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Modulating Sterics in Trimethylplatinum(IV) Diimine Complexes To Achieve C–C Bond-Forming Reductive Elimination

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Supporting Information

ABSTRACT: Tuning the aryl substituents of N,N'-diaryl-2,3-dimethyl-1,4-diaza-1,3-butadiene (DAB) ligands promotes the challenging C-C bond-forming reductive elimination from Pt^{V} diimine complexes $[(DAB)Pt(CH_3)_3(solvent)]^+$ (2) under mild conditions. Experimental results and density functional calculations indicate that 2,6-aryl substitution promotes reductive elimination by facilitating dissociation of the coordinating solvent by close to 10 kcal mol⁻¹, but too much steric bulk inhibits the formation of 2 in the one-electron outersphere oxidation of $(DAB)Pt(CH_3)_2(1).$



ransition-metal-catalyzed C-H activation/C-C bondforming reactions provide atom-economical routes for the synthesis of commodity chemicals, pharmaceuticals, natural products, and materials.¹ Palladium-based catalysts have been widely used for such transformations, in part because C-Cbond-forming reductive elimination generally proceeds efficiently from Pd centers.² The development of related Pt-catalyzed reactions is attractive because Pt^{II} is well-known to effect the C-H activation of substrates that are challenging using analogous Pd^{II} species. For example, a number of Pt^{II} complexes have been shown to promote stoichiometric and/or catalytic activation of simple alkanes, including methane.³ However, despite significant efforts in this area, Pt-catalyzed alkane C-H functionalization reactions to generate new C-C bonds have not yet been achieved.

One particularly exciting target for Pt-catalyzed C-H activation/C-C coupling would be the catalytic oxidative dimerization of CH4.4 This transformation would provide a direct method for upgrading methane to ethane, which is a key precursor to ethylene and higher alkanes. A potential catalytic cycle for Pt-catalyzed methane dimerization could start with methane C-H activation³ to form a Pt^{II}-CH₃ complex (Scheme 1, step 1). Oxidatively induced disproportionation could then produce a trimethylplatinum(IV) complex, as has been demonstrated by Bercaw⁵ and Tilset⁶ for $(DAB)Pt^{II}(CH_3)_2$ (1; DAB = N,N'-diaryl-2,3-dimethyl-1,4-diaza-1,3-butadiene) and by us for related Pd species⁷ (Scheme 1, step 2).⁸ Importantly, similar (DAB)Pt^{II} complexes are known to activate methane, although typically only by methyl group exchange.9 The final step of the catalytic cycle would then involve C-C bond-forming reductive elimination from Pt^{IV} to generate ethane (Scheme 1, step 3). Such reductive elimination is typically challenging for Pt^{IV} methyl complexes with diimine ligands,^{10,11} although it is known for related complexes with phosphine or β -diketiminate ligands and for Pd^{IV} polymethyl adducts.

Scheme 1. Proposed Catalytic Cycle for Pt-Catalyzed Methane Dimerization



We hypothesized that increased steric bulk in the diimine ligand environment would facilitate reductive elimination from $[(DAB)Pt^{IV}(CH_3)_3(solvent)]^+$ (2). This hypothesis is predicated on the observation that sterically encumbered diimine ligands accelerate CH₃I reductive elimination from Pt^{IV};¹⁴ furthermore, bulky ligands have been used to promote reductive elimination in other systems.¹⁵ In this communication we demonstrate that modification of the DAB ligands and reaction solvent can be used to achieve facile C-C reductive elimination of ethane. In addition, we show that the diimine ligand structure also strongly influences the oxidative disproportionation reaction that converts 1 to 2. These studies have facilitated the identification of a DAB ligand substitution pattern that promotes both steps 2 and 3 in Scheme 1 efficiently at room temperature.

