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Competitive Carbon–Carbon Reductive Elimination and Carbon–Iodide Bond Formation from a Pt(IV) Complex

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Although the oxidative addition of organohalides to metal centers has been very well studied, there have been few mechanistic investigations of its microscopic reverse, carbon–halide bond-forming reductive elimination.[1] Two decades ago it was reported that thermal decomposition of the octahedral bisphosphine Pt(IV) complexes containing both methyl and halide ligands, *fac*-L_2PtMe_3X (L = PMe_2Ph, X = Cl, Br, I; L = PMe_3, $PMePh_2$, $^1/_2$dppe, X = I), resulted in exclusive alkyl–alkyl reductive elimination producing ethane and the Pt(II) complexes, L_2PtMeX.[2,3] Detailed kinetic and mechanistic studies led to the proposal of the now classic mechanism that involves, for the monodentate phosphine complexes, initial phosphine dissociation with reductive elimination of ethane occurring from the resulting five-coordinate intermediate.[2] These reactions are often cited in organometallic textbooks and review articles as classic examples of carbon–carbon bond-forming reductive elimination.[1a–c]

We now report that the bidentate phosphine complex $dppePtMe_3I$ (**1**) actually undergoes an unusual competitive reaction to form methyl iodide in addition to ethane (Scheme 1). The corresponding Pt(II) products, respectively $dppePtMe_2$ (**2**) and dppePtMeI (**3**), are also produced. We have found that in solution the methyl iodide elimination is reversible, and we have taken advantage of the unique opportunity that this system provides to directly compare the kinetics, thermodynamics, and mechanisms of alkyl–alkyl and alkyl–halide reductive elimination reactions. In addition to determining energetic differences between the Pt(IV) complex and its reductive elimination products, we present evidence that pathways to both sets of products proceed through a common cationic five-coordinate intermediate formed by dissociation of iodide.

When a solution of **1** in acetone-d_6 was heated in a sealed NMR tube at 79 °C and the reaction monitored at intervals by ^1H NMR, products from both eliminations were observable, although the relative ratios of the sets of products varied with reaction time (Figure 1a). At early reaction times (less than 30% conversion of **1**), MeI (δ 2.17 (s)) and $dppePtMe_2$ (**2**) (δ 0.61 (t, 6H, J_{P-H} = 7.2 Hz, J_{Pt-H} = 71 Hz)) made up from 60 to 80% of the elimination products. The concentrations of these carbon–iodide coupling products increased to a maximum at ca. 45 min (70% conversion of **1**) and then decreased as the reaction continued. However, the signals for ethane (δ 0.82) and dppePtMeI (δ 0.80 (dd, 3H, J_{P-H} = 4.5, 7.5 Hz, J_{Pt-H} = 60 Hz)) increased steadily throughout the reaction. Even after all signals for **1** had disappeared, the concentrations of $dppePtMe_2$/MeI continued to decrease, and eventually all material was converted to the carbon–carbon coupling products, dppePtMeI/ethane.

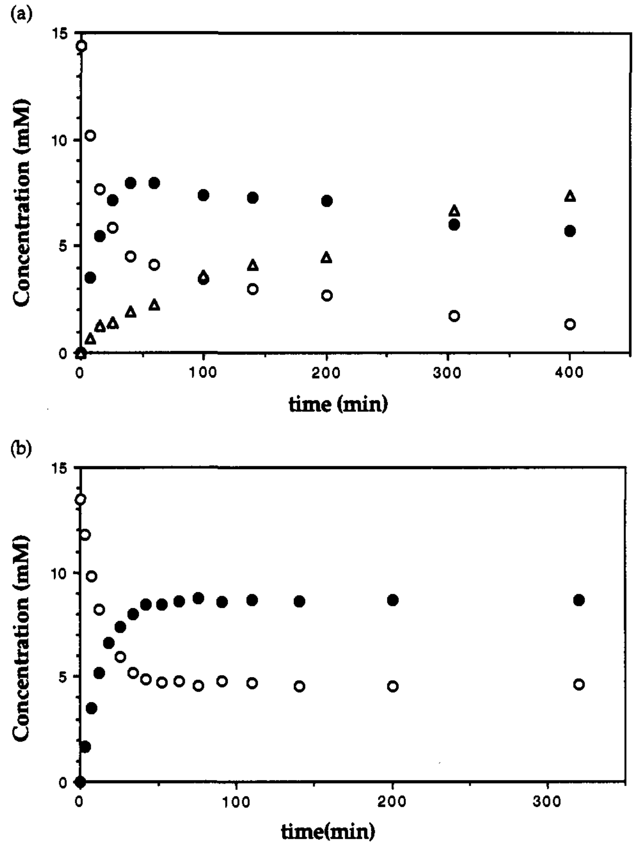
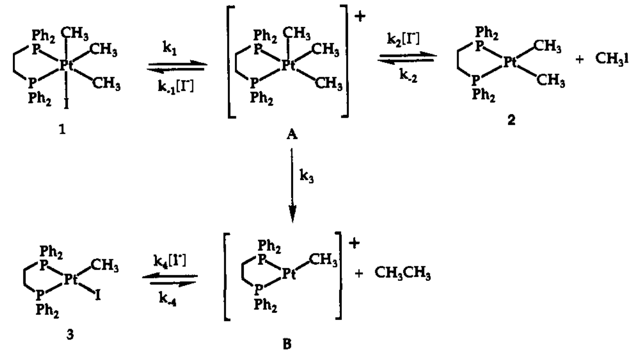


