

## Supporting Information

### ***Synthesis and Reactivity of [PCCP]-Coordinated Group 5 Alkyl and Alkylidene Complexes Featuring a Metallacyclopropene Backbone***

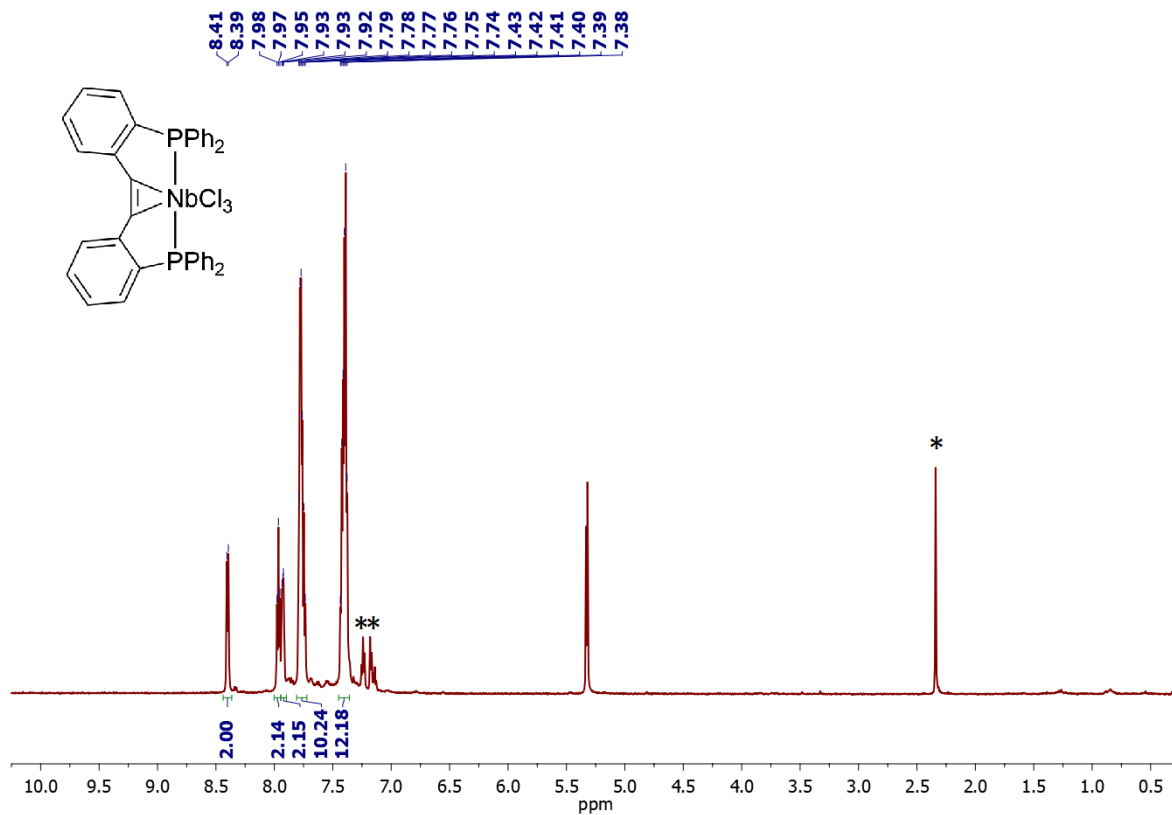
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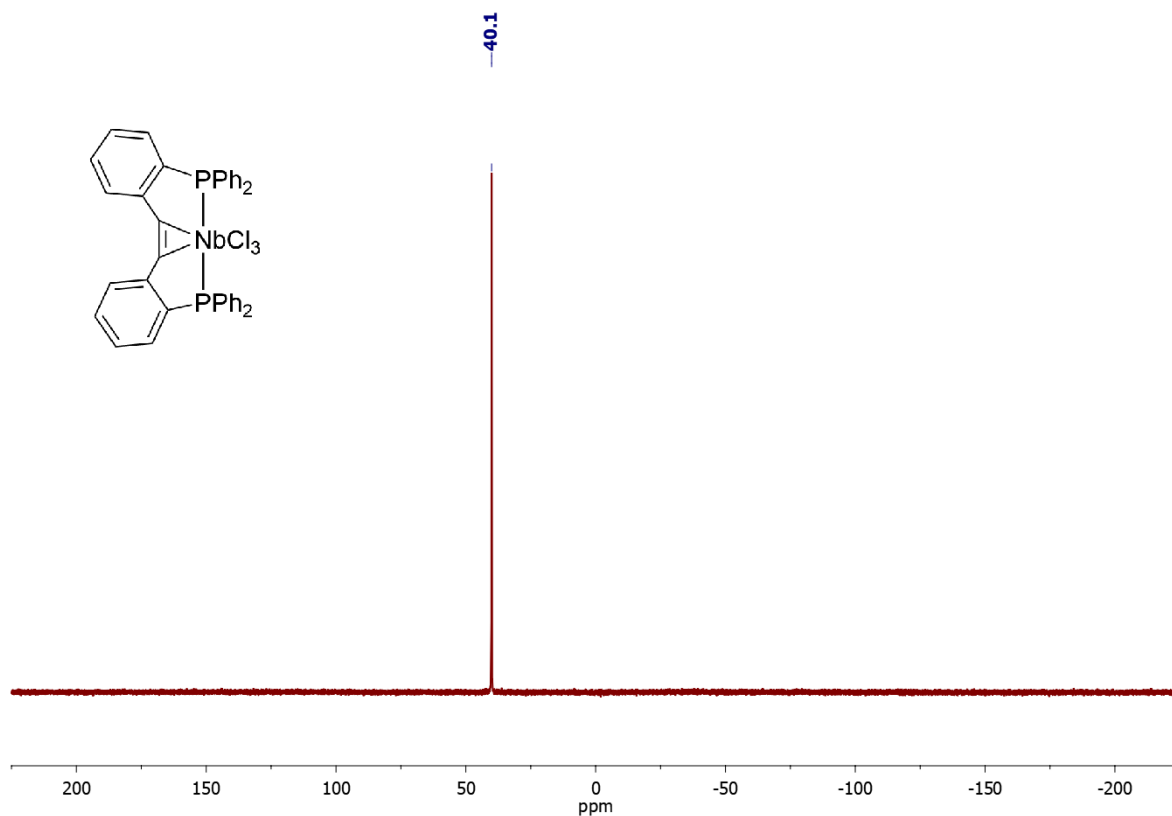
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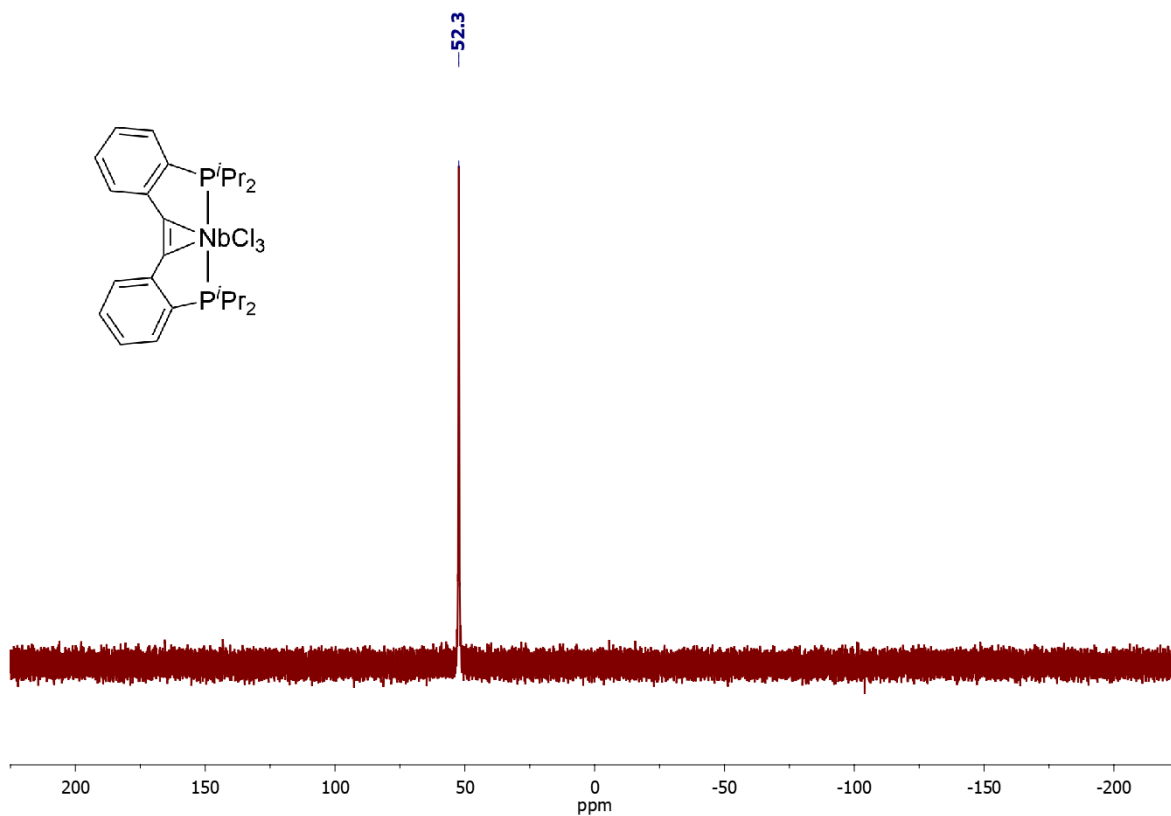
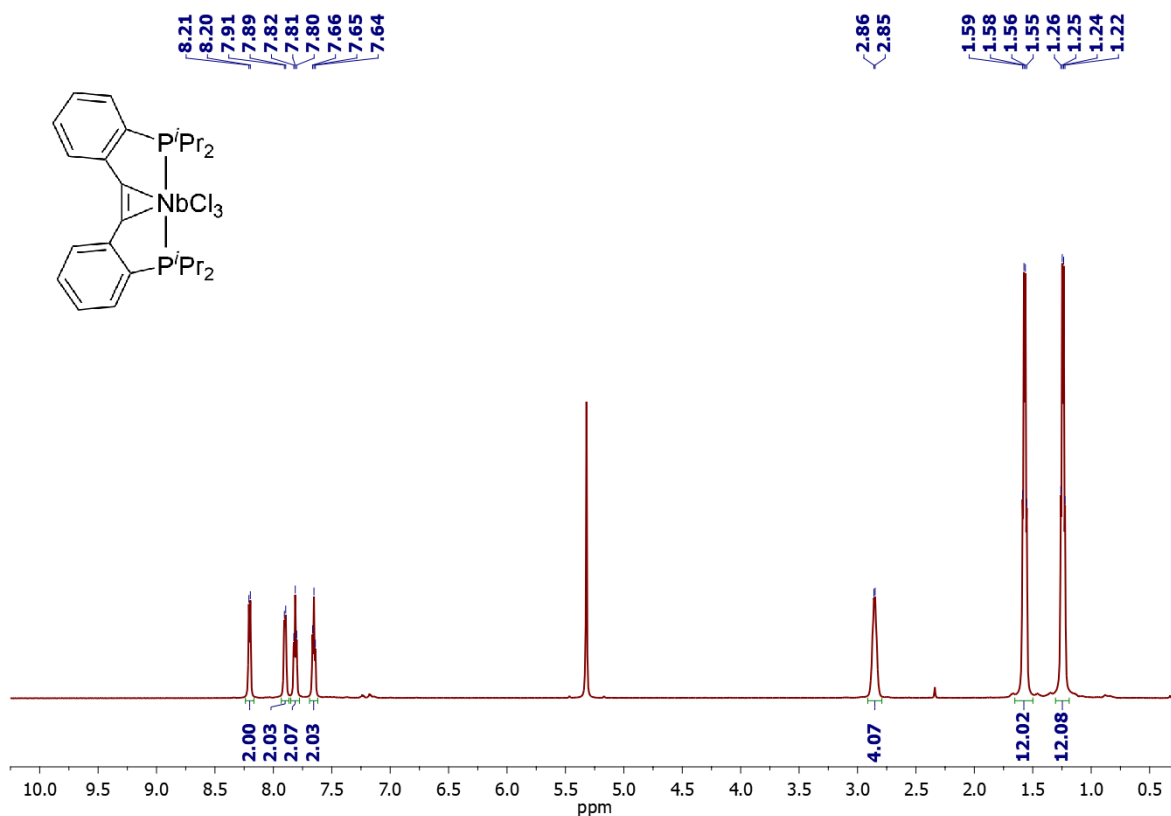
## Selected NMR Spectra

