Communication

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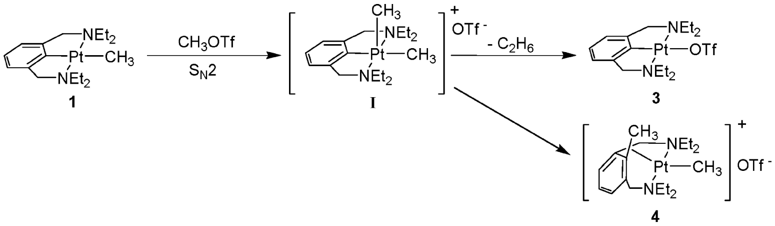

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Mechanistic Study of Competitive sp^3-sp^3 and sp^2-sp^3 Carbon−Carbon Reductive Elimination from a Platinum (IV) Center and the Isolation of a C−C Agostic Complex

Brian L. Madison, Summer B. Thyme, Sarra Keene, and B. Scott Williams*

The Joint Science Department of The Claremont Colleges, Scripps, Pitzer, and Claremont McKenna College,
W. M. Keck Science Center, 925 North Mills Avenue, Claremont, California 91711

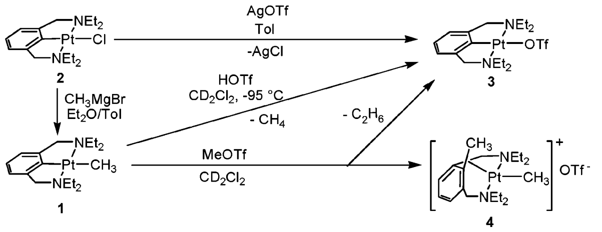
Received August 25, 2006; E-mail: williams@jsd.claremont.edu

The formation and cleavage of C−H and C−C bonds by metal complexes is presently an area that stimulates great interest because these fundamental reaction types possess numerous current and potential applications, yet our understanding of them remains limited. C−H bond activation, particularly of alkanes, is a challenging reaction, yet C−C bond cleavage, especially of "unactivated" carbon−carbon bonds, is considered to be even more difficult.[1−4] One reason for this is thought to be the high energy of the C−C σ-complex that is a suspected intermediate in C−C coupling. Herein we describe the isolation and characterization of an agostic[5] species that can be considered an analog to a true C−C σ-complex. In addition, we report a surprising competition between two carbon−carbon bond-forming processes that proceed at similar rates: a methyl−methyl coupling and a methyl−aryl coupling, with the latter analogous to those reported by Milstein and co-workers[3,6] and van Koten and co-workers.[7] This is of interest because there are very few cases where sp^2 and sp^3 reductive eliminations can be directly compared. It is believed that sp^2 couplings are much faster,[5b,8] yet there is but one computational[9] and one experimental[10] study in which relative rate constants have been determined. The faster rate of reductive elimination involving sp^2 centers has been ascribed to the higher energy required to reorient the more directional sp^3 hybrid orbitals[6] and the fact that sp^2 coupling can proceed via a more facile 1,2-shift followed by dissociation,[11] an option unavailable to sp^3−sp^3 coupling reactions

Platinum complexes of tridentate "pincer" ligands of the form [ECE], where E is a neutral, 2-electron donor and C is an aryl carbon, have a rich and long-established chemistry.[12] In particular, the Pt complexes of the form 2,6-bis (dialkyl-aminomethyl)-phenylplatinum(halide) ([NCN]PtX, Scheme 1) have been widely studied, and their derivatives are used in a wide range of catalytic reactions and as sensors.[13] However, despite nearly three decades of research involving these complexes, no simple alkyl derivatives, [NCN]PtR, have been synthesized. We have prepared the first such example, a $[NCN]PtCH_3$ complex, **1**, from the corresponding chloride, **2**, and methyl magnesium bromide in toluene in good yield (74%, Scheme 1). Other alkylating reagents resulted either in no reaction or decomposition.[14] The ^1H NMR spectrum of **1** is similar to that of **2**, but the $Pt-CH_3$ singlet (δ 0.50 ppm, $^2J_{PtH} =$ 47 Hz) indicates that the methyl group is bound to platinum *trans* to a very strongly donating ligand (the aryl ring).[15,16] The methylene protons of a given ethyl group are diastereotopic, indicating that both nitrogen "arms" remain bound to platinum.

Addition of trifluoromethanesulfonic acid (triflic acid, HOTf) to **1** at −95 °C in CD_2Cl_2 resulted in instantaneous formation of methane and a new platinum complex, **3** (Scheme 1).[17] This same complex can be generated by addition of silver triflate to the chloride complex, **2**.

Scheme 1



Addition of an excess of methyl triflate to **1** in methylene chloride-d_2 at −40 °C resulted in the formation of **3**, ethane,[18] and a new complex, **4** (Scheme 1). The NMR spectrum of the new complex, **4**, exhibits a number of unusual features. The benzylic methylene protons appear as AB doublets, and two distinct triplets in the alkyl region represent the methyl groups of the NEt_2 moieties. These data demonstrate the reduction of molecular symmetry from C_{2v} to C_s. Finally, a $Pt-CH_3$ group is observed in the product and the $^2J_{PtH}$ coupling constant of 92 Hz indicates that the methyl group is *trans* to a very weak ligand.