Figure 1. Graph of the concentrations of $dppePtMe_3I$ (**1**, ○), $dppePtMe_2$ (**2**, ●), and dppePtMeI (**3**, △) versus time at 79 °C. Concentrations of **1** and **2** were measured by integration of ^1H NMR signals against an internal standard, and the concentration of **3** was calculated by difference due to overlapping signals. (a) Without added iodide. (b) [NaI] = 0.19 M.

Scheme 1



Since there are a variety of examples in the literature which indicate that reductive elimination occurs preferentially from five-coordinate species rather than six-coordinate complexes,[2,4,5] and since the chelate effect clearly disfavors phosphine dissociation in the case of the bidentate ligand dppe, the possibility of

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(1)) For reviews and chapters on oxidative addition/reductive elimination reactions, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; Chapter 6.2. (c) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 625. (d) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; Chapter 5.

(2)) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

(3)) Although pyrolysis of *fac*-$(PMe_2Ph)_2PtMe_3Cl$ was reported in ref 2 to yield 100% ethane elimination, an earlier reference reports production of 10% MeCl/90% ethane: Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. (A)* **1969**, 2969.

(4) Proposed five-coordinate intermediates may be solvated species: (a) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227. (b) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649. (c) Saunders, D. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2133. (d) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem Soc., Dalton Trans.* **1989**, 2121. (e) Ettore, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45.

(5) Proposed five-coordinate intermediates may be solvated species: (a) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363 and references cited therein. (b) de Graaf, W.; Boersma, J; Smeets, W. J. J.; Speck, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

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dissociation of iodide was examined. When excess NaI (10^{-1} M) was added to the solution thermolysis of **1** (10^{-2} M), the initial rates of disappearance of **1** and appearance of **2** were not significantly affected. However, the rate of production of ethane and **3** was significantly inhibited. In fact, the presence of iodide caused diversion of the initial thermolysis products *exclusively* to methyl iodide and **2**. The reaction approached and reached an equilibrium[6] between **1** and **2**/MeI which was maintained for several hours at 79 °C (Figure 1b). Eventually ethane and **3** did begin to appear, and yields of these products increased very slowly but steadily over time.

The equilibrium constants for the reductive elimination of methyl iodide from **1**, $K_{eq} = [\mathbf{2}][CH_3I]/[\mathbf{1}]$, were calculated for temperatures between 69°C and 99 °C from the equilibrium concentrations maintained in the presence of excess iodide. As expected, there was no dependence of the equilibrium constants on the concentration of iodide. The following thermodynamic parameters for the methyl iodide elimination were extracted from the temperature dependence of K_{eq}: $\Delta H° = 66 \pm 2$ kJ/mol and $\Delta S° = 153 \pm 7$ J/mol·K. From these parameters it is clear that formation of methyl iodide and dppePtMe$_2$ from dppe PtMe$_3$I is not enthalpically favored. Indeed all solution-phase thermolyses proceed to give dppePtMeI and ethane as the final products.[7]

On the basis of our observations we propose a mechanism for the eliminations as shown in Scheme 1. Initial reversible loss of iodide from **1** generates the cationic intermediate **A**.[8] Intermediate **A** can then react by three routes: (i) elimination of ethane, (ii) reaction with iodide to form methyl iodide and **2**, or (iii) reaction with iodide to reform **1**. In the presence of excess iodide, these latter two pathways are accelerated and dominate, which leads to the observed equilibrium between **1** and **2**/MeI. However, since the carbon–carbon coupling is the thermodynamically favored pathway, eventually all materials are converted to ethane and dppePtMeI.