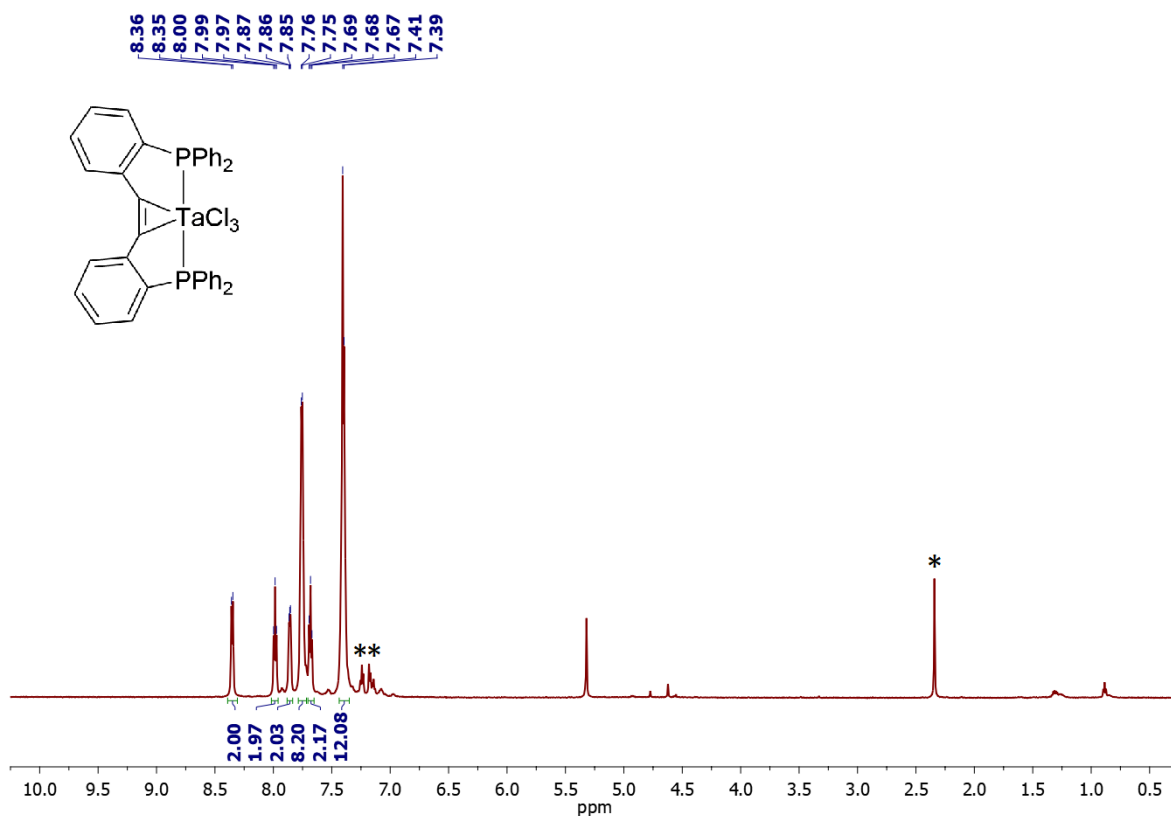


**Figure S1.**  $^1\text{H}$  NMR spectrum of **4a** (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K) (residual toluene signals are labeled with \*).

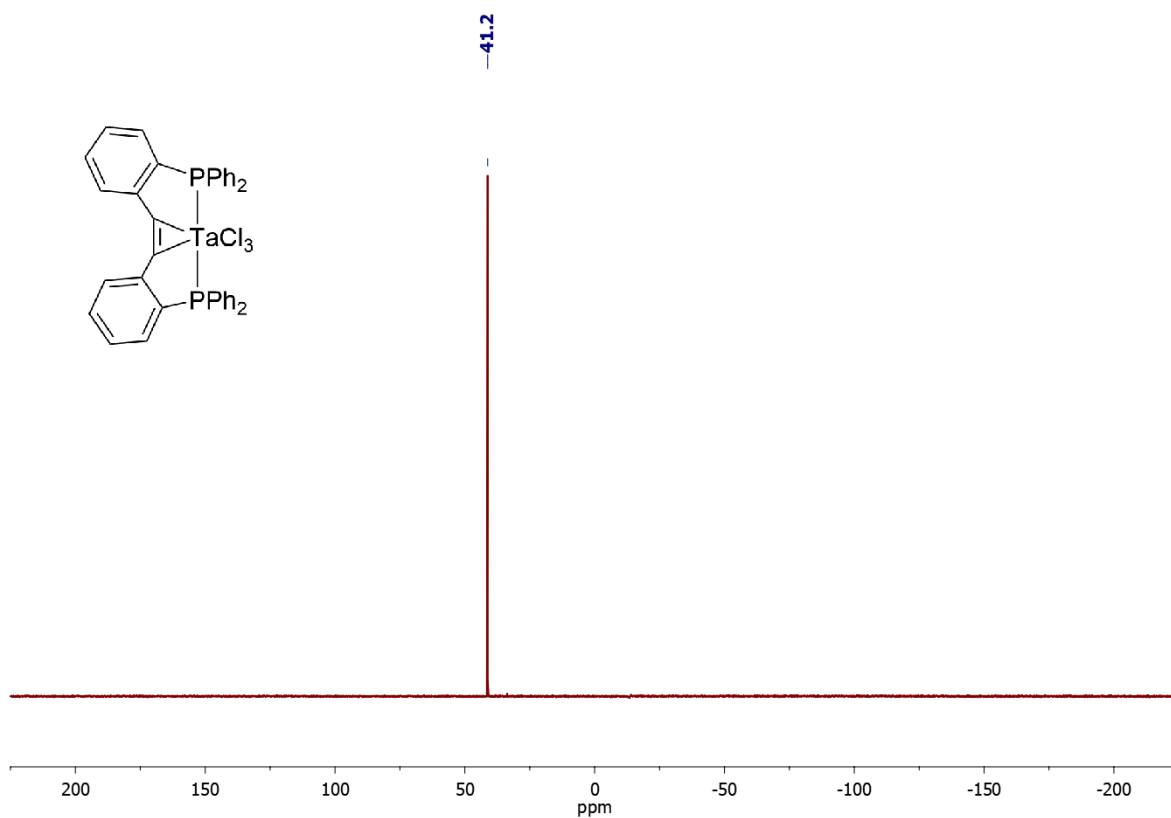


**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4a** (243 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K).

