

# Quantitative Synthesis of Pt-Si-C Cyclopropane and its Unusual Complexation with Benzene

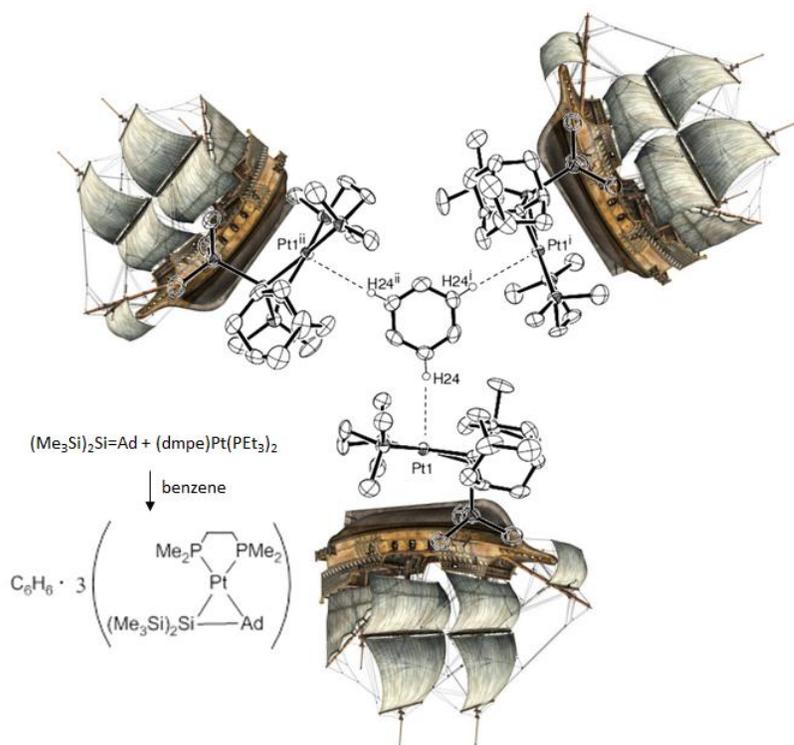
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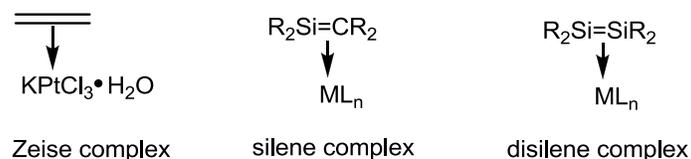
## Abstract

In this paper we report the quantitative synthesis of the first Pt-silene  $\sigma$ -complex and its unusual interaction with benzene molecule in the solid state, revealed by X-ray crystallography. Thus, three platinum complexes dock on one benzene molecule via weak van der Waals-type interactions with the benzene hydrogens. The cyclopropane nature of the complex was confirmed by  $^{29}\text{Si}$  NMR spectroscopy and molecular structure. Also, an unusual situation in  $^{31}\text{P}$  NMR was observed, in which two phosphorus atoms with different chemical environment have similar chemical shifts but different values of J-coupling with platinum.

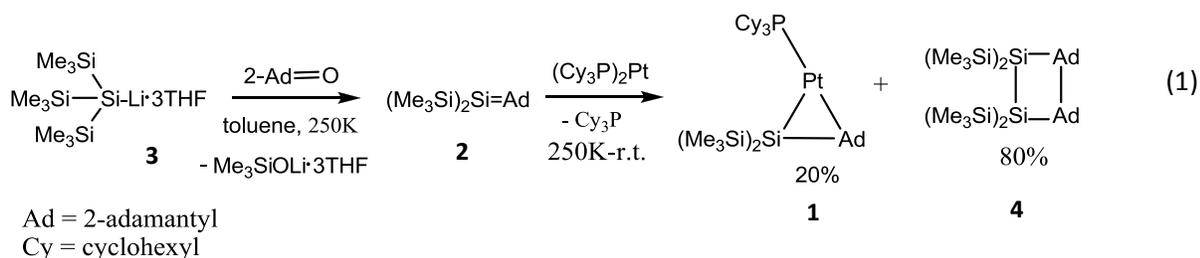
## Graphical Abstract



While the first olefin metal complex was reported already in 1831 by Zeise<sup>1</sup> the first silene<sup>2</sup> and disilene<sup>3</sup> complexes were reported only in 1988 and 1989, respectively, and also now their number and the knowledge about their properties and reactivity is still limited.



