

**Five-coordinate Platinum(IV) Complex as a Precursor to a Novel Pt(II) Olefin
Hydride Complex for Alkane Activation**

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Supporting Information

General procedures

All reactions were carried out under inert conditions using high-vacuum or drybox techniques. Pentane (THM grade, 99.9 %, 98+ % n-pentane) was purchased from Aldrich, and deuterated solvents from Cambridge Isotope Laboratories. All Solvents were dried over Na/benzophenone and vacuum transferred into medium-walled (Wilmad 504) NMR tubes. The tubes were either attached to a ground glass joint to allow for a flame seal or equipped with a Teflon valve (J. Young-type). NMR spectra were recorded on Bruker AC200, DPX200, AF300, or DRX500 instruments, and shifts are reported relative to TMS. The five-coordinate Pt(IV) complex (nacnac)PtMe₃ (**1**) was prepared as previously reported.¹

Preparation of **2**

In the drybox, **1** (11.0 mg, 16.7 μmol) was transferred into an NMR tube attached to a ground glass joint. On the vacuum line, C₆H₆ (0.75 ml) was added by vacuum transfer. After flame-sealing the tube, it was protected with a steel jacket and heated to 150 ° C in the dark for 10 min. in an oil bath. A dark yellow solution was obtained. In the drybox, the tube was cracked and the liquid transferred into a small Pyrex bomb. On the vacuum line, the C₆H₆ was removed. Pentane (0.5 ml, two times) was added and removed under vacuum. These pentane washes allowed complete removal of C₆H₆, in which **2** is extremely soluble. Finally, pentane (2 ml) was vacuum transferred into the bomb and then the solution was filtrated through glasswool to remove a small amount of grey insoluble precipitate. The pentane was removed completely under vacuum and acetonitrile (1 ml) was vacuum transferred onto the residue. From acetonitrile, a microcrystalline product is more easily obtained than from hydrocarbon solvents. Removal of the acetonitrile under vacuum yielded 6.0 mg (9.8 μmol) of compound **2** (59 % yield of crude product). This sample contained 10 % of free ligand nacnac-H, which is difficult to remove completely, since it has solubility properties extremely similar to those of **2**.

Preparation of **2-d**₂₇

2-d₂₇ was prepared in an analogous manner to **2** except that the thermolysis was carried out in C₆D₆. Using 1,3-di-*tert*-butylbenzene as an internal standard for the thermolysis of **1** (4.0 mg, 6.2 μmol) in C₆D₆ (0.3 ml), it was determined by integration of ¹H-NMR signals that **2-d**₂₇ was obtained in 50 % yield. A 5% yield of free ligand nacnac-H was obtained. Insoluble precipitate (NMR-silent) was formed which explains the non-quantitative conversion.

Slowly reducing the volume of a solution of **2-d**₂₇ in pentane (at room temperature, applying vacuum) led to the formation of crystals suitable for X-ray diffraction.

¹ Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.

Thermolysis of **1** in C₆D₁₂

We previously reported that thermolysis of **1** at 90 °C in cyclohexane-*d*₁₂ leads to the formation of ethane, methane, and a variety of unidentified platinum products over the course of half a day.¹ After the identification of **2** and **2-d**₂₇ (in the work presented here), a re-examination of the NMR spectra of these reaction mixtures made clear that the main product is **2-d**_{*n*} (0 < *n* < 27). The partial deuteration of the product obtained in cyclohexane-*d*₁₂ leads to non-integer ratios of the ¹H-NMR integrals and to the appearance of multiple peaks, which suggested a mixture of compounds. The major product is now established to be a single compound, but the degree of deuteration is ill-defined. In contrast, after 19 h at 90 °C in C₆D₆, **2-d**₂₇ is obtained selectively.

NMR characterization of **2** and **2-d**₂₇

Table S1. ¹H-NMR data for **2** (500 MHz) and **2-d**₂₇ (200 MHz). All signals appear for **2**, whereas for **2-d**₂₇ only the underlined signals are visible.