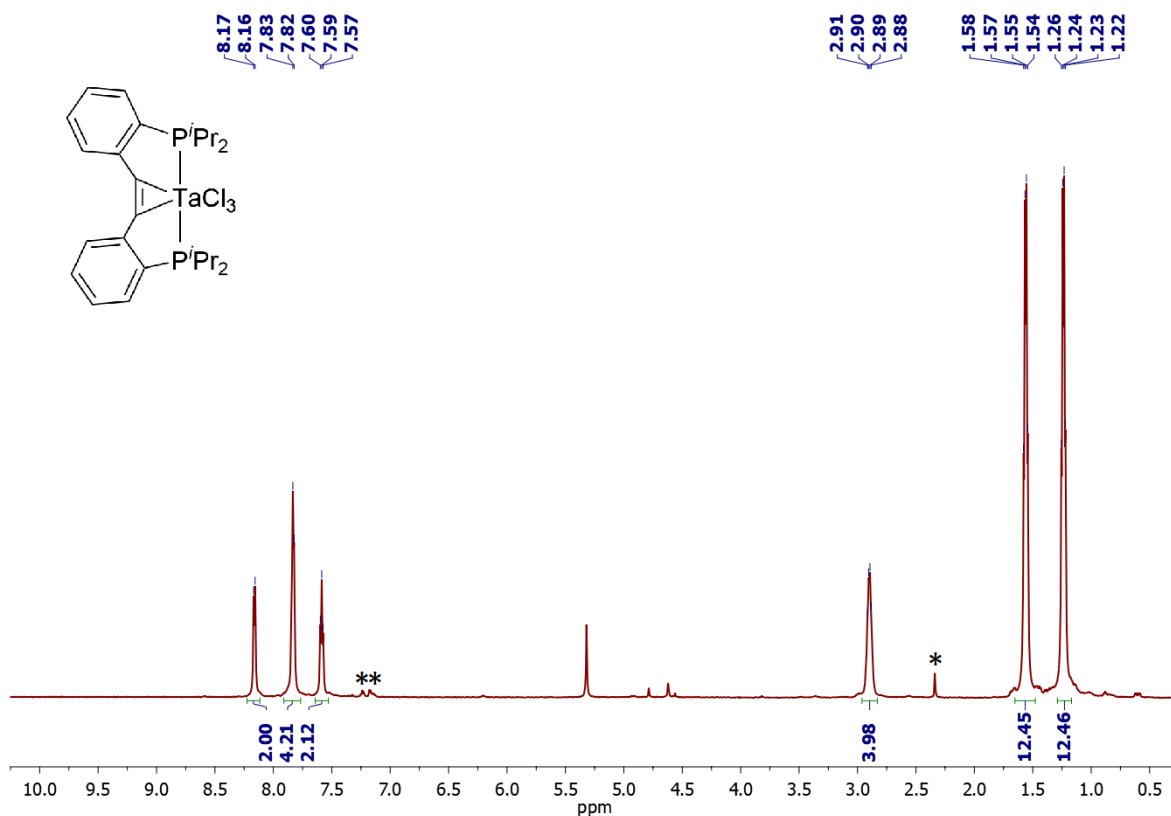




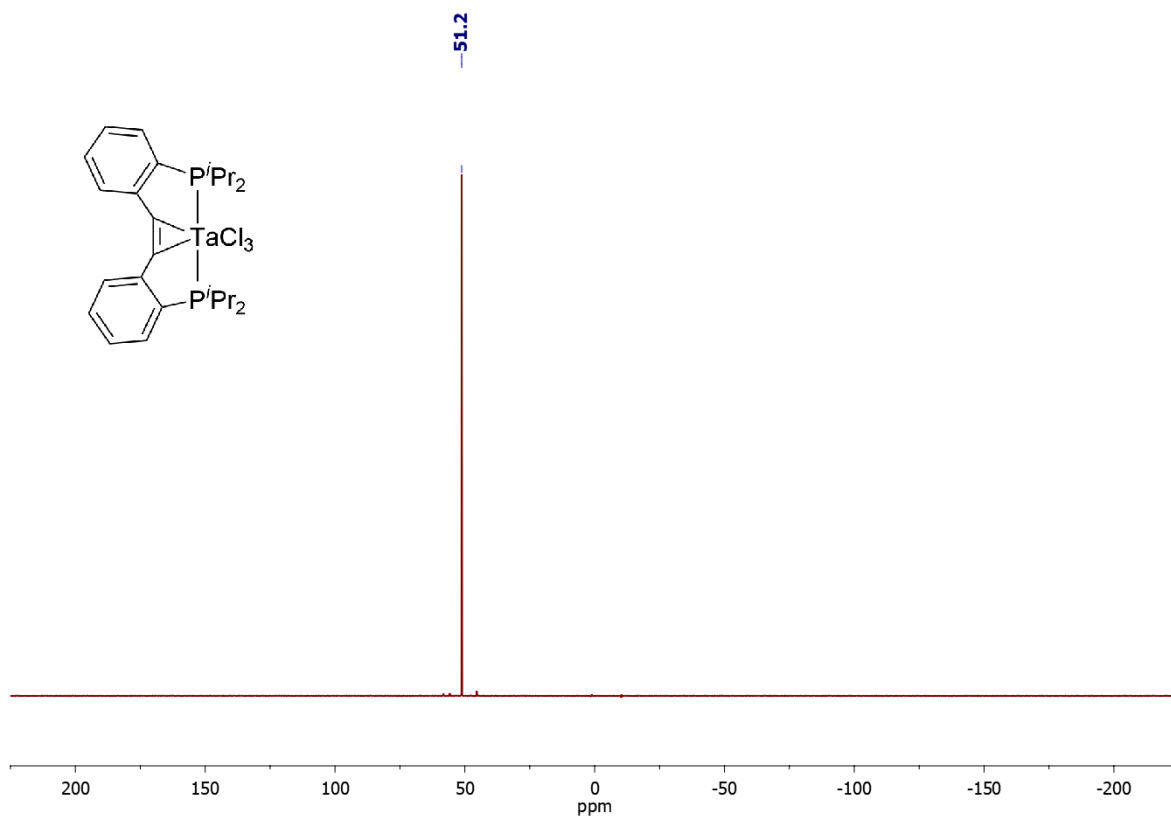
**Figure S5.**  $^1\text{H}$  NMR spectrum of **5a** (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K) (residual toluene signals are labeled with \*).



**Figure S6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5a** (243 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K).



**Figure S7.** <sup>1</sup>H NMR spectrum of **5b** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K) (residual toluene signals are labeled with \*).



**Figure S8.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5b** (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K).

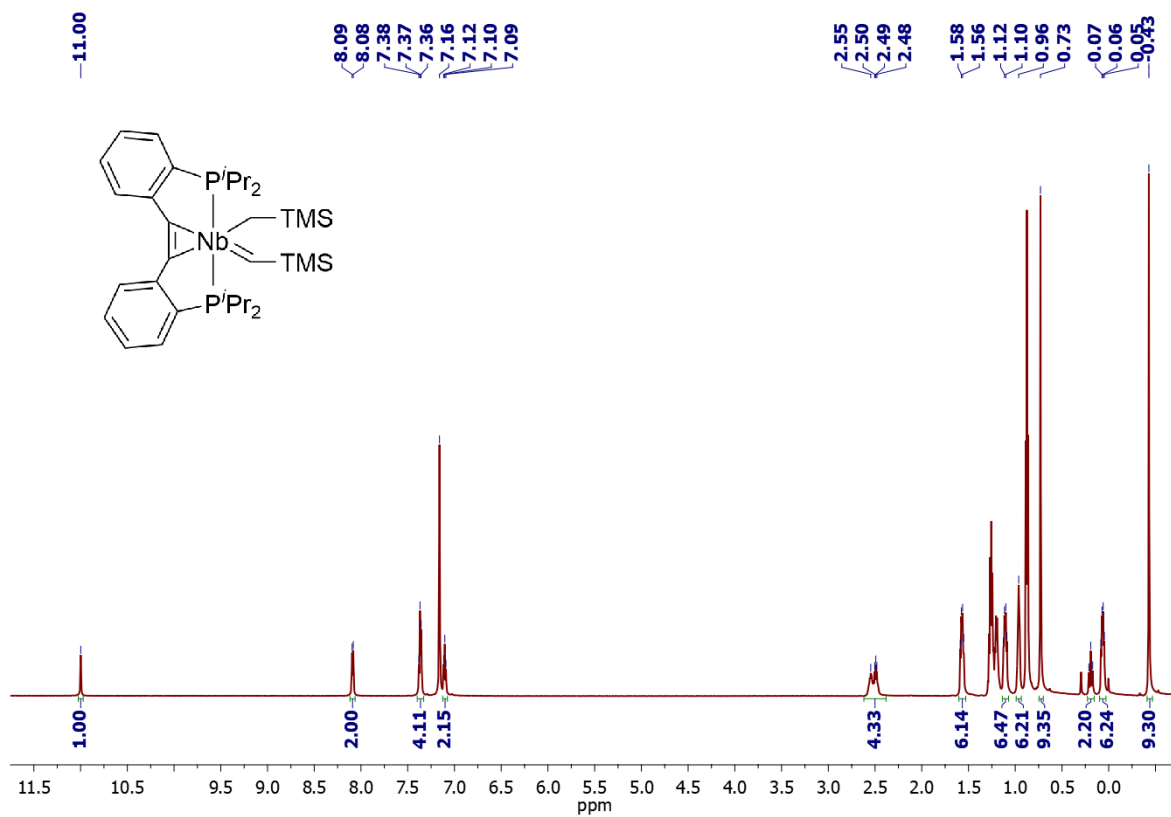


Figure S9. <sup>1</sup>H NMR spectrum of **6b** (600 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K).

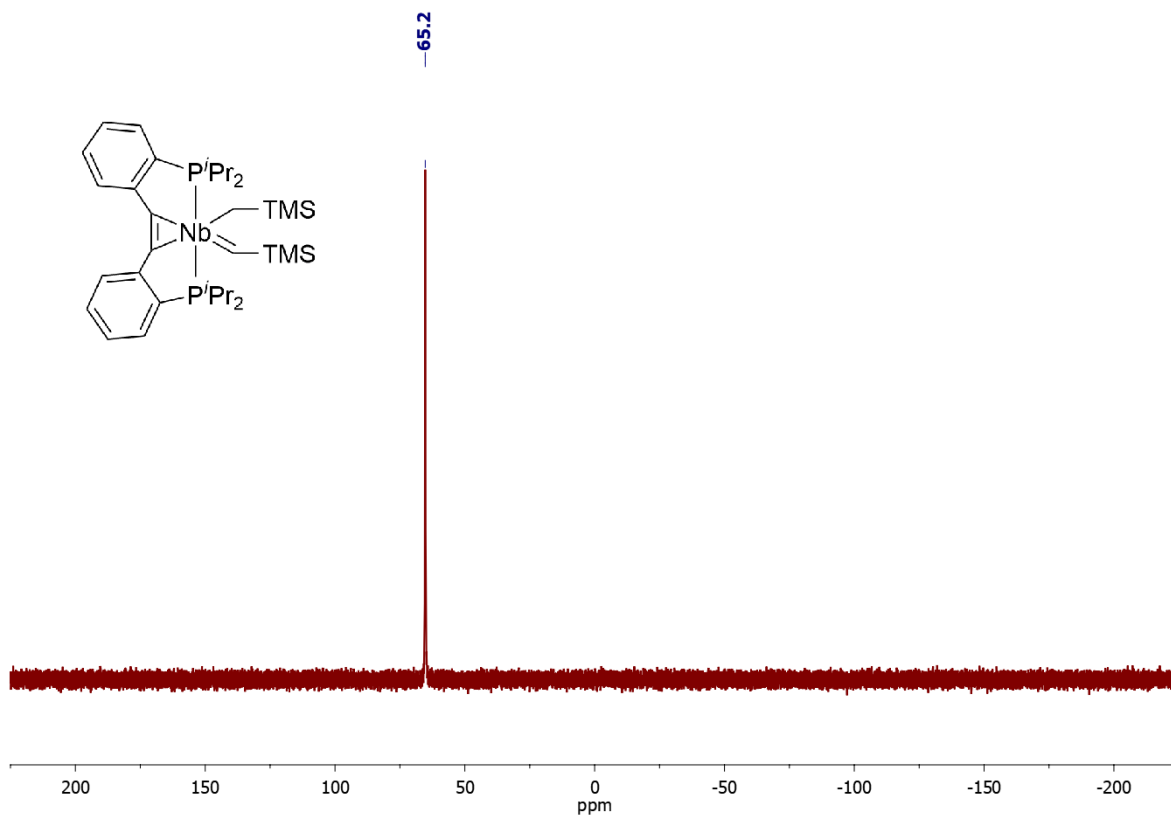
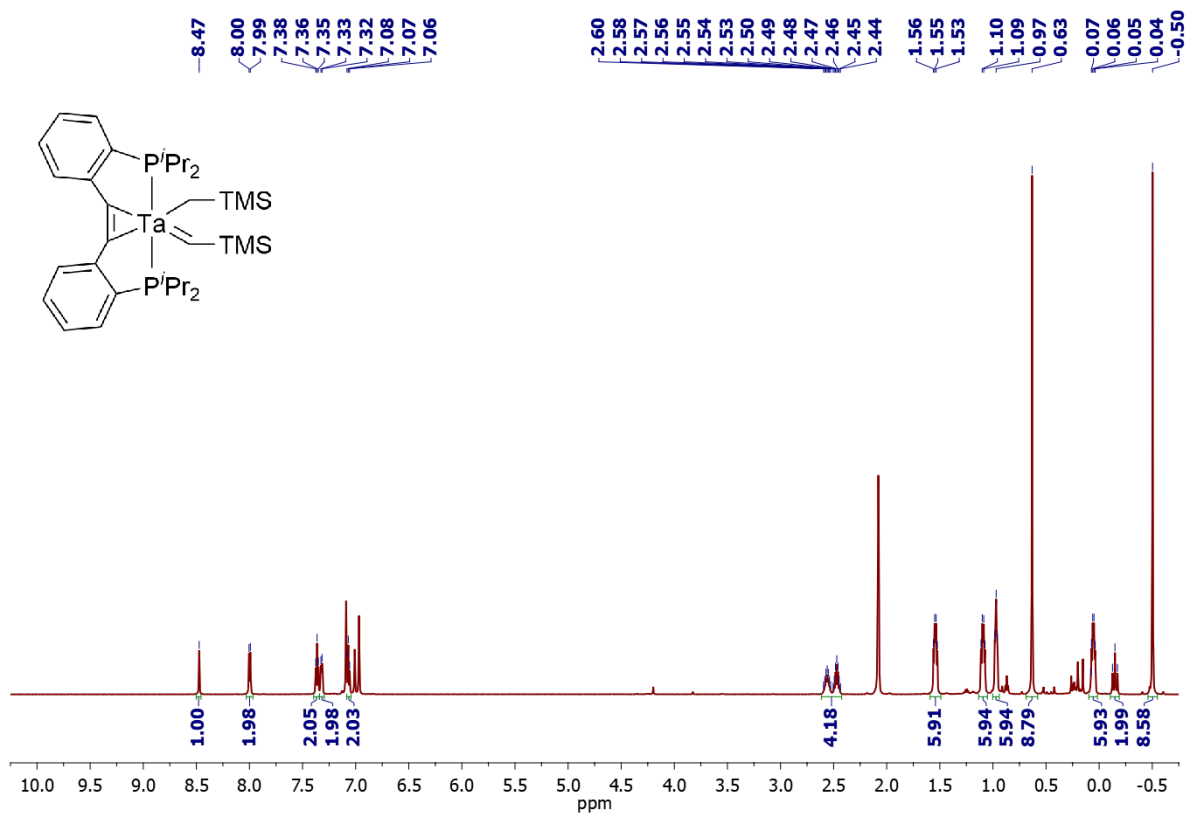
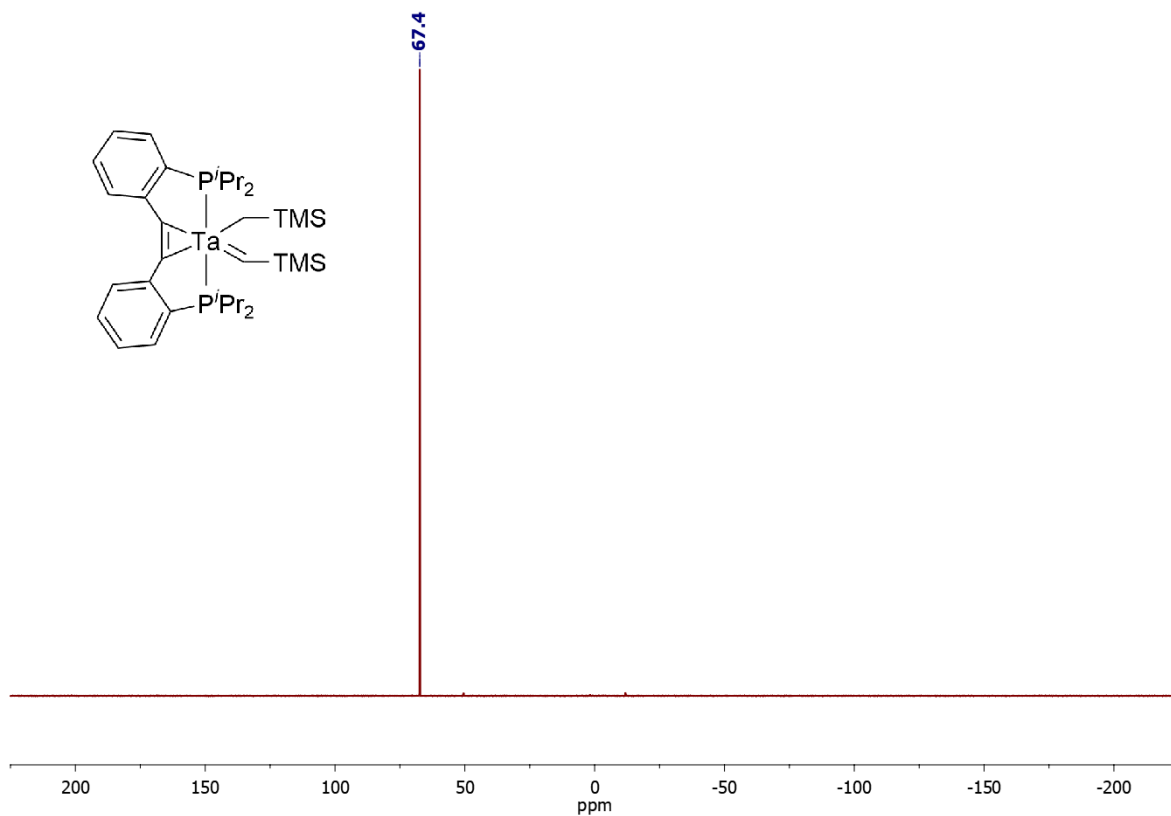