Our group reported in 2004 the synthesis of a platinum silene complex **1** – the first synthesized by a direct reaction of a silene (**2**) and an organometallic reagent Pt(PCy<sub>3</sub>)<sub>2</sub> (equation 1).<sup>4</sup> Silene **2** was generated *in situ* by reaction of tris(trimethylsilyl)silyllithium **3** and 2-adamantanone. Complex **1** could be isolated only in relatively low yield (<20%), the major product being disilacyclobutane **4**, a head-to-head dimer of **2**. This product ratio probably resulted from the low temperature (250K) at which the reaction was carried out. At this temperature the formation of **4** from **2** is irreversible and therefore only small portion of **2** could be trapped by Pt(PCy<sub>3</sub>)<sub>2</sub>. Also, the reaction was very hard to reproduce, out of ca. ten attempts only two were successful. Thus, to get higher yields and better reproducibility we looked for ways to continuously generate larger concentrations of silene **2** in solution with excess of platinum trap.



Previously, we showed that at  $T > 330\text{K}$  **4** and **2** are in equilibrium (equation 2, step a). Unfortunately, Pt(PCy<sub>3</sub>)<sub>2</sub> decomposes at  $T > 330\text{K}$ , and therefore its thermal reaction with **2** at 330K (or higher temperatures) was not productive leading to a complex mixture of products (equation 2, step b).

To synthesize a platinum silene complex in high yield we decided to use Pt-complex (dmpe)Pt(PEt<sub>3</sub>)<sub>2</sub> (dmpe = bis(1,2-dimethylphosphino)ethane) which is stable up to 410K. We used this complex recently to trap the elusive phosphasilene ((R<sub>3</sub>Si)<sub>2</sub>Si=PH) species.<sup>5</sup> Reaction in hexane of **4** with **1** in boiling hexane (342K) for 3h yielded the desired silene complex **5** quantitatively (equation 2, step c).<sup>6</sup> **5** was isolated by crystallization from hexane and its molecular structure was determined by X-ray crystallography (Figure 1).

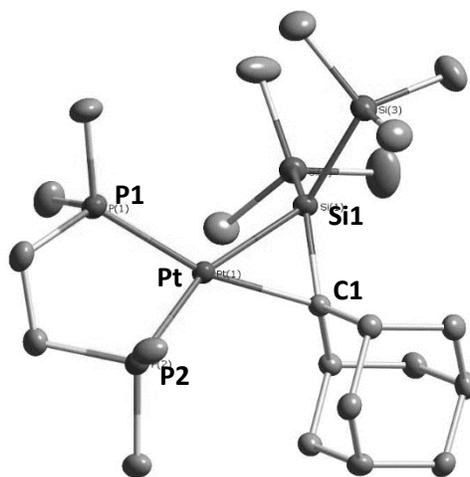
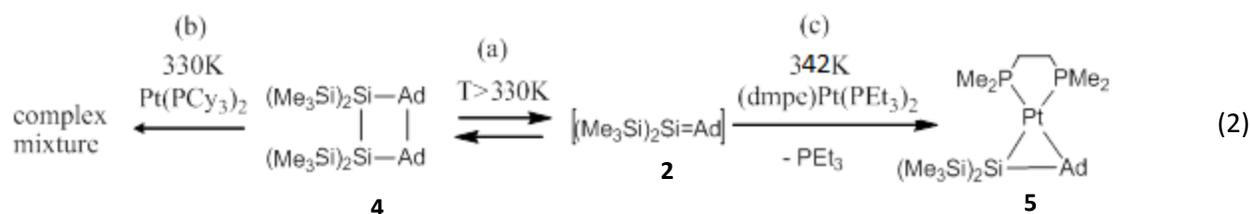


Figure 1. ORTEP drawing of the molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles and dihedral angles (°): Pt-Si1 2.353(1), Pt-C1 2.177(3), Si1-C1 1.852(3), Pt-P1 2.251(1), Pt-P2 2.303(1), P-Pt-P 85.69(3), Si1-Pt-C1 48.06(9), Si2-Si1-Si3 109.85(5), P-P-Si1-C1 9.0, P1-Pt-C1-Si1 16.6, P2-Pt-Si1-C1 104.5.