¹ H-NMR (C ₆ D ₆ , 298 K), δ (ppm)	Assignment
<u>6.8 – 7.2</u> (ca. 6 H, m, partly overlapping with solvent peak)	Aromat. CH
<u>4.97</u> (1 H, s)	β-CH
3.83 (1 H, s, J _{PtH} = 54.4 Hz)	Olefinic CH of isopropylene group
3.70 (1 H, septet, ³ J _{HH} = 7 Hz)	CH of isopropyl
3.49 (1 H, septet, ³ J _{HH} = 7 Hz)	CH of isopropyl
3.13 (1 H, s, J _{PtH} = 74.4 Hz)	Olefinic CH of isopropylene group
2.97 (1 H, septet, ³ J _{HH} = 7 Hz)	CH of isopropyl
2.04 (3 H, s, J _{PtH} = 33 Hz)	CH ₃ of isopropylene group
<u>1.90</u> (3 H s,)	α-CH ₃
<u>1.64</u> (3 H s,)	α-CH ₃
1.46, 1.38, 1.27, 1.20, 1.16, 0.77 (each 3 H, d, ³ J _{HH} = 7 Hz)	Six non-equivalent (heterotopic) CH ₃ of the isopropyl groups
- 17.69 (1 H, s, ¹ J _{PtH} = 1140 Hz)	Pt-H