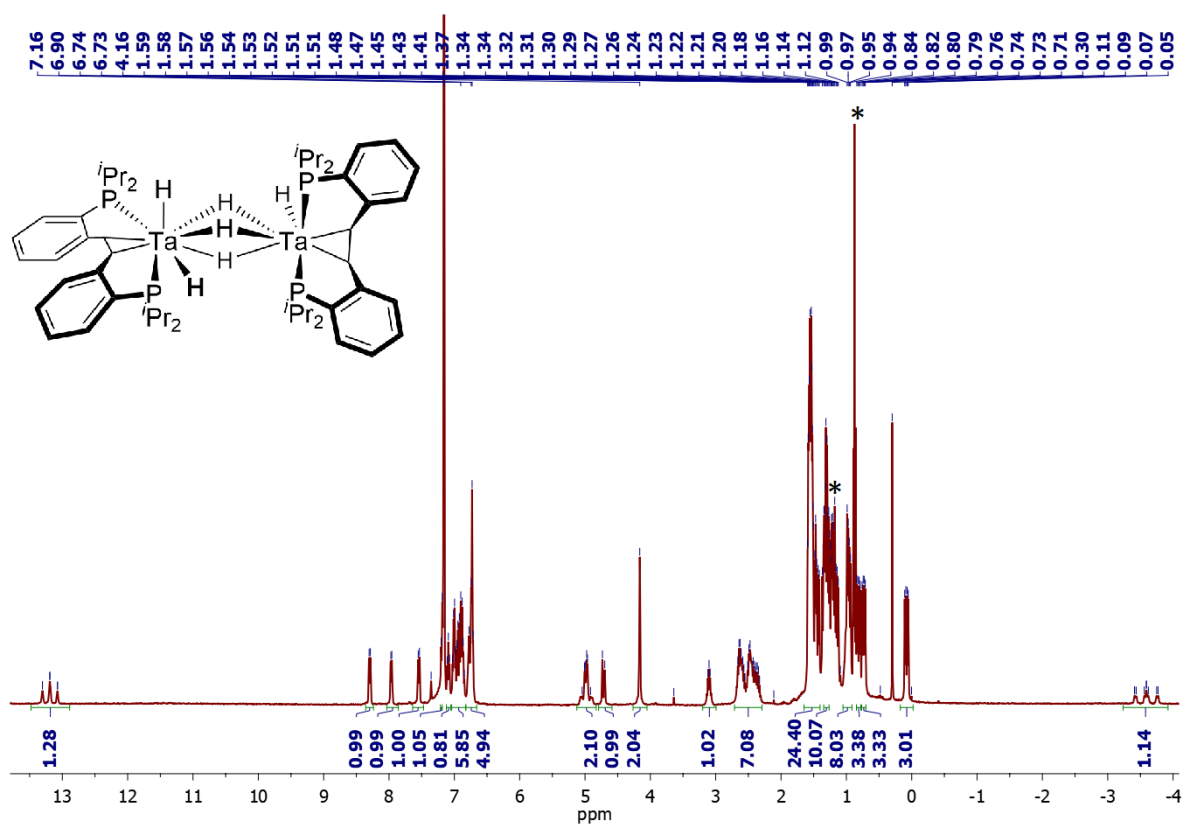
Figure S10. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **6b** (243 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K).



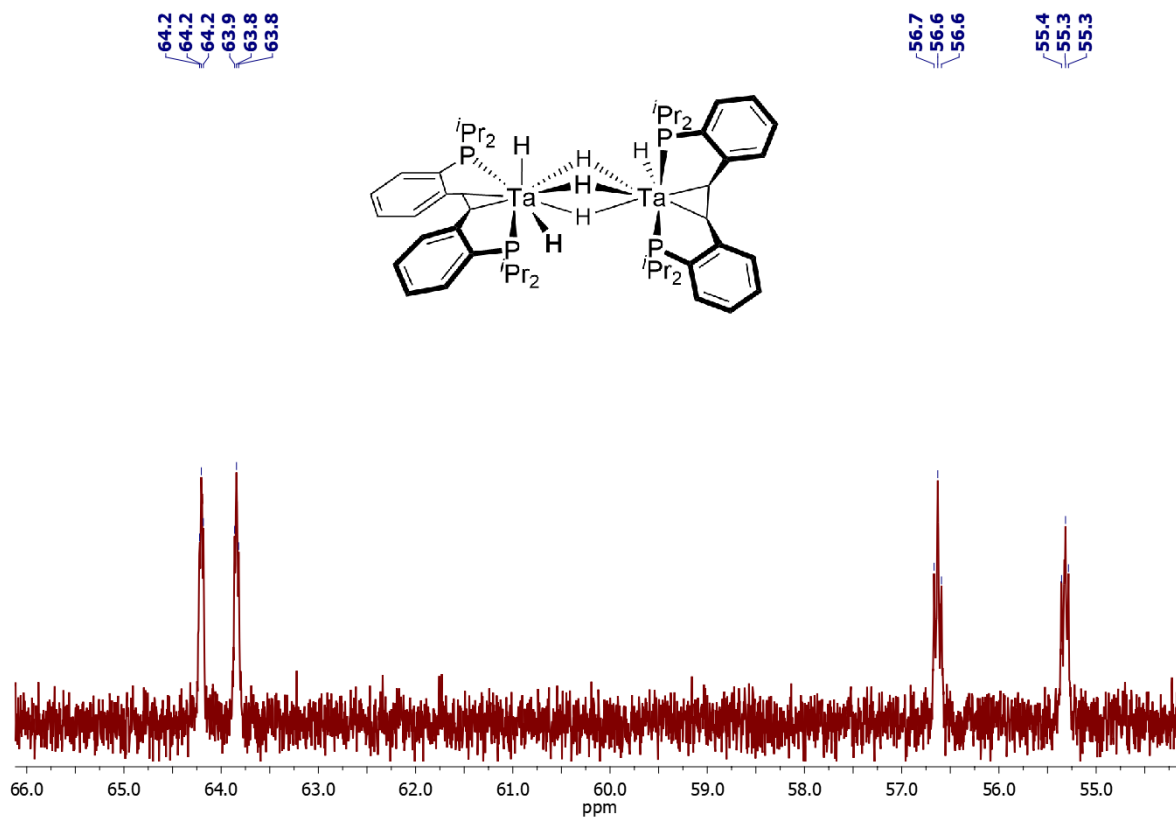
**Figure S11.** <sup>1</sup>H NMR spectrum of **7b** (600 MHz, toluene-d<sub>8</sub>, 295 K).



**Figure S12.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **7b** (243 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K).

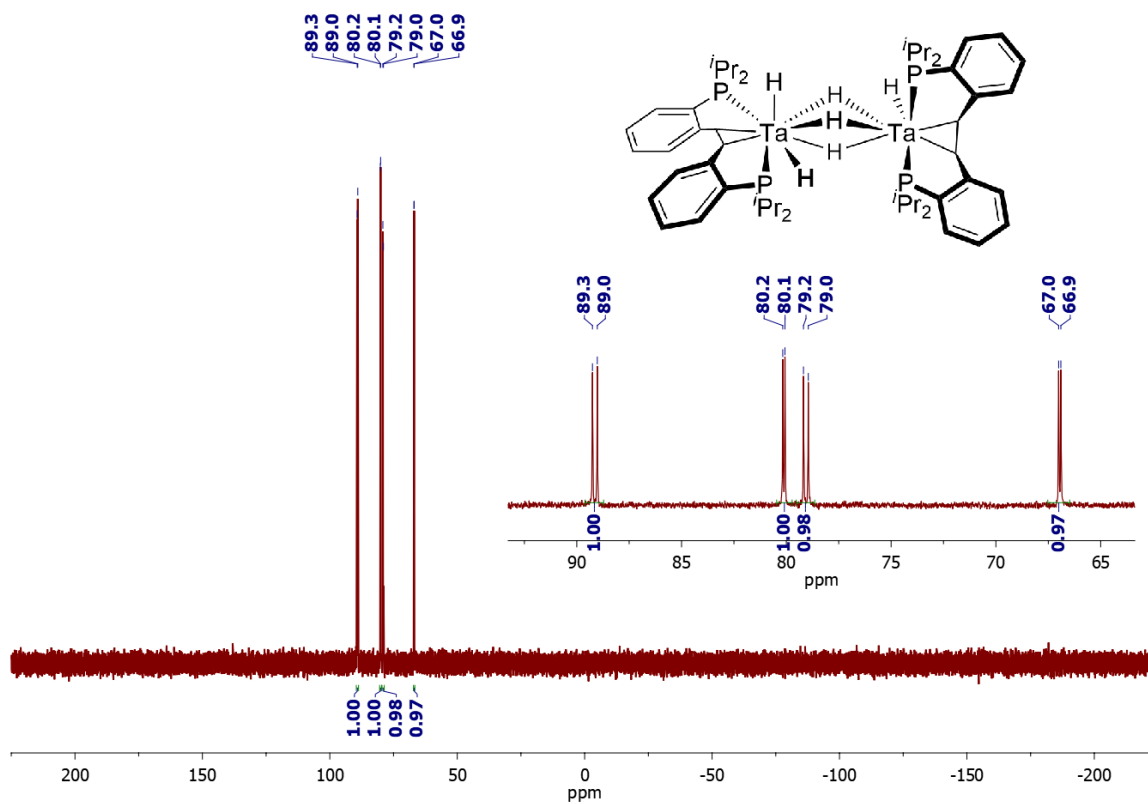


**Figure S13.** <sup>1</sup>H NMR spectrum of **8** (600 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K). Residual pentane signals are labeled with \*.

