Reactions of Indene and Indoles with Platinum Methyl Cations: Indene C-H Activation, Indole $\pi$ vs. Nitrogen Lone-Pair Coordination

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I. Crossover Experiment between 9 and 1-methylindole.
II. Conversion of 6a to 8a at high [H$^+$].
III. About H/D Exchange and Methane Isotopologs Formed in the Conversion of 3 to 4.
IV. Selected $^1$H NMR spectra for new compounds.

I. Crossover Experiment between 9 and 1-methylindole.
   A detailed procedure for this experiment is presented in the main text; figure S1 shows kinetic data collected as described.

Figure S1. Conversion of 9 to 10 in the presence of 1-methylindole.
II. Conversion of 6a to 8a at high [H⁺].

A detailed procedure for this experiment is presented in the main text; figure S2 illustrates a sample ¹H spectrum (Pt-CH₃ region, 1_10⁴ sec after mixing) containing 2a, 6a, 8a, and the intermediate structure postulated to be 7a.

Figure S2. Conversion of 2a in the presence of 5 equiv. each of BF₃ and indole. Bottom: ¹H NMR spectrum (500 MHz, TFE-d₃) for Pt-CH₃ region at t = 1_10⁴ sec. Inset: kinetic data for this reaction.
III. About H/D Exchange and Methane Isotopologs Formed in the Conversion of 3 to 4.

$^2$H NMR spectra of 4a and 4a-$d_2$ were recorded to track $^2$H incorporation in these compounds as described in the main text. Data are shown in figure S3.

Figure S3. $^2$H incorporation in the conversion of 3a to 4a

Bottom: $^1$H spectrum of 4a (600 MHz). Middle: $^2$H spectrum of 4a (76.7 MHz). Solvent has been removed en vacuo and replaced with THF-$h_3$. Top: $^2$H spectrum of 4a-$d_2$ (76.7 MHz). Solvent has been removed en vacuo and replaced with THF-$h_3$ twice. (The broad signal at ~3.3 is a decomposition product that appeared after the second cycle of solvent replacement.)
IV. Selected $^1$H NMR spectra for new compounds

Indene complex 3a:

Indene complex 3a-$d_3$
Indenyl complex 4a:

Indenyl complex 4a-d$_2$
Indole complex 8a:

Indole complex 8b:
Indole complex 8c:

2-Methylindole-π-complex 9:
2-Methylindole-N-complex 10:

1-Methylindole-\pi -complex 11:
1-Methylindole-N-complex 12: