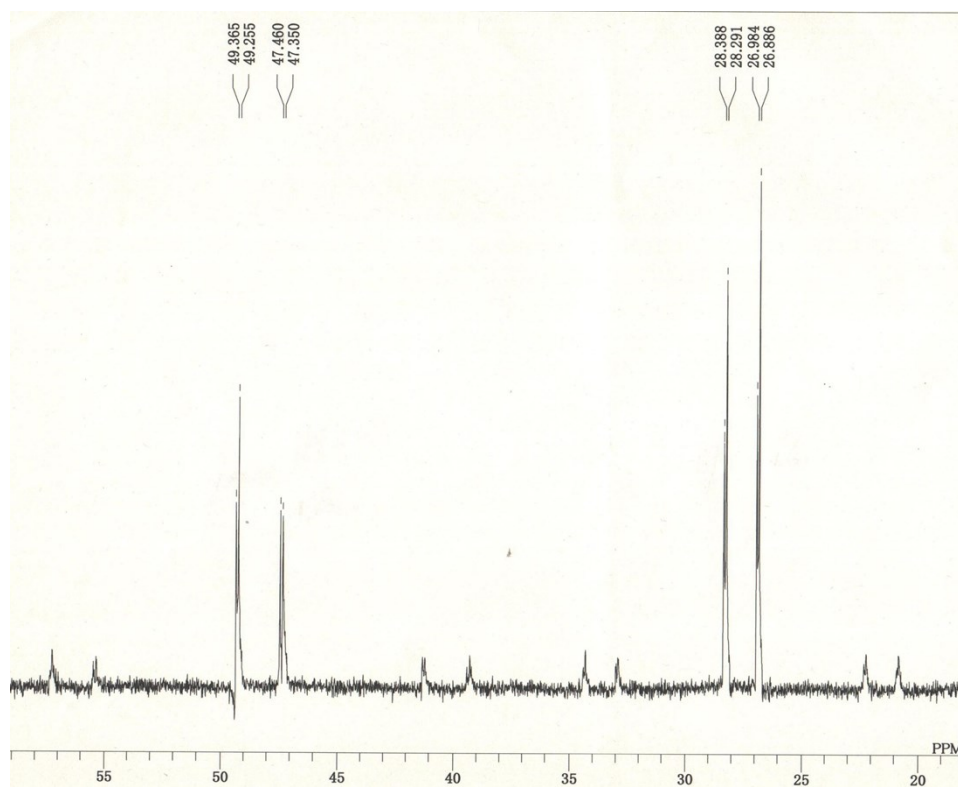
## S2. Copies of NMR spectra of the product



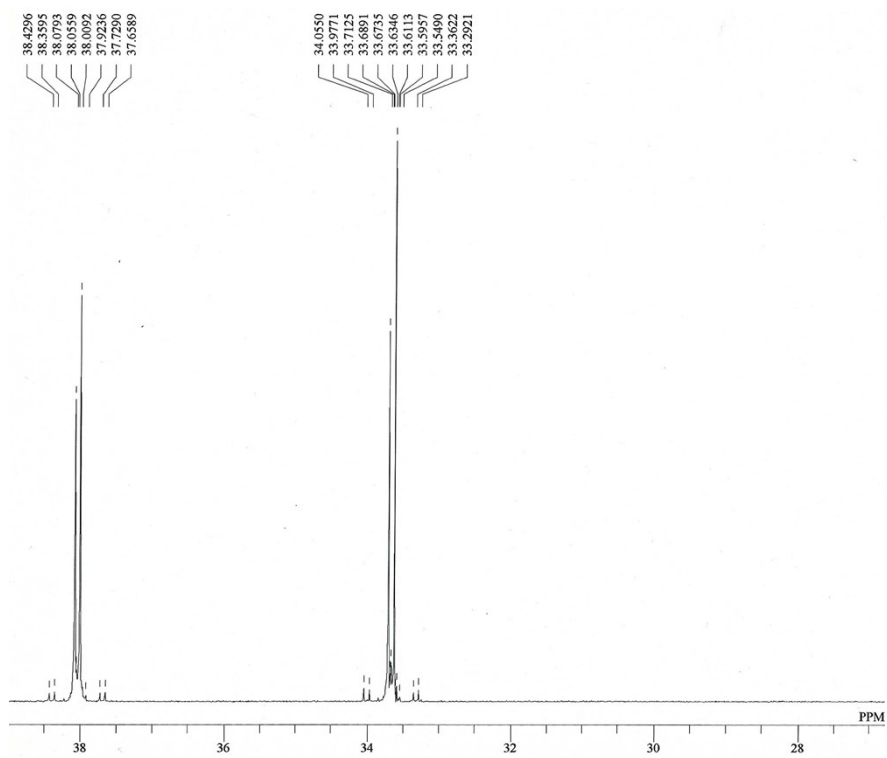
**Figure S1:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) for compound 4