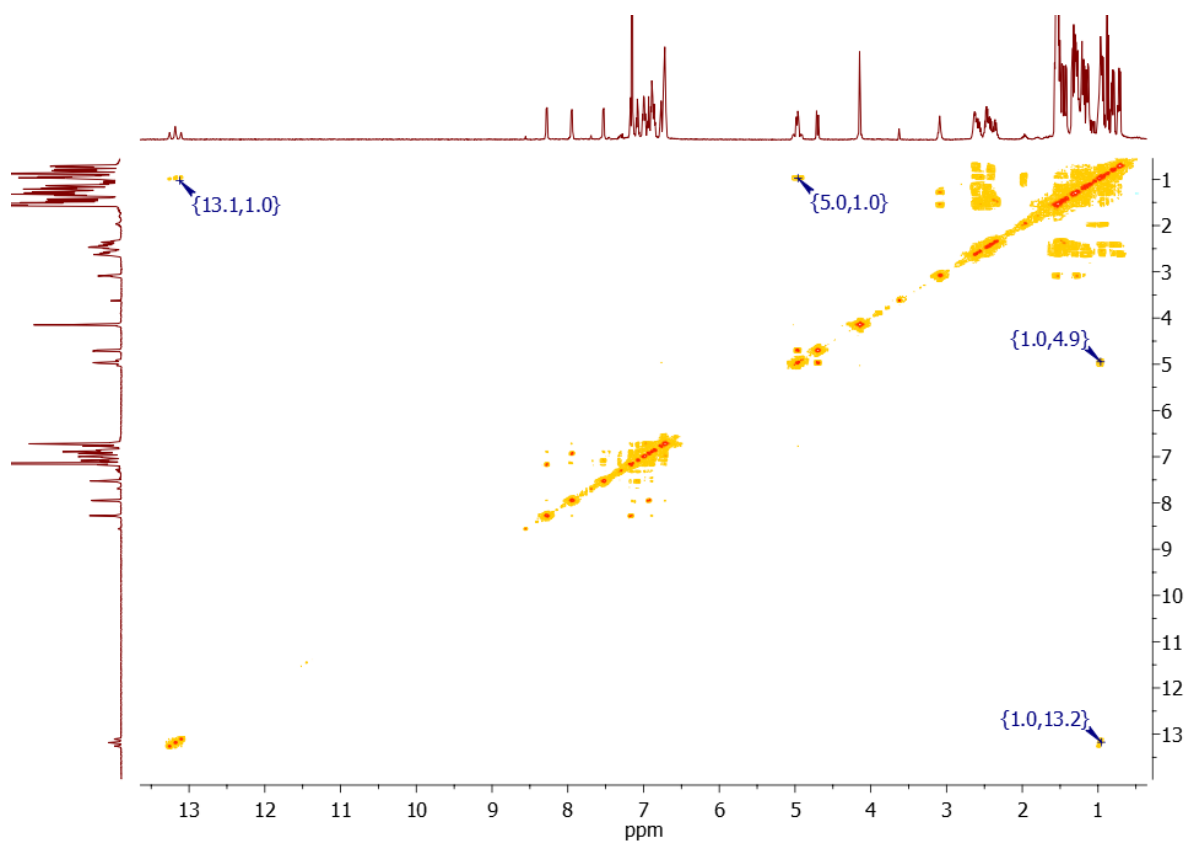


**Figure S14.** Selected region of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **8** (151 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K) showing the four signals for the metallacyclopropane carbon atoms.





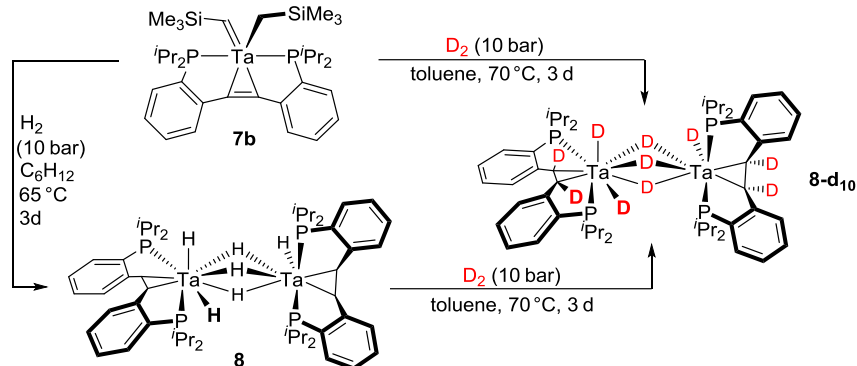
**Figure S15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8** (243 MHz,  $\text{C}_6\text{D}_6$ , 295 K).



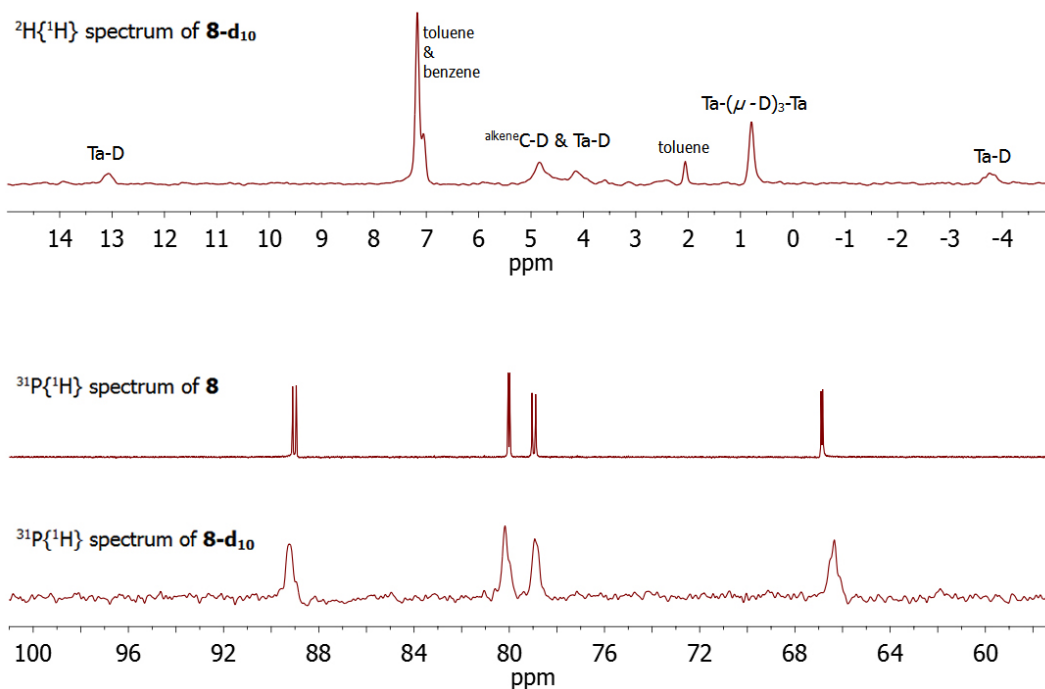
**Figure S16.** Positive region of the  $^1\text{H}$ - $^1\text{H}$ -COSY NMR spectrum of **8** (600 MHz,  $\text{C}_6\text{D}_6$ , 295 K). The crosspeaks between two of the terminal hydrides with the three  $\mu$ -hydrides at 0.98 ppm are labeled.

## Deuterium Labeling of Compound **8**

In the article, it is mentioned that the  $^1\text{H}$  NMR signal for the three bridging hydrides in **8** appears as a broad resonance at 0.98 ppm, which exhibits COSY crosspeaks with the remaining hydride signals. Although the shape of this signal indicates that a dynamic process (rendering all three bridging hydrides equivalent) is present, no changes in the spectrum were noticed upon cooling to  $-40^\circ\text{C}$ . To ascertain the signal assignment, deuterium labeling studies were carried out. The deuterium labeled compound **8-d**<sub>10</sub> was prepared either via deuteration of **7b** or via H/D-exchange starting from **8** (see Scheme S1). In both these NMR scale reactions, the samples were kept under  $\text{D}_2$  pressure (10 bar) at  $70^\circ\text{C}$  for 3 d (note: to compensate for the expected kinetic isotope effect, a slightly higher temperature was chosen in the deuteration experiments in comparison to the hydrogenation experiments). In the  $^1\text{H}$  NMR spectrum of **8-d**<sub>10</sub>, the signals assigned to the hydrides in **8** and the signals assigned to the olefinic hydrogens in **8** atoms were absent, which is in line with a 10-fold deuteration of **8**. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, significantly broadened peaks (due to unresolved deuterium coupling) were detected at the expected chemical shifts (see Figure S18). The three bridging deuterides were unambiguously identified in the  $^2\text{H}\{^1\text{H}\}$  NMR spectrum. The resonance for these deuterides (at approximately 0.98 ppm) is not coupled to the four different  $^{31}\text{P}$  nuclei (*c.f.* broad signal in the  $^1\text{H}$  NMR spectrum of **8**), which diminishes the broadening of this particular signal compared to the other deuterium signals (see Figure S18).



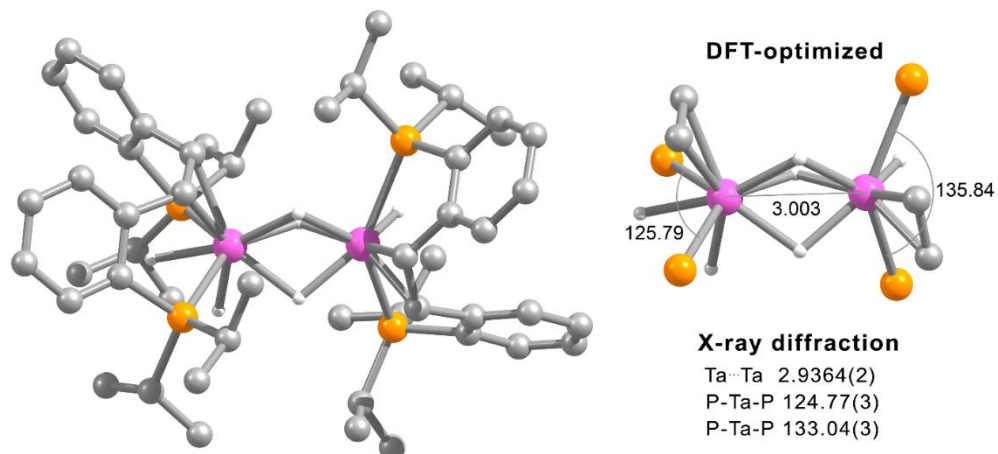
**Scheme S1.** Synthesis of **8-d**<sub>10</sub> starting from **7b** and **8** respectively.



