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Five-Coordinate Intermediates in Carbon–Carbon Reductive Elimination Reactions from Pt(IV)

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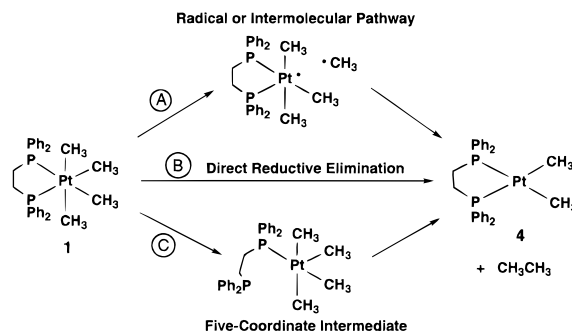*University of Washington, Seattle, Washington 98195-1700*

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Reductive elimination is a fundamental organometallic reaction and often serves as the critical product release step in homogeneously catalyzed organic reactions and metal-mediated stoichiometric transformations.[1] Although numerous studies of the mechanisms of C–C and C–H reductive elimination reactions have been carried out, it remains a challenge to predict whether such reactions will occur directly or require ancillary ligand loss or even ligand association prior to the reductive coupling.[1–7] A better understanding of the preferences for these different pathways is vital to current efforts toward rational catalyst design.

In virtually all studies of reductive elimination reactions which form alkyl C–C and C–H bonds from octahedral Pt(IV) complexes, mechanistic evidence has supported preliminary ligand loss and the generation of a five-coordinate intermediate prior to the elimination.[3–7] However, since all the compounds investigated have contained at least one ligand capable of facile dissociation (e.g. PR_3, halide), it is not clear how strong the preference is for coupling to occur from a five-coordinate intermediate. To explore the possibility of direct reductive elimination from a six-coordinate species, we have examined the thermal reactivity of the Pt(IV) complexes (dppe)PtMe$_4$ (**1**),[5] (dppbz)PtMe$_4$ (**2**),[8] and (dppe)PtMe$_3$-Et (**3**)[8] (dppe = $Ph_2PCH_2CH_2PPh_2$, dppbz = o-$Ph_2PC_6H_4PPh_2$). The chelate effect inhibits the formation of five-coordinate intermediates via phosphine dissociation. Complexes **1–3** are unusually robust for Pt(IV) phosphine alkyl compounds.[3,4] **1** has been reported to be indefinitely stable in solution at ambient temperature[5] and we have observed similar behavior for **2** and **3**. Temperatures in excess of 150 °C are required to induce the reductive elimination of ethane from **1**. Reported herein is an investigation of the mechanism of C–C reductive elimination from **1**, a Pt(IV) complex in which ligand dissociation should be substantially suppressed.

The thermolysis of **1** in solution required a period of days at 165 °C to obtain quantitative conversion to (dppe)PtMe$_2$ (**4**) and ethane.[9] The reaction exhibited first-order kinetic behavior (k_{obs}

(1) 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.

(2) For example: (a) Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8527. (b) Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209. (c) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492. (d) Milstein, D. *Acc. Chem. Res.* **1984**, *17*, 221.

(3) (a) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (b) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889 and references therein.

(4) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (b) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (In the absence of added L, 1–2% of C–C mechanisms of elimination from L$_2$PtMe$_4$ (L = MeNC, 2,6-Me$_2$-C$_6$H$_3$NC) may proceed without ligand dissociation. Significant decomposition of L under the reaction conditions hinders complete analysis of the data.)

(5) (a) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408. (b) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 4522.

(6) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961 (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (c) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (d) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156.

(7) There is support for direct reductive elimination in the coupling of *aryl* groups from Pt(IV): Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

(8) See Supporting Information for the synthesis, purification, and characterization of **2**, *fac*-**3**, and *mer*-**3**.

(9) See Supporting Information for safety precautions.

Scheme 1

= 4.2 ± 0.1 × 10^{-6} s^{-1} in benzene-d_6; k_{obs} = 3.2 ± 0.1 × 10^{-6} s^{-1} in THF-d_8). Activation parameters of $\Delta H^\ddagger$ = 43 ± 2 kcal/mol and $\Delta S^\ddagger$ = 15 ± 4 eu. were calculated using rate constants measured in benzene-d_6 over a temperature range of 165–205 °C.[10] To examine the possibility of an intermolecular mechanism for reductive elimination, a crossover study was performed in which an equimolar mixture of **1** and (dppe)Pt(CD$_3$)$_4$ (**1**-d_{12}) in benzene-d_6 was heated at 165 °C for slightly more than one half-life (50 h). Analysis by mass spectrometry revealed that the gaseous products consisted of CH$_3$CH$_3$ and CD$_3$CD$_3$ (<4% CH$_3$-CD$_3$). No scrambling of deuterium within the unreacted Pt(IV) species was observed. The Pt(II) products, however, were shown to be a mixture of **4**, **4**-d_3, and **4**-d_6 by ^{31}P{^{1}H} NMR spectroscopy.[11] That this scrambling occurs after the reductive elimination was confirmed by a separate experiment in which the thermolysis of a mixture of **4** and **4**-d_6 in benzene-d_6 at 165 °C for 12 h generated a significant amount of **4**-d_3. Exchange of alkyl groups among d^8 M(II) (M = Pt, Pd) complexes has been reported.[12]