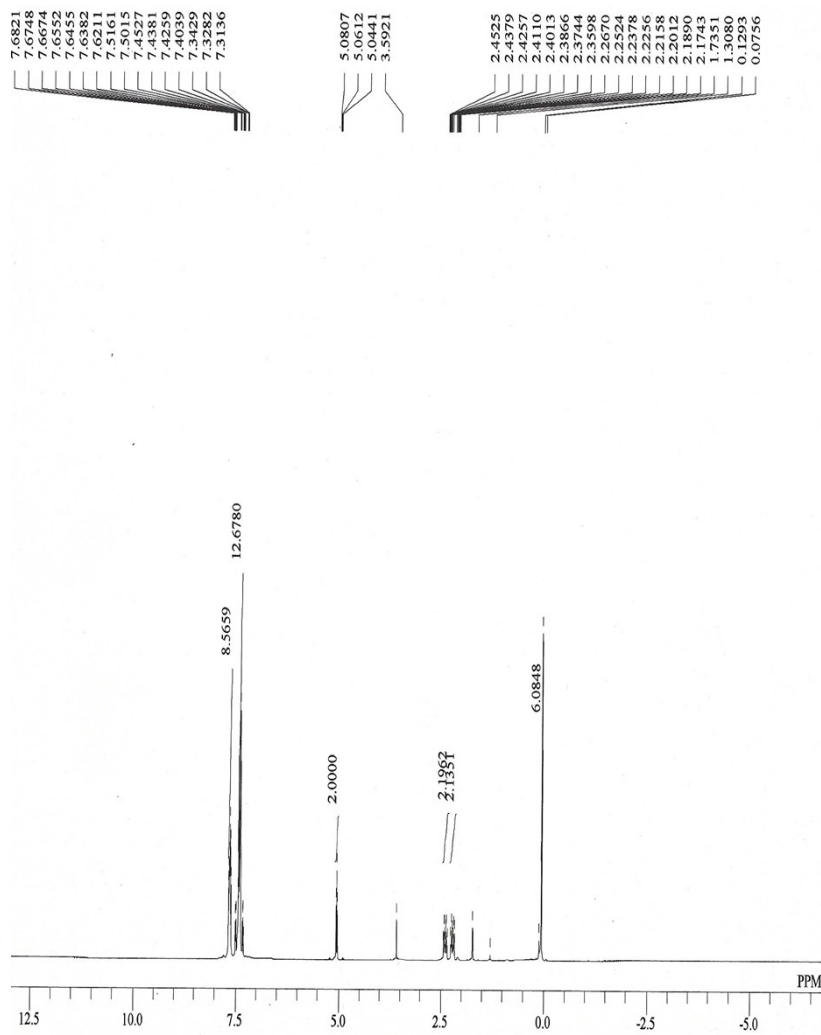
**Figure S2:**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) for compound **4**