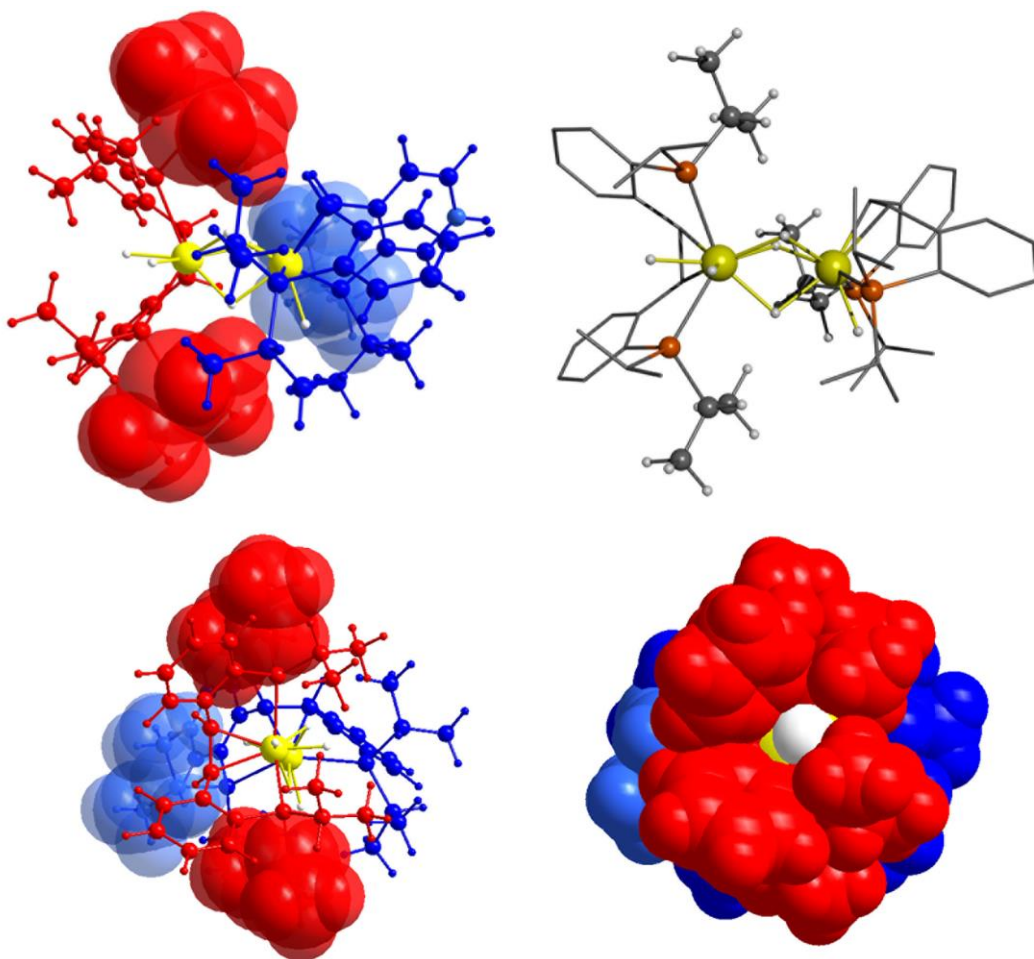
**Figure S17.**  $^2\text{H}\{^1\text{H}\}$  NMR spectrum (92 MHz,  $\text{C}_6\text{H}_6$ ) of **8-d**<sub>10</sub> together with the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **8** and **8-d**<sub>10</sub>.

## Details on DFT Calculations

DFT calculations were performed with the Gaussian 09 program suite (G09RevB.01)<sup>1</sup> using the PBE1PBE functional.<sup>2</sup> Geometry optimizations were carried out without symmetry restrictions and the stationary point were identified as minima by analytical frequency analysis. All atoms were described with the def2-TZVP basis set.<sup>3</sup> A plot of the optimized structure of **8** is shown in Figure S18. Space-filling models of **8** (illustrating the through-space repulsion between both ligands) are shown in Figure S19. Coordinates for the optimized geometry of **8** are provided as a separate mol-file.



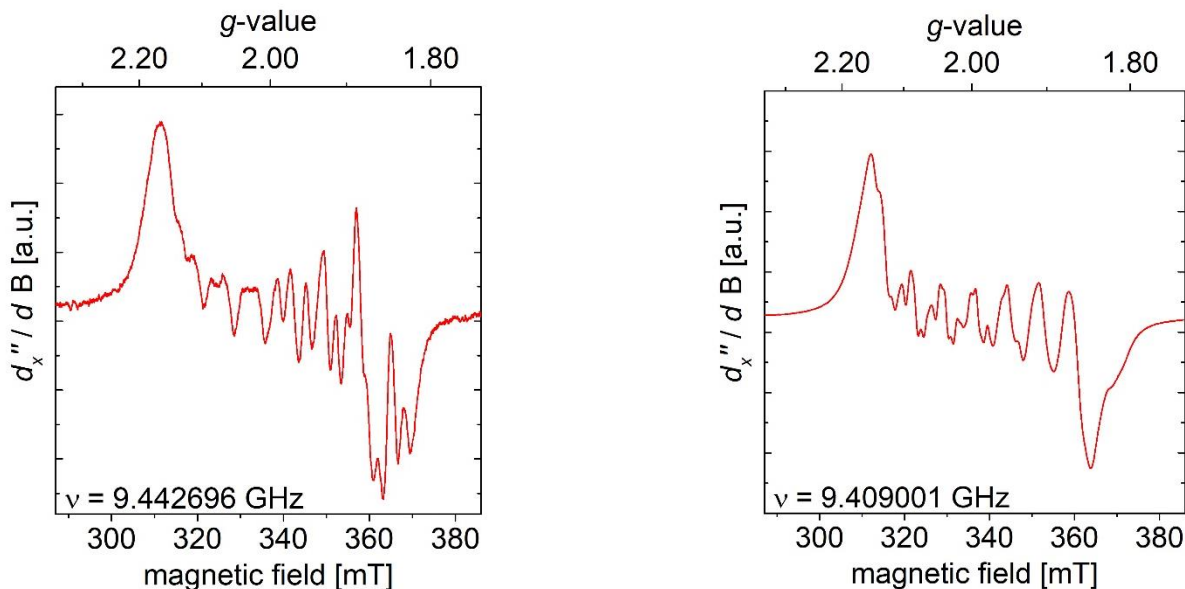
**Figure S18.** DFT-optimized structure of **8** (hydrogen atom except hydrides are omitted for clarity).



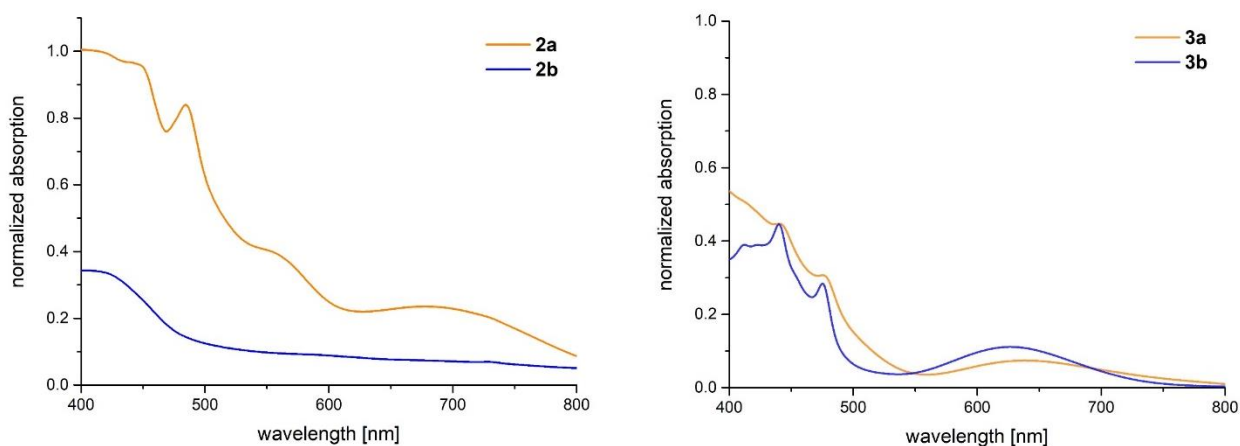
**Figure S19.** Illustration of the through-space interaction between both ligands in **8** on DFT-optimized coordinates (space-filling representations) and on the crystallographically determined coordinates (ball-and-stick representation).

## EPR and UV-Vis Spectra

Sample for EPR and UV-Vis spectra were prepared in a Glovebox by dissolving compounds **2** or **3** in rigorously dried, freshly distilled dichloroethane,  $\text{CH}_2\text{Cl}_2$  or toluene at known concentrations. These solutions were transferred to Teflon-valve quartz glass EPR tubes or Teflon-valve quartz glass UV-Vis cells prior to removal from the Glovebox.

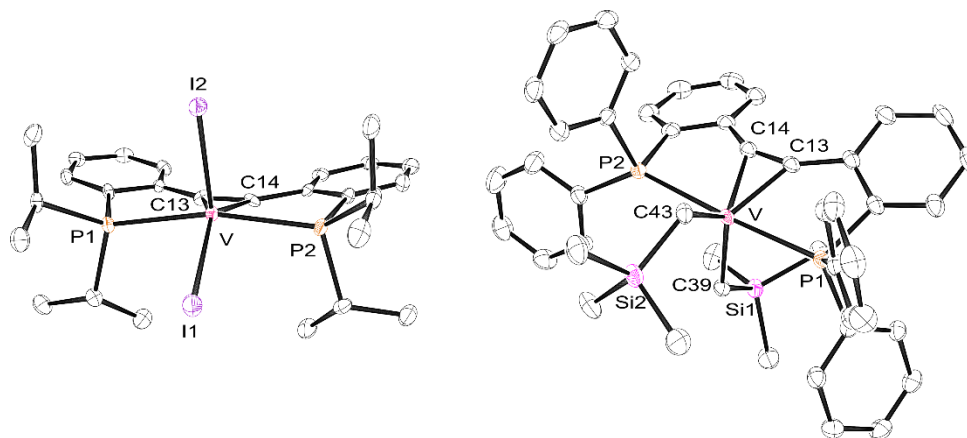


**Figure S20.** X-band EPR spectra of  $\text{Ph}[\text{PCCP}]\text{Vl}_2(\text{thf})$  **2a** (left) and  $\text{Pr}[\text{PCCP}]\text{Vl}_2$  **2b** (right) recorded in  $\text{CH}_2\text{Cl}_2$  at room temperature (microwave frequencies are denoted at the bottom of the spectra, fitted  $g_{\text{iso}}$  and  $|A_{\text{iso}}|$  values are provided in the experimental part section).

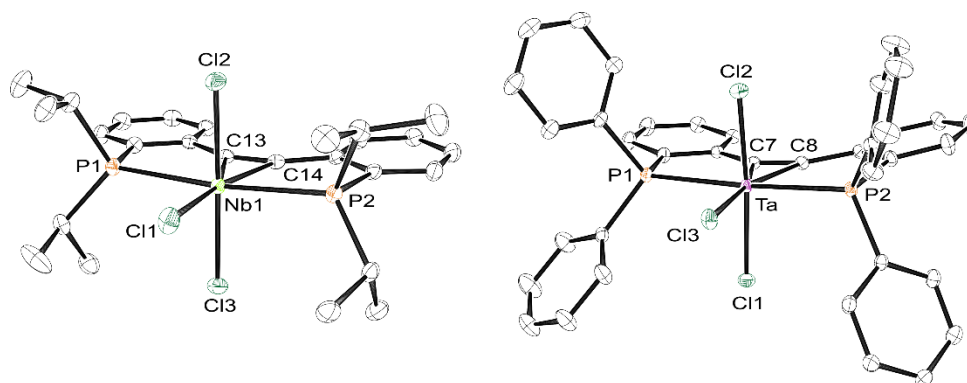


**Figure S21.** UV-Vis absorption spectra of  $\text{Ph}[\text{PCCP}]\text{Vl}_2(\text{thf})$  **2a** and  $\text{Pr}[\text{PCCP}]\text{Vl}_2$  **2b** in dichloroethane together with the UV-Vis spectra of  $\text{Ph}[\text{PCCP}]\text{V}(\text{CH}_2\text{SiMe}_3)_2$  **3a** and  $\text{Pr}[\text{PCCP}]\text{V}(\text{CH}_2\text{SiMe}_3)_2$  **3b** in toluene.