The mechanistic pathway proposed for the elimination of methyl iodide is the microscopic reverse of the popular S_N2 mechanism often proposed for oxidative addition of methyl iodide to square-planar d^8 metal centers.[5,9] Using a steady-state approximation of cationic intermediate **A** shown in the scheme, the rate equation for the reductive elimination of methyl iodide should show no iodide dependence.[10] In the presence of excess iodide, the time required to reach equilibrium was essentially independent of the iodide concentration (43 min at 79 °C).[11] In addition, this was very close to the time required to reach the maximum concentration of MeI/**2** without added iodide. The lack of significant augmentation of the rate of methyl iodide elimination in the presence of iodide ions argues against a mechanism involving direct attack of iodide on **1** to generate methyl iodide and an anionic five-coordinate intermediate. Such a mechanism would be the microscopic reverse of that which has been postulated for iodide acceleration in the oxidative addition of methyl iodide to rhodium and iridium centers.[12]

The pathway leading to carbon–carbon coupling reductive elimination is analogous to that proposed for similar palladium(IV) trimethyl iodide complexes containing bidentate neutral ligands.[5] For example, iodide dissociation to form a cationic five-coordinate intermediate was proposed to occur prior to reductive elimination of ethane from bipyPdMe$_3$I (bipy = bipyridine).[5a] The rate of elimination was enhanced by increasingly polar solvents and strongly retarded by the addition of iodide. As discussed above, carbon–carbon reductive elimination from **1** was significantly inhibited by the presence of added iodide.

In summary, the competitive production of ethane and methyl iodide by thermolysis of dppePtMe$_3$I (**1**) has allowed us to compare two pathways leading to, respectively, alkyl–alkyl and alkyl–halide bond formation. Results of our experiments involving addition of iodide to the reaction are consistent with a mechanism wherein both products are formed via a common cationic five-coordinate intermediate, **A**, produced by dissociation of iodide from **1**. Reductive elimination of ethane from **A** rivals nucleophilic attack by iodide on **A** to generate methyl iodide. Carbon–carbon bond formation was shown to be thermodynamically favored. However, the greater concentrations of methyl iodide/**2** over ethane/**3** at early reaction times in the absence of added iodide indicate that the carbon–iodide bond formation is the kinetically favored pathway. We are in the process of developing kinetic treatments of our data so as to access the activation parameters for pathways leading to both products and fully define the energetics of this dppePtMe$_3$I system. Additional mechanistic studies and attempts to observe the intermediate are underway.

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(6) While actually a *pseudoequilibrium*, the term *equilibrium* is used because the rate of conversion to **3** is slow enough that the concentrations of **1** and **2** are effectively equilibrium concentrations.

(7) Solid-state data are also in agreement with the carbon–carbon coupling being the enthalpically favored pathway. $\Delta H°$ for the solid-state reaction was found by DSC to be exothermic (−69.2 ± 0.2 kJ/mol). From ^{1}H NMR examination of the solid residues remaining after pyrolyses, ethane and methyl iodide were lost in a ratio of 82%/18%. TGA data (6.8 ± 2% weight loss) are consistent with this ratio. If we estimate that the solution and solid-state enthalpies of the C–I coupling reaction are similar, then $\Delta H°$ for the C–C coupling reaction can be approximated at −99 kJ/mol.

(8) Intermediates **A** and **B** may be solvated species.

(9) (a) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511. (b) Kubota, M.; Kiefer, G. W.; Ishikawa, R. M.; Bencala, K. E. *Inorg. Chim. Acta* **1973**, *7*, 195. (c) Thompson, W. H.; Sears, C. T., Jr. *Inorg. Chem.* **1977**, *16*, 764. (d) Burgess, J.; Hacker, M. J.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1974**, *72*, 121. (e) Ugo, R.; Pasini, A.; Fusi, A.; Cenini, S. *J. Am. Chem. Soc.* **1972**, *94*, 7364. (f) Puddephatt, R. J.; Scott, J. D. *Organometallics* **1985**, *4*, 1221. (g) Crespo, M; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (h) Aye, K. T.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518. (i) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182.

(10) At early reaction times with high iodide concentrations, **2** and MeI are the only observed products. Thus under these condiditons, k_3 can be neglected, and the following rate expression is derived using the steady-state approximation with respect to the intermediate in the scheme: $-d[\mathbf{1}]/dt = (k_1k_2[\mathbf{1}] - k_{-1}k_{-2}[\mathbf{2}][MeI])/(k_{-1} + k_2)$.

(11)) [NaI] was varied from 0.17 to 0.30 M at 79 °C. [NaI] was varied from 0.060 to 0.27 M at 89 °C, where equilibrium was consistently reached at 28 min.

(12) (a) Murphy, M. A.; Smith, B. L.; Torrence, G. P.; Aguito, A. *Inorg. Chim. Acta* **1985**, *101*, L47. (b) Hickey, C. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1609. (c) deWaal, D. J. A.; Gerber, T. I. A.; Louw, W. J. *Inorg. Chem.* **1982**, *21*, 1259. (d) Forster, D. *J. Am. Chem. Soc.* **1975**, 97, 951.