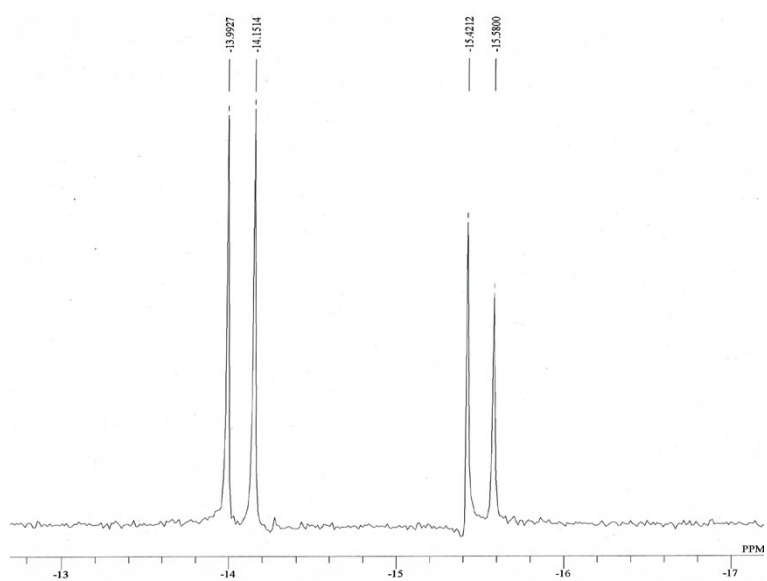
**Figure S3:**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) for compound 4



**Figure S4:**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (THF-d<sub>8</sub>) for compound 5

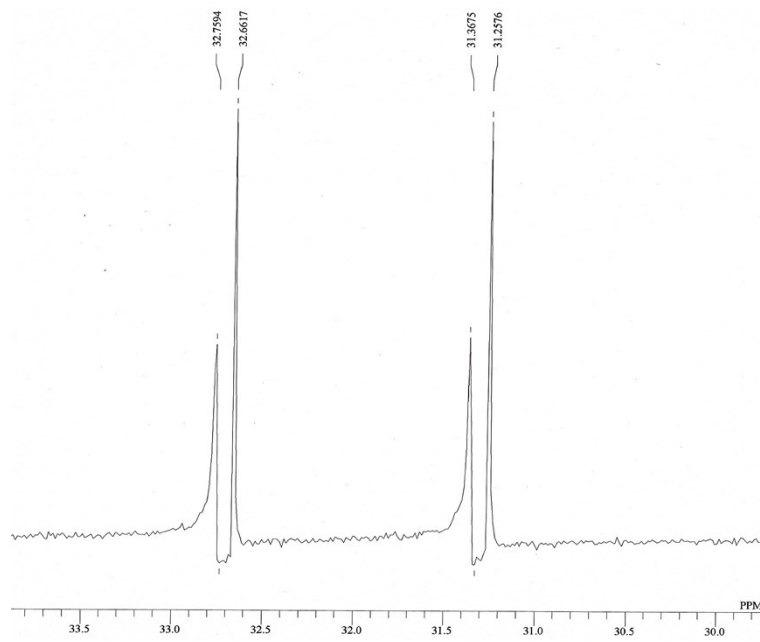


**Figure S5:**  $^1\text{H}$  NMR spectrum (THF- $d_8$ ) for compound **5**



**Figure S6:**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (THF- $d_8$ , DEPT) for compound **5**





**Figure S7:**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum ( $\text{THF-d}_8$ , INEPT) for compound **5**

**Table S1** Crystallographic data for **4**, **5** and **6**

Compounds	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> P <sub>2</sub> PtSi <sub>2</sub>	C <sub>40</sub> H <sub>50</sub> P <sub>2</sub> PdSi <sub>2</sub>	C <sub>64</sub> H <sub>108</sub> Ni <sub>2</sub> P <sub>4</sub> Si <sub>4</sub>
Formula weight	597.68	755.34	1231.12
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P 2<sub>1</sub>/c</i>	<i>P -1</i>	<i>P -1</i>
<i>a</i> (Å)	8.6370(17)	11.747(2)	11.740(2)
<i>b</i> (Å)	15.795(3)	13.118(3)	15.220(3)
<i>c</i> (Å)	18.196(4)	13.202(3)	21.430(4)
$\alpha$ (°)	90	94.02(3)	70.53(3)
$\beta$ (°)	98.15(3)	113.95(3)	80.01(3)
$\gamma$ (°)	90	95.58(3)	76.47(3)
Volume (Å <sup>3</sup> )	2457.3(9)	1836.9(7)	3490.9(14)
<i>Z</i>	4	2	2
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.616	1.366	1.171
$\mu$ (mm <sup>-1</sup> )	5.947	0.685	0.735
<i>F</i> (000)	1184	788	1328
Index ranges	-10 ≤ <i>h</i> ≤ 10, -18 ≤ <i>k</i> ≤ 18, -21 ≤ <i>l</i> ≤ 21	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -17 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 18, -25 ≤ <i>l</i> ≤ 25
Reflections collected	4372	8261	12173
Independent reflections	4187	7624	5935