Selected geometry parameters of **5**, compared to those of **1**, are given in Table 1. The Si1-C1 in **5** (1.852 Å) is slightly longer than in **1** (1.838 Å). The same trend was observed by Kira and coworkers<sup>7</sup> for diphosphino- and mono-phosphino disilene palladium complexes **6** and **7**, respectively. The P1-Pt-C1 angle in **5** (161°) is smaller than in **1** (178°), probably due to the repulsion between the two P atoms in **5** (in **1** there is only one P atom).

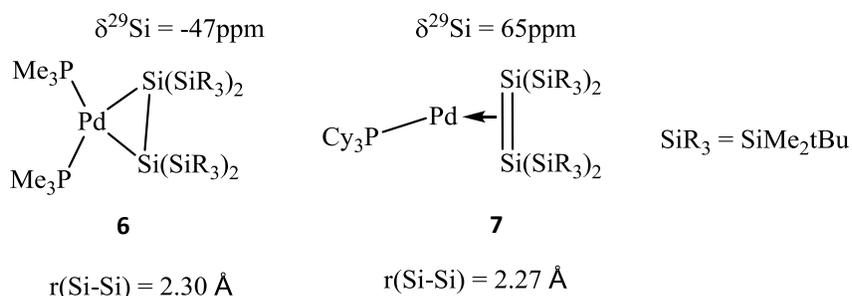
The NMR spectra of **5** and **1** are very different.  $\delta^{29}\text{Si1}$  (-66.0 ppm) and  $\delta^{13}\text{C1}$  (47.9 ppm) in **5**, are significantly upfield compared to those in **1** (6.8 and 137.8 ppm, respectively). Complex **1** was characterized by us as a hybrid between a  $\pi$ -complex and a  $\sigma$ -cyclopropane structure. In **5** the longer Si1-C1 bond and the upfield  $^{29}\text{Si}$  and  $^{13}\text{C}$  chemical shifts indicate a significantly lower  $\pi$ -character in **5** compared to **1**, i.e., **5** has a higher contribution of cyclopropane type  $\sigma$ -complex than **1**. This conclusion is consistent with the

results of Kira *et al.* observed for disilene palladium complexes **6** and **7** (shown below).<sup>6</sup> Their explanation for the differences between **6** and **7** which is based on DFT calculations was that due to electron deficiency in **7** (14 e<sup>-</sup>) compared to **6** (16 e<sup>-</sup>) complex **7** is better described as a  $\pi$ -complex, while **6** is better described as a cyclopropane type  $\sigma$ -complex. The same explanation can account for the differences between **1** (14 e<sup>-</sup> complex) and **5** (16 e<sup>-</sup> complex).

Table 1. Selected geometry parameters of **1** and **5**<sup>a</sup>

	Si1-C1	Pt-Si1	Pt-C1	Pt-P1	Pt-P2	P1-Pt-C1	Pt-Si1-C1	Pt-C1-Si1	P-Pt-P
<b>5</b>	1.852	2.353	2.177	2.251	2.303	160.6	61.0	61.0	85.7
<b>1</b>	1.838	2.298	2.161	2.268	-	177.7	61.8	69.6	-

<sup>a</sup>Bond lengths are given in Å, angles are given in °.



Interesting information was obtained from the <sup>31</sup>P NMR of **5** which should exhibit two non-equivalent phosphorous atoms: P1 *trans* to C and P2 *trans* to Si. In benzene solution these P atoms produced a typical spectrum of two doublet signals (at 24.3 ppm and at 23.7 ppm) and satellite lines due to their coupling with the <sup>195</sup>Pt nucleus (33.8% natural abundance) (Figure 2a). Surprisingly, a very different <sup>31</sup>P NMR spectrum showing a singlet at 23.5 ppm and two doublet of doublets satellite lines was recorded in hexane (Figure 2b). Apparently, in hexane the two <sup>31</sup>P NMR signals accidentally have identical chemical shifts so that a singlet signal is observed. At the same time, the two P atoms are coupled with <sup>195</sup>Pt with different J values ( $J_{\text{Pt-P1}} = 2.549 \text{ Hz}$  and  $J_{\text{Pt-P2}} = 2.206 \text{ Hz}$ ). Therefore the satellite signals for each P atom appear at different positions and they exhibit  $J_{\text{P-P}}$  coupling (doublet of doublets) (see Figure 2b and the simulated spectrum in the insert of Figure 2b).  $\delta^{29}\text{Si}$  is also different in hexane and in benzene solutions: in benzene  $\delta^{29}\text{Si1} = -66.0 \text{ ppm}$  and in hexane  $\delta^{29}\text{Si1} = -64.4 \text{ ppm}$ .