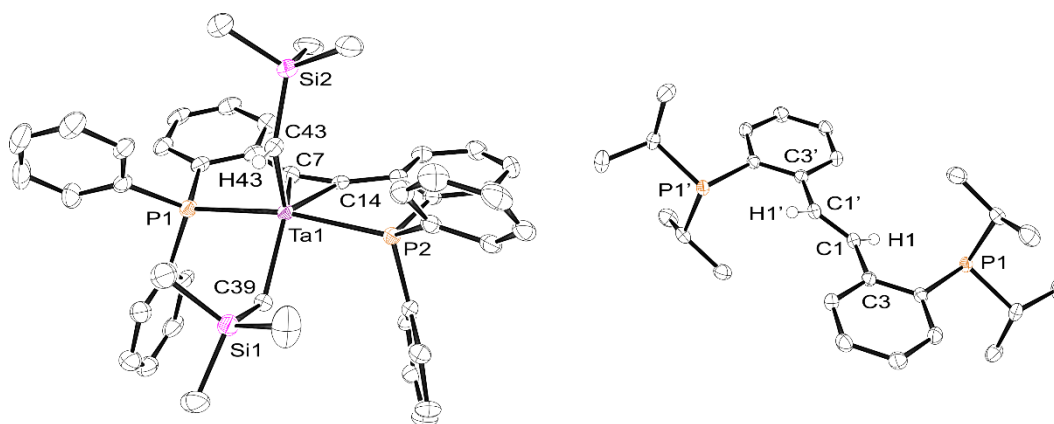
## Additional ORTEP Plots



**Figure S22.** ORTEP plots of the molecular structures of  $Pr[PCCP]Vl_2$  (**2b**) and  $Ph[PCCP]VI(CH_2SiMe_3)_2$  (**3a**) (displacement ellipsoids drawn at 50% probability, hydrogen atoms omitted). Selected structural parameter are summarized in Table 1 (see main article).



**Figure S23.** ORTEP plots of the molecular structures of  $Pr[PCCP]NbCl_3$  (**4b**, only one of the two independent molecules is shown) and  $Ph[PCCP]TaCl_3$  (**5a**) (displacement ellipsoids drawn at 50% probability, hydrogen atoms omitted). Selected structural parameter are summarized in Table 2 (see main article).



**Figure S24.** ORTEP plots of the molecular structures of  $Ph[PCCP]Ta(CHSiMe_3)(CH_2SiMe_3)$  (**7a**, only one of the two independent molecules is shown) and  $trans-Pr[PCHCHP]$  (**1b-H2**) (displacement ellipsoids drawn at 50% probability, most hydrogen atoms omitted). Selected structural parameters for **7a**:  $d(C43-H43) = 0.94(4)$  [ $0.97(4)$ ] Å;  $d(Ta1-H43) = 2.44(4)$  [ $2.45(4)$ ] Å;  $\angle Ta-C43-H43 = 107(2)$  [ $109(2)$ ]°. Other selected structural parameter for **7a** are summarized in Table 2 (see main article). Selected bond lengths (Å) and angles (°) for **1b-H2**: C1–C1' 1.335(2), C1–C3 1.4750(16), C1'–C1–C3 124.92(15).

## X-Ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Tables S1-S5. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu- $K_{\alpha}$  radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically  $\omega$ -, occasionally  $\varphi$ -scans, scan width 0.5...1°) were integrated by profile fitting.<sup>4</sup> Data were corrected for air and detector absorption, Lorentz and polarization effects<sup>5</sup> and scaled essentially by application of appropriate spherical harmonic functions.<sup>5,6,7</sup> Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling process), and augmented by a spherical correction,<sup>5,6,7</sup> or numerically (Gaussian grid).<sup>5,6,8</sup> An illumination correction was performed as part of the numerical absorption correction.<sup>6</sup>

The structures were solved by ab initio dual space methods involving difference Fourier syntheses (VLD procedure; compounds **1a**·2 CH<sub>2</sub>Cl<sub>2</sub>, **7b**·*n*-pentane and **1b**-H<sub>2</sub>),<sup>9</sup> by intrinsic phasing (compound **6b**·*n*-pentane)<sup>10</sup> or by the charge flip procedure (all other compounds)<sup>11</sup> and refined by full-matrix least squares methods based on  $F^2$  against all unique reflections.<sup>12</sup> All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. The positions of some hydrogen atoms (all hydrogens except those of the methyl groups of **1b**-H<sub>2</sub>, all the hydrides and those of all the M-C(H)SiMe<sub>3</sub> and M-CH<sub>2</sub>SiMe<sub>3</sub> ligands) were taken from difference Fourier syntheses and refined. Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied.<sup>13,14</sup>

The positions of the hydrides and the olefinic hydrogens in **8** were located from the difference Fourier syntheses and refined freely. The position of some of the hydrides was further verified by removing them from the model and using the thus obtained incomplete model as input file for XHydex.<sup>15</sup> The positions of the missing hydrides were then calculated on basis of the potential energy surface of the molecule. As expected, the calculated positions and the freely refined positions were virtually identical.

Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures of **3b**·0.5 *n*-pentane **7a**·*n*-pentane with the BYPASS procedure,<sup>16</sup> as implemented in PLATON (squeeze/hybrid).<sup>17</sup> Partial structure factors from the solvent masks were included in the refinement as separate contributions to  $F_{\text{calc}}$ .

Crystals of **2b** were twinned; the structure was solved using only reflections with small overlap factors (typically < 0.4). Final refinement was carried out against all single and composite reflections involving both domains (refined twin fractions 0.60:0.40).

CCDC 1947155 - 1947169 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.

**Table S1.** Crystal data and details of the structure determinations for **1a** · 2 CH<sub>2</sub>Cl<sub>2</sub>, **1b** and **2a**.

Compound	Ph[PCCP] · 2 CH <sub>2</sub> Cl <sub>2</sub> ( <b>1a</b> · 2 CH <sub>2</sub> Cl <sub>2</sub> )	Pr[PCCP] ( <b>1b</b> )	Ph[PCCP]Vl <sub>2</sub> (thf) ( <b>2a</b> )
Empirical Formula	C <sub>40</sub> H <sub>32</sub> Cl <sub>4</sub> P <sub>2</sub>	C <sub>26</sub> H <sub>36</sub> P <sub>2</sub>	C <sub>42</sub> H <sub>36</sub> I <sub>2</sub> OP <sub>2</sub> V
Formula Weight	716.39	410.49	923.39
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	8.3364(3)	8.29860(14)	12.14223(5)
<i>b</i> / Å	10.0476(3)	12.6444(2)	22.50431(11)
<i>c</i> / Å	10.8008(5)	13.1978(2)	13.53498(5)
$\alpha$ / °	86.468(3)	114.6886(18)	
$\beta$ / °	83.524(3)	98.8110(15)	91.9154(4)
$\gamma$ / °	78.672(3)	93.9722(14)	
<i>V</i> / Å <sup>3</sup>	880.68(6)	1229.65(4)	3696.40(3)
<i>Z</i>	1	2	4
<i>F</i> <sub>000</sub>	370	444	1820
<i>d</i> <sub>c</sub> / Mg · m <sup>−3</sup>	1.351	1.109	1.659
$\mu$ / mm <sup>−1</sup>	0.456	1.646	16.423
max, min transmission factors	1.0000, 0.8697 <sup>a</sup>	1.000, 0.758 <sup>b</sup>	0.628, 0.287 <sup>b</sup>
X-ray radiation, $\lambda$ / Å	Mo- <i>K</i> $\alpha$ , 0.71073	Cu- <i>K</i> $\alpha$ , 1.54184	Cu- <i>K</i> $\alpha$ , 1.54184
data collect. temperature / K	120(1)	120(1)	120(1)
$\theta$ range / °	2.5 - 32.5	3.8 - 70.8	3.8 - 67.2
index ranges <i>h</i> , <i>k</i> , <i>l</i>	±12, −15 ... 14, −16 ... 15	±10, ±15, ±16	±14, ±26, ±16
reflections measured	26430	45999	181274
unique [ <i>R</i> <sub>int</sub> ]	5959 [0.0532]	4688 [0.0281]	6623 [0.0338]
Observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4420	4393	6498
parameters refined [restraints]	218 [22]	261[0]	433 [0]
GooF on <i>F</i> <sup>2</sup>	1.044	1.028	1.069
<i>R</i> indices [ <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )] <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0466, 0.0980	0.0313, 0.0840	0.0379, 0.0964
<i>R</i> indices (all data) <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0711, 0.1111	0.0335, 0.0858	0.0385, 0.0968
difference density: max, min/e · Å <sup>−3</sup>	0.545, −0.337	0.391, −0.221	2.385, −2.438
CCDC deposition number	1947155	1947156	1947157

<sup>a</sup> semi empirical absorption correction. <sup>b</sup> numerical absorption correction.

**Table S2.** Crystal data and details of the structure determinations for **2b**, **3a** · Et<sub>2</sub>O · 1/2 C<sub>5</sub>H<sub>12</sub> and **3b** · 1/2 C<sub>5</sub>H<sub>12</sub>.

Compound	<sup>Pt</sup> [PCCP]VI <sub>2</sub> ( <b>2b</b> )	<sup>Ph</sup> [PCCP]V(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> · Et <sub>2</sub> O · 1/2 C <sub>5</sub> H <sub>12</sub> ( <b>3a</b> · Et <sub>2</sub> O · 1/2 C <sub>5</sub> H <sub>12</sub> )	<sup>Pt</sup> [PCCP]V(CH <sub>2</sub> SiMe <sub>3</sub> ) <sub>2</sub> · 1/2 C <sub>5</sub> H <sub>12</sub> ( <b>3b</b> · 1/2 C <sub>5</sub> H <sub>12</sub> )
Empirical Formula	C <sub>26</sub> H <sub>36</sub> I <sub>2</sub> P <sub>2</sub> V	C <sub>52.50</sub> H <sub>66</sub> OP <sub>2</sub> Si <sub>2</sub> V	C <sub>36.50</sub> H <sub>64</sub> P <sub>2</sub> Si <sub>2</sub> V
Formula Weight	715.23	882.11	671.93
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	30.1712(11)	13.0092(3)	12.43100(10)
<i>b</i> / Å	7.81727(18)	13.8752(4)	15.97136(15)
<i>c</i> / Å	23.4961(6)	15.1785(4)	19.77068(16)
$\alpha$ / °	90	66.463(3)	90
$\beta$ / °	92.157(2)	80.0542(19)	90.9004(7)
$\gamma$ / °	90	80.7466(19)	90
<i>V</i> / Å <sup>3</sup>	5537.8(3)	2461.28	3924.79(6)
<i>Z</i>	8	2	4
$\bar{F}_{000}$	2808	940	1456
<i>d<sub>c</sub></i> / Mg · m <sup>-3</sup>	1.716	1.190	1.137
$\mu$ / mm <sup>-1</sup>	2.716	3.028	3.620
max, min transmission factors	0.7967, 0.7914 <sup>a</sup>	1.000, 0.625 <sup>b</sup>	0.969, 0.753 <sup>b</sup>
X-ray radiation, $\lambda$ / Å	Mo- <i>K</i> $\alpha$ , 0.71073	Cu- <i>K</i> $\alpha$ , 1.54184	Cu- <i>K</i> $\alpha$ , 1.54184
data collect. temperature / K	120(1)	120(1)	120(1)
$\theta$ range / °	2.2 - 32.4	3.2 - 70.8	3.6 - 70.9
index ranges <i>h, k, l</i>	-44...45, $\pm$ 11, $\pm$ 35	$\pm$ 15, $\pm$ 16, $\pm$ 18	$\pm$ 15, -19...18, $\pm$ 24
reflections measured	84933	63700	103146
unique [ <i>R</i> <sub>int</sub> ]	13814 [0.0772]	9366 [0.0357]	7534 [0.0551]
observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	9548	8213	6843
parameters refined [restraints]	289 [0]	588 [72]	382 [0]
Goof on <i>F</i> <sup>2</sup>	0.929	1.040	1.035
<i>R</i> indices [ <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )] <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0372, 0.0732	0.0450, 0.1290	0.0341, 0.0798
<i>R</i> indices (all data) <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0665, 0.0768	0.0520, 0.1344	0.0386, 0.0818
difference density: max, min/e · Å <sup>-3</sup>	1.635, -0.801	1.246, -0.808	1.315, -0.381
CCDC deposition number	1947158	1947159	1947160

<sup>a</sup> semi empirical absorption correction. <sup>b</sup> numerical absorption correction.