A series of $(DAB)Pt^{II}(CH_3)_2$ complexes (1A-D) have been prepared with differently substituted aryl rings: 4-methyl (A),

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Chart 1. Yields of Reductive-Elimination Products, C_2H_6 and 3, from Thermolysis of 2 in Acetone- d_6 for 8.5 h at 60 °C (Scheme 2)^{*a*}



^aThe 1,4-diaza-1,3-butadiene ligands **A**–**D** are shown.

3,5-dimethyl (B), 2,6-dimethyl (C), and 2,6-diisopropyl (D) (shown in Chart 1).^{16,17} The cationic Pt^{IV} solvento complexes $[(DAB)Pt^{IV}(CH_3)_3(solv)]^+$ (2A–D) were then generated by treating 1A–D with 1 equiv of CH₃I followed by AgPF₆ in acetone- d_6 (eq 1).^{18,19} The ¹H NMR spectra of 2A,B in acetone- d_6 at ambient temperature exhibit two distinct Pt–CH₃ resonances in the expected 2:1 ratio. In contrast, 2C,D show a single Pt–CH₃ signal, indicating that the three methyl ligands are in fast exchange.^{10b} This exchange is expected to proceed via the five-coordinate cationic intermediate I-1 (Scheme 2, top).²⁰ As such, these data suggest that I-1 is significantly more accessible in the more sterically crowded complexes 2C,D.

$$\begin{pmatrix} \mathsf{N} \\ \mathsf{N} \\ \mathsf{N} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \end{pmatrix} \xrightarrow{\mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{I} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{I} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{I} \\ \mathsf{C} \\ \mathsf{H}_{\mathsf{C}}^{\mathsf{I}} \\ \mathsf{I} \\ \mathsf{$$

Consistent with literature precedent, compounds **2A**,**B** are quite thermally stable.^{10,11} For example, no decay was observed after heating for 24 h in acetone-*d*₆ at 60 °C. Even after 18 h at 100 °C, C_2H_6 was not detected and only minimal (<5%) decomposition was seen (Chart 1). Thus, the $\Delta G^{\dagger}_{60 \ ^{\circ}C}$ value for C–C bond-forming reductive elimination from **2A**,**B** is >30 kcal mol⁻¹.

In contrast, the ortho-aryl-substituted diimine complexes **2C**,**D** quantitatively eliminate ethane over 8.5 h at 60 °C in acetone- d_{6} , in 96(6) and 91(6)% yields, respectively (Chart 1).²¹ This reaction proceeds with concomitant formation of the corresponding Pt^{II} monomethyl solvento complexes [(DAB)Pt^{II} CH₃(solv)]⁺ in 82(6)% (3C) and 72(5)% (3D) yield (Pt yields are less than quantitative due to some competing decomposition). The kinetics of C–C coupling were monitored by ¹H NMR spectroscopy. First-order rate constants were observed for the decay of 2C ([1.6(3)] × 10⁻⁴ s⁻¹) and 2D ([4.2(6)] × 10⁻⁴ s⁻¹) at 60 °C. These correspond to energy barriers ($\Delta G_{60 °C}^{-}$) of 25.4(1) and 24.7(1) kcal mol⁻¹ for 2C,D, respectively.²²

DFT calculations were conducted to gain insights into the marked reactivity difference between the complexes with and without 2,6-substituents on the aryl rings. Gas-phase reaction coordinates for reductive elimination from isomeric **2B** and **2C**



Scheme 2. Mechanism for the Fluxionality of 2C,D and Their Reductive Elimination of Ethane

Figure 1. Reaction coordinate for C_2H_6 elimination (gas-phase free energies in kcal mol⁻¹) from DFT calculations.¹⁷

(with solv = acetone) were computed using the B3LYP functional in Gaussian 03 and the basis sets LANL2TZ on Pt and $6-31G^{**}$ on C, H, N, and O (Figure 1).²³ Since it is well-known that reductive elimination reactions from six-coordinate Pt^{IV} trimethyl complexes proceed via initial ligand dissociation,^{10,24} we first calculated the free energies for loss of acetone to give I-**1B** or I-1C. This step is 5.5 kcal mol⁻¹ uphill for **2B** but is roughly isoergic for **2C**. These results are consistent with the NMR data discussed above, indicating much more facile loss of solvent from **2C**.