The results of the crossover experiment are inconsistent with C–C reductive elimination proceeding by an intermolecular mechanism (pathway A in Scheme 1). It is considerably more difficult to distinguish between the possible intramolecular mechanisms of direct reductive elimination (pathway B) and predissociation of one end of the phosphine chelate[13] followed by reductive elimination from a five-coordinate species (pathway C). These are kinetically indistinguishable and the measured activation parameters are compatible with either. However, strong support for phosphine dissociation (pathway C) is provided by thermolysis of (dppbz)PtMe$_4$ (**2**).[8] With a benzene backbone, dppbz is a more rigid diphosphine chelate than dppe and is expected to have a smaller propensity for chelate opening.[14,15] Complex **2** was heated at 165 °C in THF-d_8 and after 300 h had

(10) Eyring and kinetic plots provided in Supporting Information.

(11) ^{31}P{^{1}H} NMR (C$_6$D$_6$): **4** (δ 47.35, J_{Pt-P} = 1779 Hz); **4**-d_6 (δ 47.49, J_{Pt-P} = 1769 Hz); **4**-d_3 (δ 47.42, J_{Pt-P} = 1774 Hz). The signals were not baseline separated and integration was not feasible.

(12) Exchange of methyl, aryl, and halide ligands between d^8 M(II) centers: Casado, A. L.; Casares, J. A.; Espinet, P. *Organometallics* **1997**, *16*, 5730 and references therein.

(13) An initial opening of a chelate ring has been proposed in the mechanisms of some substitution and oxidative addition reactions. (a) Basallote, M. G.; Durán, J.; Fernández-Trujillo, M. J.; González, G.; Máñez, M. A.; Martínez, M. *Inorg. Chem.* **1998**, *37*, 1623 and references therein. (b) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yetson, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260. (c) Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, *10*, 2209 and references therein. (d) Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664. (e) Landgrafe, C.; Sheldrick, W. S.; Südfeld, M. *Eur. J. Inorg. Chem.* **1998**, 407.

(14) (a) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205. (b) Sweigart, D. *Inorg. Chim. Acta* **1974**, 317.

(15) The bite angles for dppe and dppbz are similar (85° and 83°, respectively). Dierkes, P.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519.

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Scheme 2
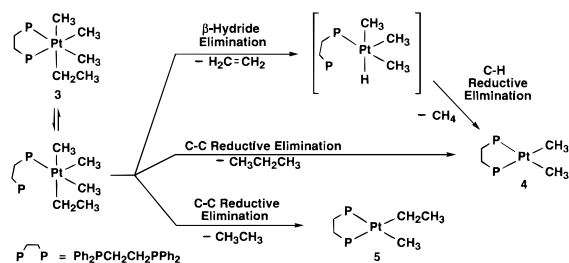
proceeded to only 4% conversion.[16] For comparison, 4% conversion of **1** (a first-order process) would require only ca. 3.5 h under the same conditions. Thus, replacement of dppe with the more rigid chelate dppbz significantly inhibits the rate of ethane elimination.

Predissociation of the dppe phosphine linkage from Pt(IV) was shown to be kinetically competent in the Pt(IV) C−C reductive elimination reaction by examination of the thermal behavior of the trimethylethyl analogue, (dppe)PtMe$_3$Et (**3**). This compound provides the potential for β-hydride elimination to compete with or even eclipse C−C reductive elimination under thermolysis conditions.[17] As β-hydride elimination is known to require an open coordination site at the metal center,[1] the observation of such reactivity for **3** would imply that phosphine dissociation is occurring on the time scale of the reaction or faster.

Complex **3** (as a nonequilibrium mixture of *fac* and *mer* isomers) was prepared by the reaction of EtMgBr and (dppe)-PtMe$_3$I in toluene and isolated in low yield after extensive purification procedures.[8] Pt−C bond cleavage processes were not observed until **3** was heated above 100 °C in benzene-d_6. Such thermal stability is unusual for a Pt(IV) ethyl complex, and is undoubtedly related to the absence of an easily accessible open coordination site at the metal.[17] When heated to 165 °C in benzene-d_6, **3** undergoes reaction to form the organic products ethylene, methane, propane and ethane, and the Pt(II) products (dppe)PtMe$_2$ (**4**) and (dppe)PtMeEt (**5**). The disappearance of **3** is a first-order process with $k_{obs} = (1.2 \pm 0.1) \times 10^{-4}$ s^{-1} at 165 °C. The yields of **4** and **5** are 91% and 4%, respectively.[18] The organic products were identified by ^{1}H NMR and GC/MS and the ratio of ethylene to propane to ethane was 75:18:7 (GC analysis).