**Table S3.** Crystal data and details of the structure determinations for **4a** · CH<sub>2</sub>Cl<sub>2</sub>, **4b** · C<sub>6</sub>H<sub>5</sub>Cl and **5a** · CH<sub>2</sub>Cl<sub>2</sub>.

Compound	<sup>Ph</sup> [PCCCP]NbCl <sub>3</sub> CH <sub>2</sub> Cl <sub>2</sub> ( <b>4a</b> · CH <sub>2</sub> Cl <sub>2</sub> )	<sup>Pr</sup> [PCCCP]NbCl <sub>3</sub> · C <sub>6</sub> H <sub>5</sub> Cl ( <b>4b</b> · C <sub>6</sub> H <sub>5</sub> Cl)	<sup>Ph</sup> [PCCCP]TaCl <sub>3</sub> CH <sub>2</sub> Cl <sub>2</sub> ( <b>5a</b> · CH <sub>2</sub> Cl <sub>2</sub> )
Empirical Formula	C <sub>39</sub> H <sub>30</sub> Cl <sub>5</sub> NbP <sub>2</sub>	C <sub>32</sub> H <sub>41</sub> Cl <sub>4</sub> NbP <sub>2</sub>	C <sub>39</sub> H <sub>30</sub> Cl <sub>5</sub> P <sub>2</sub> Ta
Formula Weight	830.73	722.30	918.77
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	11.98115(3)	24.6584(3)	11.99348(7)
<i>b</i> / Å	17.03945(4)	14.14141(18)	17.03997(9)
<i>c</i> / Å	17.64788(4)	19.6272(3)	17.65784(9)
$\beta$ / °	92.5385(2)	105.4082(14)	92.6247(5)
<i>V</i> / Å <sup>3</sup>	3599.316(15)	6598.09(16)	3604.92(3)
<i>Z</i>	4	8	4
<i>F</i> <sub>000</sub>	1680	2976	1808
<i>d</i> <sub>c</sub> / Mg · m <sup>-3</sup>	1.533	1.454	1.693
$\mu$ / mm <sup>-1</sup>	7.200	0.807	3.537
max, min transmission factors	0.835, 0.535 <sup>a</sup>	1.000, 0.713 <sup>a</sup>	0.989, 0.716 <sup>a</sup>
X-ray radiation, $\lambda$ / Å	Cu- <i>K</i> $\alpha$ , 1.54184	Mo- <i>K</i> $\alpha$ , 0.71073	Mo- <i>K</i> $\alpha$ , 0.71073
data collect. temperature /K	120(1)	120(1)	120(1)
$\theta$ range / °	3.6 - 70.8	2.2 - 32.5	2.1 - 32.4
index ranges <i>h, k, l</i>	±14, ±20, ±21	-36...37, -20...21, -28...29	±17, ±25, ±26
reflections measured	209497	170039	143802
unique [ <i>R</i> <sub>int</sub> ]	6918 [0.0272]	22903 [0.0865]	12576 [0.0319]
Observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	6824	16540	11727
parameters refined [restraints]	424 [10]	887 [332]	424 [0]
Goof on <i>F</i> <sup>2</sup>	1.046	1.026	1.051
<i>R</i> indices [ <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )] <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0220, 0.0509	0.0417, 0.0691	0.0195, 0.0401
<i>R</i> indices (all data) <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0223, 0.0511	0.0731, 0.0785	0.0224, 0.0410
difference density: max, min/e · Å <sup>-3</sup>	0.779, -0.784	0.715, -0.592	1.207, -1.140
CCDC deposition number	1947161	1947162	1947163

<sup>a</sup> numerical absorption correction.

**Table S4.** Crystal data and details of the structure determinations for **5b**, **6b** · C<sub>5</sub>H<sub>12</sub> and **7a**.

Compound	<sup>P</sup> [PCCP]TaCl <sub>3</sub> <b>(5b)</b>	<sup>P</sup> [PCCP]Nb(CHSiMe <sub>3</sub> ) (CH <sub>2</sub> SiMe <sub>3</sub> ) · C <sub>5</sub> H <sub>12</sub> <b>(6b</b> · 2C <sub>5</sub> H <sub>12</sub> )	<sup>Ph</sup> [PCCP]Ta(CHSiMe <sub>3</sub> ) (CH <sub>2</sub> SiMe <sub>3</sub> ) <b>(7a</b> · C <sub>5</sub> H <sub>12</sub> )
Empirical Formula	C <sub>26</sub> H <sub>36</sub> Cl <sub>3</sub> P <sub>2</sub> Ta	C <sub>39</sub> H <sub>69</sub> NbP <sub>2</sub> Si <sub>2</sub>	C <sub>56</sub> H <sub>73</sub> P <sub>2</sub> Si <sub>2</sub> Ta
Formula Weight	697.79	748.97	1045.21
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> <i>m</i> <i>n</i> 2 <sub>1</sub>	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	11.77248(5)	16.09027(10)	36.5324(7)
<i>b</i> / Å	13.83456(7)	9.01200(6)	14.74615(17)
<i>c</i> / Å	17.42868(8)	14.45411(9)	39.0565(9)
$\beta$ / °	97.1867(4)		114.639(3)
<i>V</i> / Å <sup>3</sup>	2816.26(2)	2095.93(2)	19124.5(7)
<i>Z</i>	4	2	16
<i>F</i> <sub>000</sub>	1384	804	8640
<i>d</i> <sub>c</sub> / Mg · m <sup>-3</sup>	1.646	1.187	1.452
$\mu$ / mm <sup>-1</sup>	4.314	0.445	5.629
max, min transmission factors	1.000, 0.530 <sup>a</sup>	1.000, 0.698 <sup>a</sup>	1.000, 0.494 <sup>a</sup>
X-ray radiation, $\lambda$ / Å	Mo- <i>K</i> $\alpha$ , 0.71073	Mo- <i>K</i> $\alpha$ , 0.71073	Cu- <i>K</i> $\alpha$ , 1.54184
data collect. temperature / K	120(1)	120(1)	120(1)
$\theta$ range / °	2.2 - 32.4	2.5 - 32.4	3.3 - 71.1
index ranges <i>h</i> , <i>k</i> , <i>l</i>	±17, ±20, ±26	±24, ±13, -20...21	±44, ±18, -41...47
reflections measured	232263	73661	212438
unique [ <i>R</i> <sub>int</sub> ]	10018 [0.0460]	7523 [0.0366]	18316 [0.0781]
Observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	9675	7393	15707
parameters refined [restraints]	297 [0]	230 [1]	951[0]
GooF on <i>F</i> <sup>2</sup>	1.241	1.097	1.037
<i>R</i> indices [ <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )] <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0241, 0.0400	0.0186, 0.0442	0.0360, 0.0650
<i>R</i> indices (all data) <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0260, 0.0405	0.0193, 0.0445	0.0477, 0.0683
asymmetry parameter		-0.022(6)	
difference density: max, min/e · Å <sup>-3</sup>	0.714, -0.645	0.333, -0.298	0.959, -1.259
CCDC deposition number	1947164	1947165	1947166

<sup>a</sup> numerical absorption correction.

**Table S5.** Crystal data and details of the structure determinations for **7b** · C<sub>5</sub>H<sub>12</sub>, **8** and **1b-H<sub>2</sub>**.

Compound	<sup>P</sup> r[PCCP]Ta(CHSiMe <sub>3</sub> ) (CH <sub>2</sub> SiMe <sub>3</sub> ) · C <sub>5</sub> H <sub>12</sub> <b>(7b</b> · C <sub>5</sub> H <sub>12</sub> )	<sup>P</sup> r[PCHCHP]Ta(H) <sub>2</sub> (μ-H) <sub>3</sub> Ta(H) <sup>P</sup> r[PCHCHP] <b>(8)</b>	<i>trans</i> - <sup>P</sup> r[PCHCHP] <b>(1b-H<sub>2</sub>)</b>
Empirical Formula	C <sub>39</sub> H <sub>69</sub> P <sub>2</sub> Si <sub>2</sub> Ta	C <sub>52</sub> H <sub>82</sub> P <sub>4</sub> Ta <sub>2</sub>	C <sub>26</sub> H <sub>38</sub> P <sub>2</sub>
Formula Weight	837.01	1192.95	412.50
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>P m n 2</i> <sub>1</sub>	<i>P 2</i> <sub>1</sub> / <i>c</i>	<i>P</i> − 1
<i>a</i> / Å	16.08690(11)	18.61861(8)	6.10715(13)
<i>b</i> / Å	9.00887(6)	12.82823(5)	7.20048(19)
<i>c</i> / Å	14.46090(10)	21.13733(15)	14.3716(3)
<i>α</i> / °			96.9714(19)
<i>β</i> / °		90.3598(5)	101.4601(18)
<i>γ</i> / °			99.436(2)
<i>V</i> / Å <sup>3</sup>	2095.74(2)	5048.42(5)	603.21(2)
<i>Z</i>	2	4	1
<i>F</i> <sub>000</sub>	868	2400	224
<i>d</i> <sub>c</sub> / Mg · m <sup>−3</sup>	1.326	1.570	1.136
<i>μ</i> / mm <sup>−1</sup>	2.780	9.290	1.678
max, min transmission factors	0.968, 0.643 <sup>a</sup>	0.863, 0.441 <sup>a</sup>	1.000, 0.838 <sup>a</sup>
X-ray radiation, <i>λ</i> / Å	Mo- <i>Kα</i> , 0.71073	Cu- <i>Kα</i> , 1.54184	Cu- <i>Kα</i> , 1.54184
data collect. temperature / K	120(1)	120(1)	120(1)
<i>θ</i> range / °	2.3 - 32.4	4.0 - 70.9	3.2 - 70.7
index ranges <i>h, k, l</i>	±23, ±13, ±21	±22, ±15, −25...22	±7, ±8, ±17
reflections measured	63888	272824	22417
unique [ <i>R</i> <sub>int</sub> ]	7520 [0.0421]	9703 [0.0492]	2309 [0.0277]
Observed [ <i>I</i> > 2σ( <i>I</i> )]	7371	9176	2203
parameters refined [restraints]	230 [1]	579 [9]	156 [0]
Goof on <i>F</i> <sup>2</sup>	1.104	1.043	1.068
<i>R</i> indices [ <i>F</i> <sub>0</sub> > 4 σ( <i>F</i> <sub>0</sub> )] <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0190, 0.0366	0.0293, 0.0672	0.0271, 0.0659
<i>R</i> indices (all data) <i>R</i> ( <i>F</i> ), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0201, 0.0369	0.0318, 0.0685	0.0288, 0.0668
asymmetry parameter	0.012(2)		
difference density: max, min/e · Å <sup>−3</sup>	0.790, −1.467	1.733, −1.599	0.323, −0.182
CCDC deposition number	1947167	1947168	1947169

<sup>a</sup> numerical absorption correction.

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