

TpPt(IV)Me(H)₂ Forms a σ -CH₄ Complex That Is Kinetically Resistant to Methane Liberation

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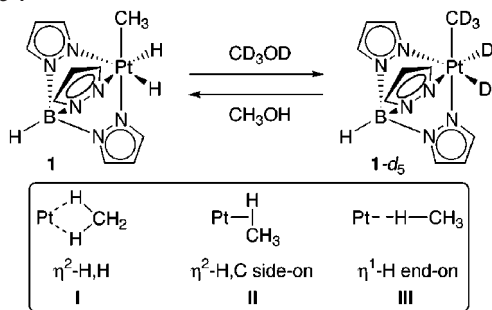
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The challenge of selective, transition-metal catalyzed functionalization of alkanes¹ has attracted increasing attention ever since the development of the classical Shilov system, which employs Pt^{II}/Pt^{IV} salts in aqueous media, and particularly the recent demonstration that methane can be catalytically activated by an organometallic complex of Pt(II).² An important conceptual advance in the field has been the proposed existence of a σ -alkane complex^{3,4} on the reaction pathway of either metal insertion into the C–H bond or alkane elimination from the metal center. It has been a desirable goal to structurally and kinetically characterize such weakly bound metal–alkane intermediate complexes. Unfortunately, direct observation of σ -alkane intermediates in the oxidative addition reaction required ultrafast spectroscopic techniques^{4f} and low-temperature gas matrices.^{4d,g} Furthermore, in the reductive elimination reaction the thermal instability of these intermediates did not allow for dissecting the two-step pathway and studying the formation of the σ -complex as an independent kinetic event without the accompanied liberation of the alkane product.

We recently reported on the synthesis of an air- and moisture-stable alkylidihydrido platinum(IV) complex, TpPtMe(H)₂ (**1**, Tp = hydridotris(pyrazolyl)borate).⁵ Here we report that although **1** has a very high energy barrier for the liberation of methane, it readily forms a σ -CH₄ Pt(II) complex, whose existence is strongly indicated by the observed inverse kinetic isotope effect⁶ in the H/D exchange reaction at 55 °C. To the best of our knowledge, this is the first example of a hydridoalkylmetal complex that undergoes isotopic scrambling at elevated temperatures without concomitant liberation of either alkane or dihydrogen.^{3,4} Nevertheless, in the presence of PMe₃, complex **1** undergoes facile reductive elimination to produce TpPt(II)Me(PMe₃) and dihydrogen rather than methane.

Scheme 1



The thermal stability of **1** (Figure 1) was evident from the fact

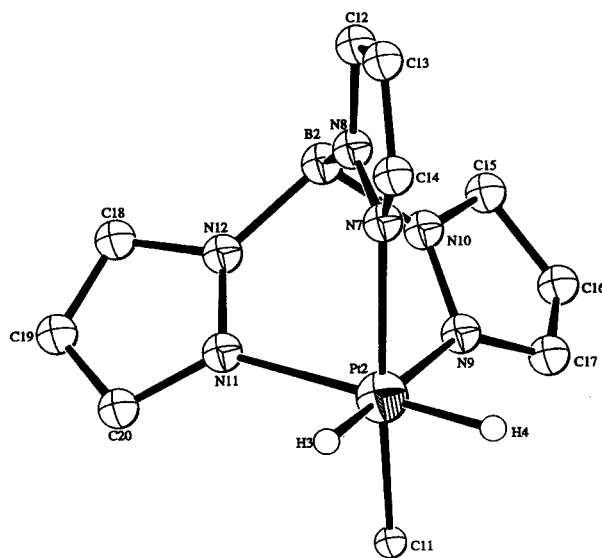


Figure 1. ORTEP diagram of TpPtMe(H)₂, **1**. Selected bond distances (Å) and bond angles (deg): Pt(2)–C(11) 2.01(8), Pt(2)–N(9) 2.19(2), Pt(2)–N(11) 2.20(2), Pt(2)–N(7) 2.20(2), C(11)–Pt(2)–N(7) 177(2), C(11)–Pt(2)–N(9) 91(2), C(11)–Pt(2)–N(11) 96(2), N(9)–Pt(2)–N(11), 84.0(8), N(9)–Pt(2)–N(7) 88.1(9), N(11)–Pt(2)–N(7) 86.7(9). The hydride ligands (H3 and H4) were placed in calculated positions. For more details, see the Supporting information.

that no NMR spectral changes could be observed even after heating at 55–70 °C in CH₃OH for several hours. However, when **1** was heated at the same temperatures in either CD₃OD or in a 1:1 mixture of C₆H₆ and CD₃OD, the hydride and methyl signals disappeared completely from the ¹H NMR spectrum with no change in the Tp signals. Remarkably, when the resultant **1-d₅** was heated under the same conditions in CD₃OH, it was converted back to **1** quantitatively (Scheme 1). Clearly, liberation of methane with or without C–H activation of benzene does not occur under these conditions.