In the transition structures (**TS**) for H_3C-CH_3 coupling, the two reacting methyl groups straddle the N₂Pt equatorial plane with a C···C distance of ~1.95 Å. Distortion along the imaginary mode in one direction and reoptimization of the minimum energy geometries returned the five-coordinate square-pyramidal complexes **I-1B** and **I-1C**. In the other direction, a slight decrease in the C···C distance led to C₂H₆-bound complexes **I-2B** and **I-2C** as local minima (Scheme 2). Displacement of coordinated C₂H₆ with acetone then completes the reaction sequence to form **3B** or **3C**.

The overall gas-phase free energy barrier for C_2H_6 formation from 2C is 21.8 kcal mol⁻¹ at 298 K, which is in reasonable agreement with the experimental value ($\Delta G^{\dagger}_{60\,^{\circ}C} = 25.4$ kcal mol⁻¹ in acetone solution). The barrier for 2B is computed to be 5.4 kcal mol⁻¹ higher than that of 2C, again consistent with experiment ($\Delta \Delta G^{\dagger}_{60\,^{\circ}C} > 5.6$ kcal mol⁻¹). The calculations show that the difference in energy between the transition structures is almost entirely due to $\Delta \Delta G^{\circ}$ for acetone dissociation (5.5 kcal mol⁻¹). Thus, the ortho substituents accelerate reductive elimination by facilitating access to the five-coordinate intermediate I-1, rather than by promoting the actual C–C bond-forming step.

Scheme 3. Oxidation of $(DAB)Pt^{II}Me_2(2)$ with $AcFc^+$



The DFT calculations indicate that C-C coupling from 2 should be faster in more weakly coordinating solvents.²⁵ Indeed, in nitromethane- d_{3} , reductive elimination to C_2H_6 from 2C proceeds within 8 h at room temperature ($k = [5.7(5)] \times 10^{-5} \text{ s}^{-1}$ and $\Delta G^{\ddagger}_{25^{\circ}C} =$ 23.2(1) kcal mol⁻¹). The use of CD_2Cl_2 resulted in quantitative reductive elimination to C_2H_6 within 1 h at room temperature (k = $7.6(14) \times 10^{-4} \text{ s}^{-1}$; $\Delta G^{\ddagger}_{25 \,^{\circ}\text{C}} = 21.7(1) \text{ kcal mol}^{-1}$.²⁶ This order of facility of reductive elimination, dichloromethane > nitromethane > acetone, parallels the lower donor ability of these solvents.²⁷ This is almost as fast as reductive elimination from the 1,2-bis(diphenylphosphino)ethane (dppe) complex (dppe)Pt- $(CH_3)_3(OTf)$, which occurs upon warming to room temperature in acetone (though complexes of this type have not been shown to activate C-H bonds).^{10b} Furthermore, although **2A**,**B** are both stable to heating in nitromethane- d_3 at 60 °C (<10%) decomposition over 16 h), both undergo reductive elimination to C_2H_6 when heated in CD_2Cl_2 at 50 °C over 48 h.

We next sought to apply these ligand effects in the two-step oxidative disproportionation/reductive elimination sequence proposed for methane dimerization (Scheme 1, steps 2 and 3). The PtII dimethyl complexes 1C,D provided very different results. Reaction of the 2,6-diisopropyl derivative 1D with 1 equiv of acylferrocenium $(AcFc^{+})$ in acetone- d_6 proceeded slowly at room temperature, and the expected Pt^{IV} intermediate 2D was formed only in low yield (<20% out of a theoretical 50% maximum yield). Furthermore, after heating for 8 h at 60 °C, C_2H_6 was formed in only 17(2)% yield along with substantial quantities of CH₄. In marked contrast, the 2,6-dimethyl complex 1C reacted instantaneously and cleanly with AcFc⁺ at room temperature in acetone- d_6 to form 0.5 equiv of 2C and 0.5 equiv of **3C** (Scheme 3, top path). The latter then liberated C_2H_6 in high yield after 8 h at 60 °C. These findings indicate that while sterically encumbered diimine ligands are necessary for facile solvent dissociation prior to reductive elimination, too much steric bulk can hinder the oxidative disproportionation.