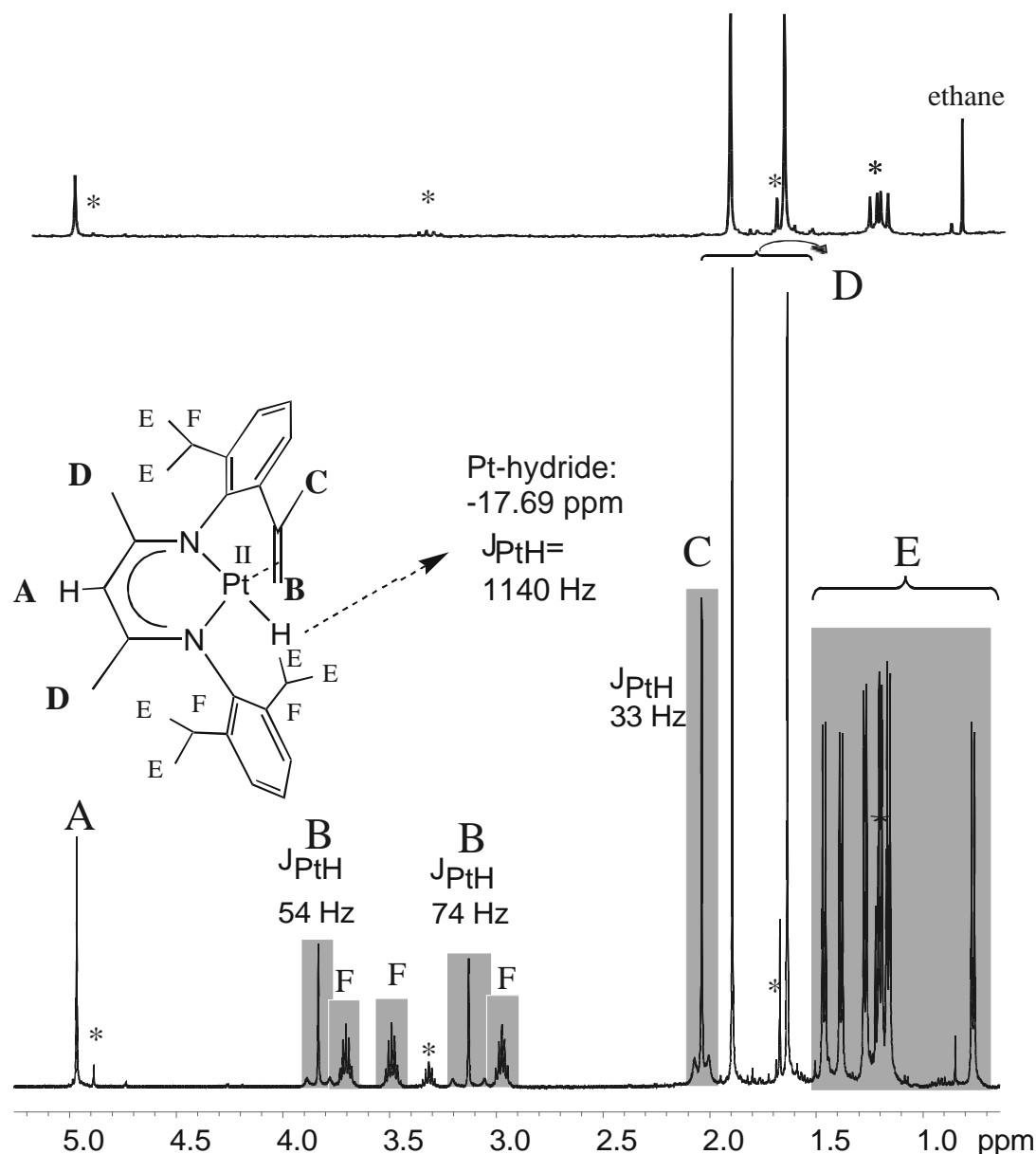


Figure S1. ^1H -NMR Spectra of the reaction products from the thermolysis of $(\text{nacnac})\text{PtMe}_3$ (**1**) in C_6D_6 (top, 200 MHz, **2-d₂₇**) and C_6H_6 (below, 500 MHz, **2**). Also shown is the assignment of the signals. The aromatic C-H signals, identical for both experiments, and the hydride signal observed in the C_6H_6 experiment are not shown. Complete data are given in table S1. Free ligand nacnac-H is denoted with an asterisk (*). Signals for ethane (shown) and methane (δ 0.16 ppm, not shown) were observed in the C_6D_6 experiment. Ethane and methane were not visible in the particular C_6H_6 experiment shown here, since all volatiles were vacuum transferred before C_6D_6 was added for the acquisition of the ^1H -NMR spectrum.

Activation of hydrocarbon solvents by **2** or **2-d₂₇**

The solutions typically contained 1-3 mg of **2** (or **2-d₂₇**) in 0.25 ml of solvent (C_6D_6 , pentane- d_{12} , or pentane- h_{12}). These solutions were heated (in the dark, 85 °C) in medium-walled, flame-sealed NMR tubes. Both visual inspection and the NMR data indicated that no significant decomposition occurred over the course of the reaction. This was confirmed with the use of an internal standard having a sterically protected hydrogen (the 2-H of 1,3-di-*tert*-butylbenzene, Aldrich).²

The incorporation of deuterium atoms from **2-d₂₇** into protiated solvent is clearly seen when **2-d₂₇** is heated in pentane. After 68 h at 85 °C, a 2H -NMR spectrum showed that no deuterium was left in the platinum complex. Deuteration of pentane was clearly seen in the 2H -NMR spectrum (Figure S2). The deuterium was incorporated into the terminal position of pentane and into the secondary positions, but the terminal position was favored over the statistical (1:1) distribution by a factor of 6. Examination of this same tube by 1H -NMR spectroscopy (500 MHz) showed the formation of **2**. No additional products (for example pentene) were seen by 2H or 1H -NMR spectroscopy.

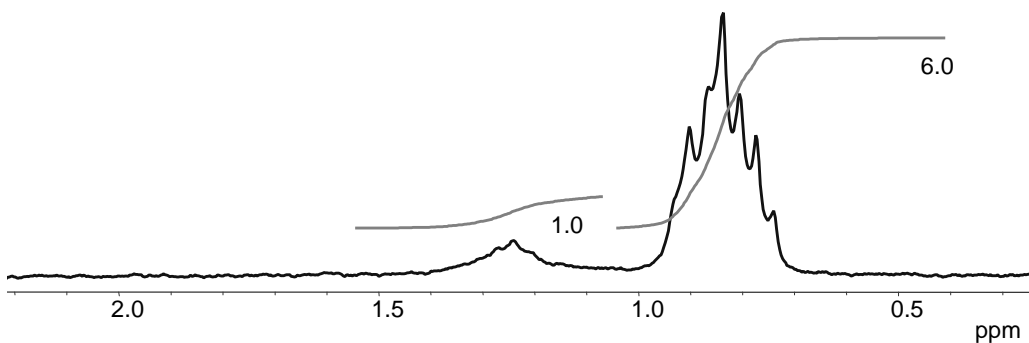


Figure S2. 2H -NMR (30.72 MHz) of the partially deuterated pentane produced by heating **2-d₂₇** in pentane at 85 °C for 68 h. Integration shows that incorporation of deuterium into the terminal position versus the secondary positions of pentane was favored over the statistical (1:1) distribution by a factor of 6.

² To allow for reliable integration, a relaxation delay of 200 s was used in these NMR experiments. After reacting **2** for 36 h in pentane- d_{12} (85 °C), the total concentration of platinum complex (**2** + **2-d₂₇**) was still identical to that observed before the reaction, as judged by integration of the central CH (ligand backbone) signal versus the internal standard. The isopropyl groups on the ligand were 80% deuterated at that time. After much longer reaction times, a minor decrease in intensity of the central CH was observed. No additional peaks appeared.