Since the observed H/D exchange points at the existence of a σ -alkane intermediate,^{7,8} the rates of this exchange were further pursued. Thus, a solution of **1** in CD₃OD (0.8 mL) was heated in an NMR probe at 55 °C and the progress of the reaction was monitored by ¹H NMR for 6 h until both the hydride (δ –19.85) and methyl (δ 1.06) signals could no longer be detected. Since the time for the disappearance of the hydride signal (less than 5 min) was much shorter than that of the methyl signal (several hours), we considered the H/D exchange between hydride ligands and solvent molecules as a fast preequilibrium step and neglected its contribution to the kinetic isotope effect. After completion of the reaction, the solvent was carefully removed under high vacuum, CD₃OH (0.8 mL) was added, and the resulting solution of **1-d₅** was heated in the NMR probe as described above. Pseudo-first-order kinetics were observed

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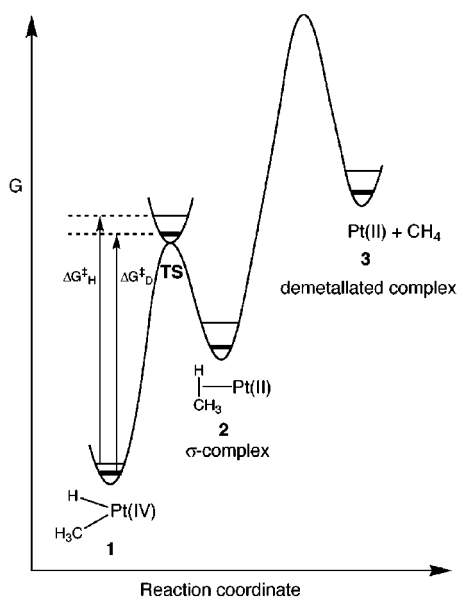


Figure 2. Proposed potential energy surface for the reductive elimination of methane from **1**. The zero-point energy differences between hydrogen containing species (thin line) and their deuterium analogues (thick line) are assumed to follow the general order of: $\Delta G_{\text{HD}}(\mathbf{1}) < \Delta G_{\text{HD}}(\text{TS}) < \Delta G_{\text{HD}}(\mathbf{2})$.

in both the conversion of **1** to **1-d**₅ ($k_{\text{obs}}^{\text{D}} = 2.42(3) \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} \sim 48 \text{ min}$) and the reversion of **1-d**₅ to **1** ($k_{\text{obs}}^{\text{H}} = 1.84(5) \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} \sim 63 \text{ min}$), $k_{\text{H}}/k_{\text{D}} = 0.76$.

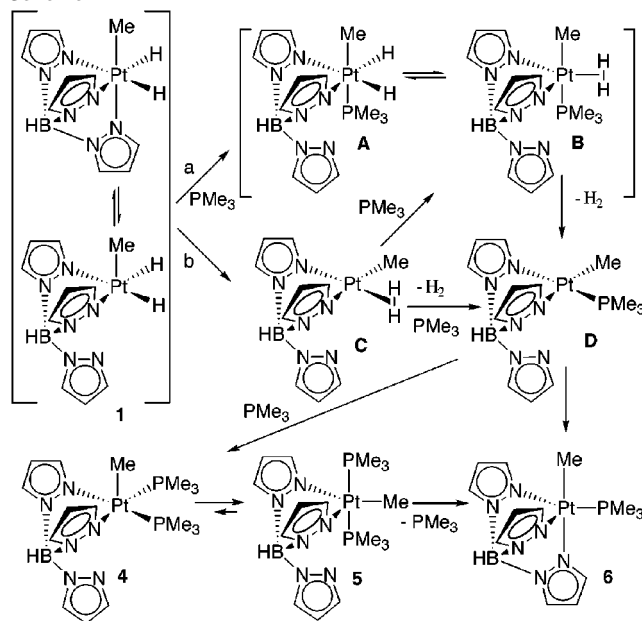
An inverse kinetic isotope effect can occur in a reaction that is characterized by a single rate-determining step with a product-like transition state.^{6a,b} For the reductive coupling in hydridoalkylmetal complexes, the inverse kinetic isotope effect could stem from the fact that the energy barrier for breaking a deuterium–metal bond is lower than that of a proton–metal bond. Such effects were previously observed for the loss of alkanes from hydridoalkyl complexes via a proposed σ -alkane intermediate ($k_{\text{H}}/k_{\text{D}}$ ranging from 0.29 to 0.80).^{3a,d,4a,b,9} The isotope effect in these reports was obtained by measuring the relative rates of alkane liberation. By contrast, no liberation of methane could be detected in our case. Therefore, we propose that our observed inverse kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 0.76$) should reflect the ΔG^{\ddagger} of the reductive coupling step (in which a σ -methane Pt(II) complex is formed)^{6c,10} but not the ΔG^{\ddagger} of the overall process (in which a dealkylated Pt(II) complex and free methane are formed).¹⁰ Accordingly, the proposed energy diagram (Figure 2) illustrates that the conversion of **1** to the σ -methane Pt(II) complex, **2**, has a lower barrier than that of the conversion of **2** to the dealkylated Pt(II) complex, **3**, and free methane. In previous reports on σ -alkane, the barriers for the transition from **2** to **3** appeared to be either lower or comparable to that of the transition from **1** to **2**.¹¹ Due to the energetically unfavorable high electron density on a metal in 18e Pt(II) species, we assume that complex **2** is a 16e species with an η^2 -Tp rather than an η^3 -Tp binding mode.