The substantial differences in reactivity between 1C and 1D can be rationalized on the basis of the mechanism in Scheme 3. Initial $1e^-$ outer-sphere oxidation by AcFc⁺ to give the putative Pt^{III} intermediate $[(DAB)Pt^{III}(CH_3)_2]^+$ is expected to be endoergic;²⁸ thus, the overall sequence is driven by the relative rates of the subsequent steps. $[(DAB)Pt^{III}(CH_3)_2]^+$ can react with AcFc⁺ and an additional 1 equiv of 1 with concomitant methyl transfer to generate 2 and 3 (path a).²⁹ Alternatively, $[(DAB)Pt^{III}(CH_3)_2]^+$ can undergo $Pt^{III}-CH_3$ bond homolysis (path b), as has been observed upon oxidation of phosphine-ligated palladium methyl complexes.^{7b,30} Path a appears to occur rapidly and cleanly for the *o*methyl-substituted aryldiimine complex 1C. In contrast, the additional steric congestion from the isopropyl groups in **1D** significantly lowers the rate of methyl transfer between platinum centers (path a). This decreases the rate of disappearance of **1D** and allows Pt-C bond homolysis (path b) to become competitive, thereby providing significant quantities of CH_4 .

In summary, an effective ligand-based approach for promoting C-C bond-forming reductive elimination from Pt^{IV} diimine complexes under mild conditions has been described. Tuning the steric properties of the ligand in concert with the reaction solvent can lower the barrier for C-C bond formation by close to 10 kcal mol^{-1} . The lower barrier for reductive elimination is due to the ease of accessing the five-coordinate intermediate, rather than a greater facility for C-C bond formation. Furthermore, with an appropriate choice of ligand, this reaction can be exploited in the context of the oxidative disproportionation of Pt^{II} dimethyl complexes. Promoting these reactions for diimine-ligated Pt complexes is valuable, because these complexes are particularly effective for C–H activation reactions. Studies are in progress to couple these oxidative disproportionation and reductive elimination steps with methane activation. More generally, this work provides an attractive strategy for the development of new Ptcatalyzed C-C coupling reactions.

ASSOCIATED CONTENT

Supporting Information. Text, figures, and tables giving experimental details, ¹H NMR spectra, characterization data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) An analogue of 2D without methyls on the diazabutadiene backbone and with a triflate counterion has been reported. $^{10\rm{b}}$

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(21) Puddephatt et al. have reported that a close analogue of $2D^{10b,18}$ is stable to reductive elimination, but they may not have explored elevated temperatures. Their analogue is lacking methyl groups on the diimine backbone and has a triflate rather than a solvent ligand.

(22) To test whether the difference between **2A**,**B** and **2C**,**D** could be due to ion pairing or anion coordination, the decay of a solution of **2C** in acetone- d_6 at 60 °C was monitored with and without 20 equiv of NaOTf. Nearly identical rates were observed, indicating that the anion does not play a major role. In addition, **2B** generated in CD₃NO₂ with a B(C₆F₅)₄⁻ counterion still did not produce C₂H₆ at 60 °C over 18 h.

 $\left(23\right)$ Similar trends were observed using the B3PW91 and M06 functionals.

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(25) In the more strongly coordinating solvent acetonitrile, complex 2C (solv = acetonitrile) was found to be more stable toward reductive elimination than in acetone.

(26) Complexes $3A_{,B}$ were stable in CD_3NO_2 over 24 h at 60 °C. In CD_2Cl_2 , these complexes underwent slow decomposition after 24 h at 50 °C; however, only traces of C_2H_6 were observed in either case.

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