Data/restraints/parameters	4372/97/235	8261/0/410	12173/0/667
GOF (F <sup>2</sup> )	1.127	1.070	0.794
$R_I [I > 2\sigma(I)]$	0.1075	0.0333	0.0566
$wR_2$ (all data)	0.2326	0.0977	0.1228

$$R_I = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$


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**Table S2** Selected bond lengths (Å) and bond angles (°) for **4**, **5** and **6**

Selected bond lengths for <b>4</b>				Selected bond lengths for <b>5</b>			
Pt1-P1	2.303(4)	Pt1-P2	2.300(4)	Pd1-P2	2.352(8)	Pd1-P1	2.341(1)
Pt1-Si2	2.346(4)	Pt1-Si1	2.355(4)	Pd1-Si2	2.372(8)	Pd1-Si1	2.338(1)
Si1-C8	1.891(13)	Si1-C7	1.900(14)	Si1-C29	1.885(2)	Si1-H1A	1.4366
Si1-C1	1.915(15)	Si2-C6	1.875(13)	P1-C21	1.821(3)	P1-C14	1.854(2)
Si2-O1	1.678(9)	Si2-O2	1.686(10)	P2-C1	1.829(2)	P2-C13	1.838(2)
Selected bond lengths for <b>6</b>							
Ni1-P1	2.149(1)	Ni1-P2	2.143(1)	Ni2-P3	2.146(1)	Ni2-P4	2.144(2)
Ni1-Si1	2.261(7)	Ni1-Si4	2.274(8)	Ni2-Si2	2.274(1)	Ni2-Si3	2.260(1)
Si1-Si3	2.351(2)	Si2-Si4	2.353(2)	Si3-C7	1.911(6)	Si1-C1	1.915(5)
Selected bond angles for <b>4</b>							
P2-Pt1-Si2	95.53(12)		P2-Pt1-P1	85.39(13)			
Si2-Pt1-P1	173.99(13)		P2-Pt1-Si1	175.17(12)			
Si2-Pt1-Si1	83.24(13)		C8-Si1-C7	106.5(6)			
C8-Si1-Pt1	112.6(4)		C6-Si2-Pt1	111.6(4)			
C6-Si2-O1	106.6(5)		Pt1-Si2-O2	116.5(3)			
C16-C15-P1	110.9(10)		C13-P1-C14	101.5(7)			
Selected bond angles for <b>5</b>							
P2-Pd1-Si2	173.87(2)		P1-Pd1-Si1	174.05(2)			
P1-Pd1-P2	84.88(3)		Si2-Pd1-Si1	80.03(3)			
P2-Pd1-Si1	98.72(3)		P1-Pd1-Si2	96.88(3)			

P2-C13-C14	108.30(16)	C21-P1-C15	106.38(11)
C1-P2-C7	102.56(10)	Pd1-P2-C13	106.03(8)

Selected bond angles for **6**

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P1-Ni1-P2	90.52(7)	P3-Ni2-P4	90.45(7)
Si1-Ni1-Si4	80.41(6)	Si2-Ni2-Si3	80.27(6)
P1-Ni1-Si1	159.44(7)	P3-Ni2-Si3	159.14(7)
P1-Ni1-Si4	98.00(7)	P3-Ni2-Si2	97.76(7)
Si1-Si3-Ni2	115.52(8)	Si2-Si4-Ni1	117.79(8)
P1-C14-C13	113.2(4)	P4-C40-C39	112.1(4)
C21-P1-C15	104.5(3)	C47-P4-C41	103.2(3)

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