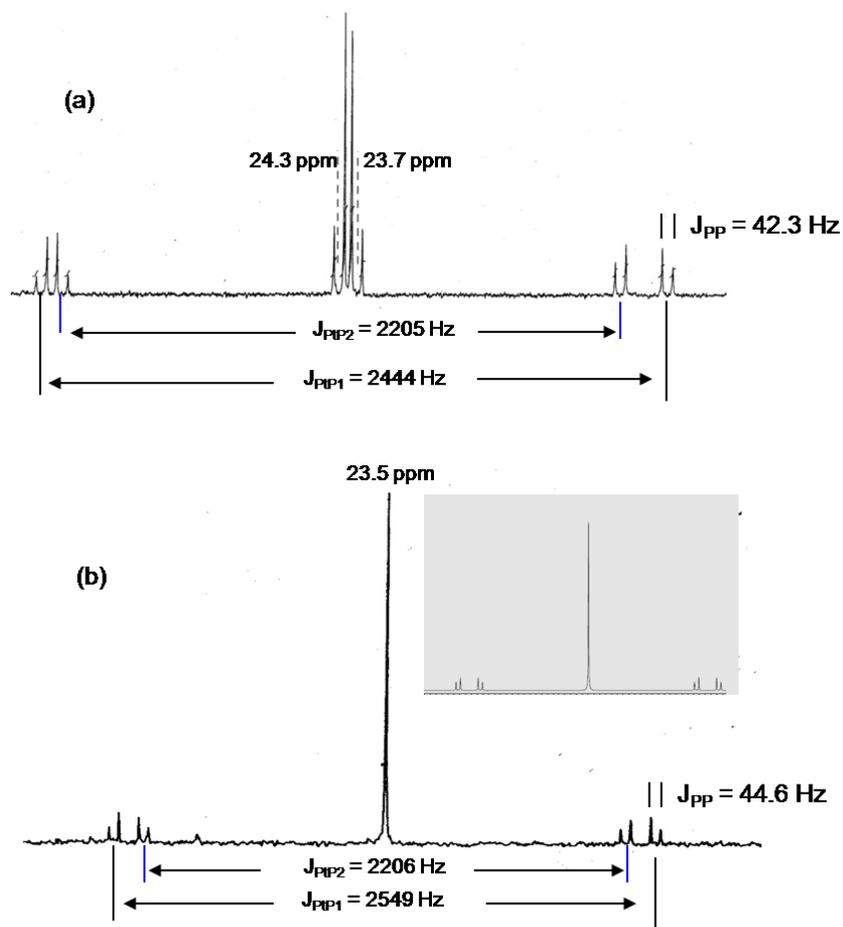


Figure 2.  $^{31}\text{P}$  NMR spectra of **5**. (a) in benzene; (b) in hexane (insert – simulated spectrum)

In attempt to understand the solvent effect, we crystallized **5** from benzene and to our surprise the X-ray crystal structure was very different from the structure obtained by crystallization from hexane shedding light on the differences in the NMR spectra, discussed above.

The X-ray analysis of the crystals of **5** obtained from a hexane solution revealed a monomolecular structure (Figure 1). In contrast, the X-ray analysis of the crystals obtained from a benzene solution of **5** revealed an unusual complex of one benzene molecule with three molecules of **5** as shown in Figure 3 (equation 3).