The mechanism that most reasonably accounts for the observed organic and Pt(II) products from thermolysis of **3** is depicted in Scheme 2. Preliminary dissociation of a phosphine chelate arm is followed by competitive β-hydride elimination and C−C reductive elimination from the five-coordinate intermediate. The β-hydride elimination path leads to ethylene and (dppe)PtMe$_3$H. This Pt(IV) alkyl hydride would be expected to undergo rapid reductive elimination of methane at 165 °C and so should not be observed. The C−C reductive elimination pathways proceed to ethane and propane. The majority of **3** proceeds via β-hydride elimination and propane reductive elimination as evidenced by the high yield of (dppe)PtMe$_2$ (**4**) and the significant production of ethylene and propane. The minor ethane reductive elimination pathway gener-

ates the Pt(II) ethylmethyl complex (**5**). Such a Pt(II) ethyl complex may also undergo β-hydride elimination to generate ethylene.[19] However, as 95% of the Pt was accounted for, the vast majority of the ethylene results from β-hydride elimination from the Pt(IV) species **3** rather than the Pt(II) complex **5**.

Additional support for phosphine dissociation from (dppe)Pt tetraalkyl species at high temperatures is the observation of isomerization to an equilibrium mixture of *fac*-**3** and *mer*-**3** during the reaction at 165 °C. At 100 °C, isomerization is complete within 4 h and occurs without further reaction to generate Pt(II) complexes. The *mer* isomer is favored ($K_{eq} = 6.3$ at 100 °C). Isomerization of Pt(IV) octahedral complexes is most commonly proposed to occur via fluxional five-coordinate intermediates.[6c,20,21]

In summary, despite the strong chelate effect of dppe, complex **1** appears to undergo reductive elimination by a mechanism that involves ligand dissociation and C−C coupling from a five-coordinate intermediate (Scheme 1, pathway C). The observation of isomerization and β-hydride elimination for the (dppe)Pt(IV) ethyl complex **3** establishes the kinetic viability of dppe chelate arm opening at Pt(IV). That the C−C reductive elimination from **1** is occurring via the five-coordinate chelate opened species is supported by the dramatic rate reduction observed when dppe is replaced by the more rigid chelating ligand dppbz.

Thus, there are as yet no definitive examples of C−C reductive elimination of alkyl groups from Pt(IV) that undergo direct coupling from the six-coordinate species. This is a critical aspect to consider in catalyst development, as an open site should be accessible from a six-coordinate Pt(IV) complex to promote C−C reductive elimination. In addition, due to the presence of an open coordination site, β-hydride elimination is likely to be a significant competing pathway for alkyl groups undergoing C−C coupling in such systems. Finally, based on the principle of microscopic reversibility, C−C oxidative addition to square planar Pt(II) should require preliminary ligand dissociation and addition of the C−C bond to a "formally" three-coordinate Pt(II) species.[22] Such reactivity has been documented for C−H activation reactions at Pt(II) centers.[23−25]

Studies to further investigate the importance of five-coordinate intermediates in C−C and C−H reductive elimination from d^6 octahedral complexes are underway in our laboratory. The use of both different metals and ligand sets may change the energy barriers associated with the strong five-coordinate preference.

Supporting Information Available: Synthesis and characterization of **2** and **3**; kinetic plots for the thermolysis of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Thermolyses of **2** were carried out in the presence of 2% cross-linked polyvinylpyridine (PVP, an acid scavenger).[3a] In the absence of PVP, greater initial reactivity was observed with the amount dependent on sample (after 100 h, 9−17% conversion). With continued heating, thermolyses without PVP distinctly slowed (from 100 to 500 h, only 5−13% conversion). A trace Lewis acid impurity in **2** (consumed over time or scavenged by PVP) is suspected. The addition of PVP had no effect on the thermolysis rate of **1**.

(17) (PMe$_2$Ph)$_2$Pt(Me)(Et)$_2$I undergoes competitive β-hydride elimination and C−C reductive elimination at 33 °C. Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613.

(18) (a) Yields were measured by integration against an internal standard in the ^{1}H NMR spectrum. The remaining 5% may be accounted for by some decomposition of **5** to intractable Pt(0).[19] (b) Small amounts of **1** (2−5%) were present in the samples of **3**. However, only 15% of **1** had reacted after the thermolysis of **3** was complete (12 h), so the contribution was negligible.

(19) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, C. D.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805 and references therein.

(20) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1973**, *12*, 362. (b) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548.

(21) Five-coordinate intermediates have also been proposed in the isomerization of octahedral Ir(III) complexes. Wehman-Ooyevaar, I. C. M.; Drenth, W.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1993**, *32*, 3347.

(22) van der Boom, M. E.; Kraatz, H.-B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873.

(23) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.

(24) Direct oxidative addition of C−H bonds to square planar (dmpe)Pt-(Me)X has been proposed. However, a mechanism involving preliminary opening of the phosphine chelate could not be eliminated. Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493.

(25) (a) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (c) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379. (d) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713.