Since **1** was found to be thermally resistant to liberation of methane, we attempted to facilitate this transformation with a strong donor ligand (e.g., PMe_3). Surprisingly, however, addition of PMe_3 (1.0 equiv) in one portion to a CD_2Cl_2 solution of **1** in an NMR tube at room temperature caused immediate evolution of hydrogen gas. While the formation of H_2 was confirmed by the ^1H NMR signal of H_2 at δ 4.62, which disappeared completely upon purging the mixture with argon for 2 min, no signal attributed to free CH_4 in the range of δ 0–0.5 could be detected. Following the reaction by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR revealed that the overall conversion of **1**

to the isolable product **6** involved two intermediates, **4** and **5** (Scheme 2).¹² The presence of two PMe_3 ligands in both intermediates was evident from their ^1H NMR integration ratios. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two singlets with Pt satellite coupling representing the two intermediates: **4**, δ –24.74 ($^1J_{\text{Pt-P}} = 1796.6$) and **5**, δ –10.98 ($^1J_{\text{Pt-P}} = 2755.9$). The two *trans*-oriented PMe_3 in **5** was highly suggested by the observation of virtual coupling¹³ between the two P nuclei in the ^1H NMR: both proton signals associated with Pt– CH_3 (δ 0.35, t, $^3J_{\text{PH}} = 7.2$, $^2J_{\text{Pt-H}} = 74.5$) and Pt– $\text{P}(\text{CH}_3)_3$ (δ 1.12, t, $J_{\text{PH}} = 3.4$, $^3J_{\text{Pt-H}} = 30.9$) in **5** appear as a triplet. By contrast, the broad and unresolved Pt– CH_3 signal in **4**¹² was consistent with a *cis* geometry and fluxional movement of the two sterically demanding PMe_3 ligands. The repulsive interaction between two *cis*-oriented phosphines is known to be considerable, particularly in Tp complexes.¹⁴

In the above-described experiment, a $\sim 1:1$ mixture of **1** and intermediate **4** was immediately formed upon addition of PMe_3 , **4** then isomerized to **5** within 60 min,^{12b} and the latter slowly converted to **6**. Furthermore, addition of a small amount of PMe_3 to **6** converted it back to **4**, which then isomerized to **5**. These observations led us to carry out an alternative experiment in which PMe_3 (1.2 equiv) was added slowly over a period of $\sim 60 \text{ min}$ to a CD_2Cl_2 solution of **1**. Complete consumption of **1** was observed, leading to a $\sim 9:1$ ratio of **6** and **5** within 4 h.^{12b} These results are intriguing, particularly in light of the recent report that $\text{Tp}^*\text{Pt}(\text{CH}_3)_2\text{H}$ undergoes reductive elimination to form Pt(II) with the assistance of HBAr_4 ¹⁵ and that another close analogue of **1**, $(\text{triphos})\text{Ir}(\text{C}_2\text{H}_5)(\text{H})_2$, liberates ethane rather than dihydrogen in the presence of a sulfur-containing ligand.¹⁶

Scheme 2



Although mechanistic studies have suggested that reductive elimination from octahedral Pt(IV) complexes involves predisassociation of one ligand to form a five-coordinate intermediate,^{4b,17} the alternative routes involving concerted reductive coupling,¹⁸ or ligand association prior to or during the reductive coupling step have also been proposed.^{3d,19} Since complex **1** is stable in protic and aprotic solvents at 55–70 °C, it is conceivable that η^3 -Tp to η^2 -Tp interconversion and PMe_3 association to form intermediates **A** and **B** (pathway a, Scheme 2) could occur prior to the extrusion of H_2 to give **D**.^{19,20} An alternative (pathway b) involves formation of an η^1 - H_2 Pt(II), **C**,¹¹ prior to the coordination of PMe_3 to produce

D. Intermediate **C**, $\eta^2\text{-TpPt(II)Me(H}_2\text{)}$, which is isoelectronic of $\eta^2\text{-TpPt(II)H(CH}_3\text{)}$, **2**, could afford **D** either via a concerted or a stepwise ligand substitution of dihydrogen with PMe_3 .²⁰

In conclusion, complex **1** provides an unprecedented opportunity to study the initial step in the reductive elimination of hydridoalkyl-metal complexes as an isolated kinetic event.¹⁰ Both experimental and theoretical studies to further understand the parameters governing the selectivity of C–H and H–H reductive coupling are currently underway. Other issues, such as the use of **1** for C–H meta-thesis reactions,²¹ will be reported in due course.

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Supporting Information Available: Experimental details and spectroscopic data for **4**, **5**, and **6** and complete crystallographic data for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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