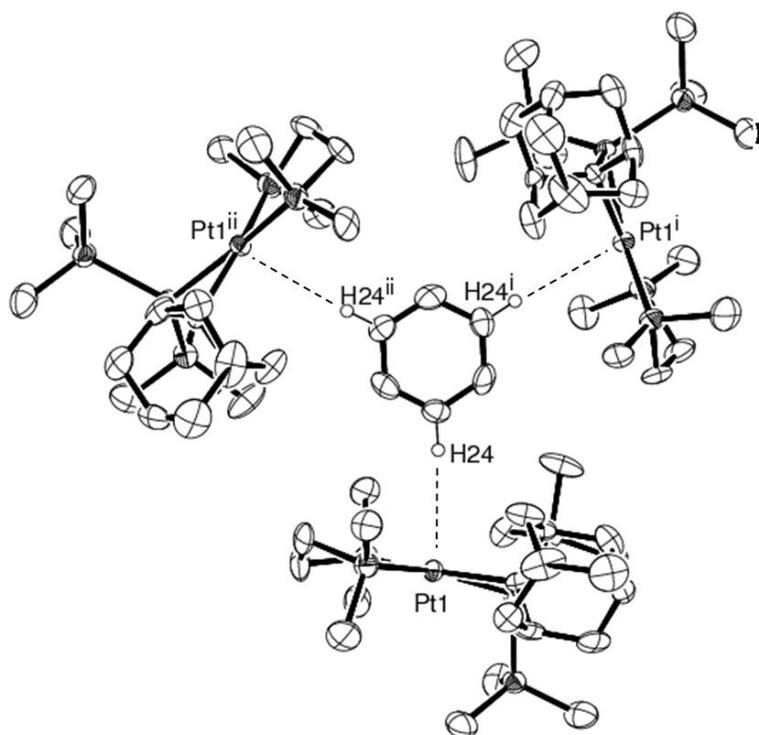
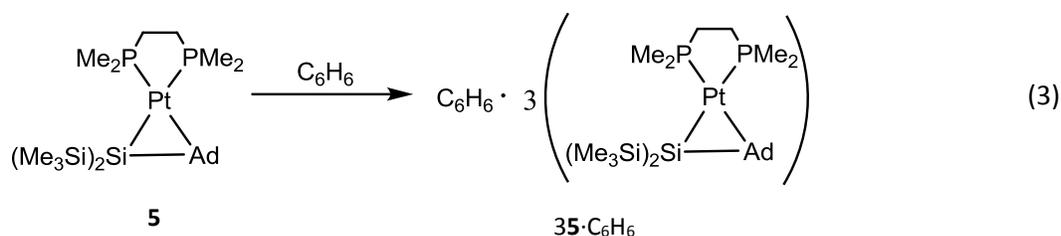


Figure 3. ORTEP drawing of the molecular structure of  $\mathbf{35 \cdot C_6H_6}$ . Hydrogen atoms (except three) are omitted for clarity. Selected bond lengths (Å), bond angles and dihedral angles (°): Pt-Si1 2.344(3), Pt-C1 2.171(11), Si1-C1 1.834(11), Pt-P1 2.251(4), Pt-P2 2.295(4), P-Pt-P 85.89(13), Si1-Pt-C1 47.8(3), Si2-Si1-Si3 111.8(2), P-P-Si-C 13.0, Pt-H(24)-C(2)-C(3) 152.6.

In the crystal three hydrogen atoms of a benzene molecule are bonded to one molecule of **5** each. The benzene molecule and the three Pt atoms are located on the same plane. The Pt-H distance is 3.03 Å indicating a weak van der Waals interaction (sum of the van der Waals radii of Pt and H is 2.95 Å;<sup>8</sup> the range of covalent Pt-H bonds is 1.4-1.9 Å<sup>9</sup>). The weakness of the Pt-H interaction in the complex is demonstrated

by the fact that the benzene can be removed from the complex by its dissolution in hexane followed by solvent evaporation.

The geometrical parameters of  $35\cdot\text{C}_6\text{H}_6$  are slightly different from those of **5**, which may explain the different NMR spectra of **5** in hexane and in benzene. E.g., in  $35\cdot\text{C}_6\text{H}_6$   $r(\text{Pt-P}2) = 2.295$  and in **5**  $r(\text{Pt-P}2) = 2.303$ ; in  $35\cdot\text{C}_6\text{H}_6$   $\angle(\text{Si}2\text{-Si}1\text{-Si}3) = 112^\circ$  and in **5**  $\angle(\text{Si}2\text{-Si}1\text{-Si}3) = 110^\circ$ , the angle between the P-Pt-P and Si-Pt-C planes is  $8.9^\circ$  in **5** and  $12.6^\circ$  in  $35\cdot\text{C}_6\text{H}_6$ , etc. The most significant difference is in the Si1-C1 bond: in  $35\cdot\text{C}_6\text{H}_6$   $r(\text{Si}1\text{-C}1) = 1.834 \text{ \AA}$  and in **5**  $r(\text{Si}1\text{-C}1) = 1.852 \text{ \AA}$ , i.e., in  $35\cdot\text{C}_6\text{H}_6$  the  $r(\text{Si}1\text{-C}1)$  is similar to that in **1** ( $1.838 \text{ \AA}$ ). This similarity does not mean that  $35\cdot\text{C}_6\text{H}_6$  is a  $\pi$ -complex, since its  $^{29}\text{Si}$  NMR ( $-66 \text{ ppm}$ ) in benzene solution clearly indicate that it is a  $\sigma$ -complex.

We are aware that in solution the structure can be different, but likely hydrogens of benzene (and other aromatic solvents) interact with platinum the same way also in solution, which will lead to the differences in the NMR spectra and perhaps also in reactivity,<sup>10</sup> which needs to be studied.

In summary, we synthesized new Pt-silene  $\sigma$ -complex in high yield and found its unusual complexation with benzene.

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  6. A hexane solution of  $(\text{dmpe})\text{Pt}(\text{PEt}_3)_2$  (5 ml, 0.1 mmol/ml) was mixed with benzene solution of disilacyclobutane **4** (5 ml, 0.154 g, 0.25 mmol) at room temperature in a vacuum vessel. The vessel was kept in an oil bath at  $100^\circ\text{C}$  for 3h. Evaporation of volatiles and crystallization from hexane resulted in formation of 0.27 g of **5** (85%) as colorless crystals. NMR (in  $\text{C}_6\text{H}_6$  with  $\text{DMSO-}d_6$  capillary),  $\delta$  in ppm:  $^1\text{H}$ : 0.39 (s, 18H,  $\text{Me}_3\text{Si}$ ), 0.73-1.35 (m, 16H, dmpe), 2.0-2.66 (m, 14H, Ad);  $^{13}\text{C}$ : 47.8 ( $J_{\text{P}1\text{-C}} = 8.7 \text{ Hz}$ ,  $J_{\text{P}2\text{-C}} = 5 \text{ Hz}$ ,  $J_{\text{Pt-C}} = 67.5 \text{ Hz}$ , CPT), 3.13 ( $J_{\text{Pt-C}} = 20 \text{ Hz}$ ,  $\text{Me}_3\text{Si}$ ), 11.05-41.6 (all the rest);  $^{29}\text{Si}$ :  $-66.0$  ( $J_{\text{Si-Pt}}=493.8 \text{ Hz}$ ,  $J_{\text{Si-P}1} = 71.7 \text{ Hz}$ ,  $J_{\text{Si-P}2} = 6.8 \text{ Hz}$ , SiPt),  $-14.7$  ( $J_{\text{Si-Pt}} = 38 \text{ Hz}$ ,  $J_{\text{Si-P}} = 3.8 \text{ Hz}$ ,  $\text{Me}_3\text{Si}$ )  $^{31}\text{P}$ : 24.3 ( $J_{\text{Pt-P}} = 2205 \text{ Hz}$ ), 23.7

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( $J_{\text{Pt-P}} = 2444\text{Hz}$ ). NMR (in hexane with DMSO- $d_6$  capillary),  $\delta$  in ppm:  $^{29}\text{Si}$ : -64.4 ( $J_{\text{Si-Pt}} = 414\text{ Hz}$ ,  $J_{\text{Si-P1}} = 30\text{ Hz}$ , SiPt), -14.1 ( $J_{\text{Si-Pt}} = 29\text{ Hz}$ ,  $J_{\text{Si-P}} = 4\text{ Hz}$ ,  $\text{Me}_3\text{Si}$ )  $^{31}\text{P}$ : 23.5 ( $J_{\text{Pt-P}} = 2206\text{ Hz}$ ), 23.5 ( $J_{\text{Pt-P}} = 2549\text{ Hz}$ ).

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