Compound **4** could be described as either an arenium complex (**4″**, Chart 1), analogous to that reported by van Koten et al.,[19] or as a C−C agostic complex (**4′**), as per the compounds reported by Milstein et al.[3,20]

The spectral characteristics of **4** indicate an agostic complex (**4′**). First, the increase of the $^2J_{PtH}$ coupling of the Pt-bound methyl group from 47 (**1**) to 92 Hz (**4**) suggests that the ligand *trans* to methyl in **4** is exceptionally weak. Second, the increase in the $^{195}Pt-^{13}CH_3$ coupling from 636 (**1**) to 982 Hz (**4**) indicates a ligand *trans* to methyl roughly as donating as a triflate group in **3**.[17] Third, in the complex reported by van Koten et al., the signal assigned to the aryl methyl group exhibits discernible $^{195}Pt-^1H$ satellites, whereas that of **4** does not. Finally, the $^{195}Pt-^{13}C$ coupling constants to the aryl (14 Hz) and methyl (56 Hz) carbons of the agostic moiety indicate very little interaction.

The reaction of **1** and CH_3OTf at −40 °C in CD_2Cl_2 to form **3**, ethane, and **4** was monitored by ^1H NMR spectroscopy and was found to be first order in both **1** and CH_3OTf, with a second-order rate constant of $k = 2.05(15) \times 10^{-4}\ M^{-1}\ s^{-1}$.[21] The reaction produced **3** and **4** in an 88:12 ± 2% ratio, which was consistent throughout the reaction. Similar product ratios were obtained with CH_3I and $[(CH_3)_3O][BF_4]$. In none of these cases could any intermediates be detected by ^1H NMR spectroscopy, even at low temperature (−90 to −40 °C).

Ethane and **3** presumably form via the nucleophilic attack by **1** on CH_3OTf to generate a five-coordinate intermediate $[NCN]Pt(CH_3)_2^+$ (**I**) from which reductive elimination of ethane occurs.[22,23] Three possible mechanisms were considered to explain the formation of **4** from **1** and CH_3OTf (Scheme 2). While nucleophilic attack by platinum on methyl triflate to form an intermediate, **I**, on the

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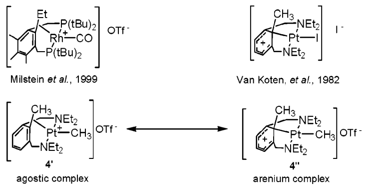
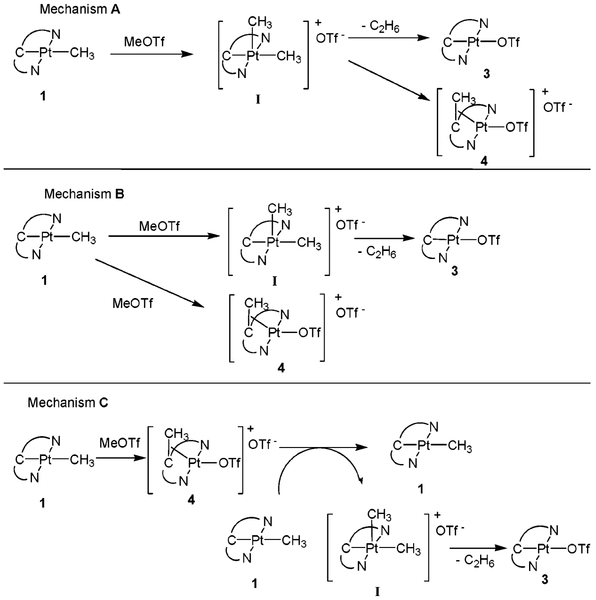
Chart 1



Scheme 2



pathway to both sp^3−sp^3 and sp^2−sp^3 coupling seemed plausible (mechanism **A**), that would imply that methyl−methyl and methyl−aryl coupling from **I** were competitive. Because both reactions are irreversible at room temperature, the activation barriers and rate constants must be very similar. Because of these surprising implications, a second mechanism (mechanism **B**) was considered in which direct nucleophilic attack by the aryl ligand at methyl triflate leads directly to **4** without the intermediacy of **I**.

A third possibility (mechanism **C**) is that **4** is formed as the sole initial product from **1** and MeOTf and that **3** is formed by nucleophilic attack of **1** upon the aryl-bound methyl group of **4** to generate **I**, which would lead to **3** and ethane. Mechanism **C** was ruled out because **1** and **4** were shown not to react with one another in an independent experiment. To distinguish between **A** and **B**, **1** was allowed to react with CD_3OTf (−40 °C, CD_2Cl_2). If mechanism **B** was followed, all of the Ar−Me in the resultant **4-d_3** would be Ar−CD_3. In mechanism **A**, since **I-d_3** is five-coordinate, its fluxionality would be expected to scramble the deuterium label between the Ar−Me and Pt−Me positions.[23,24] When CD_3OTf was added to **1**, 80% of the deuterium in **4-d_3** appears in the Ar−Me position and 20% of the deuterium appears in **4-d_3** in the Pt−Me position, which is inconsistent with mechanism **B**, indicating that the five-coordinate cation **I** lies on the reaction coordinate to both products.[25]

A common intermediate to form **3** and **4** is consistent with the fact that the ratio of these reactions is the same for the CH_3OTf and CH_3I reactions. The ratio of **4**:**3** is, therefore, the ratio of the rates of aryl−methyl and methyl−methyl reductive elimination *from the same complex*. The 7:1 ratio observed at −40 °C is in keeping with the 2.4:1 ratio observed by Ozerov et al. for the related Ar−Ar versus Ar−CH_3 coupling from Pt at +40 °C.[10] These results support the oft-cited but poorly documented more facile reductive elimination of sp^2 versus sp^3 carbons, but show that the preference for sp^2 coupling is such that the reaction rates can be competitive.

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Supporting Information Available: Experimental procedures and characterization are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (c) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (d) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.
(2) Brayshaw, S. K.; Sceats, E. L.; Green, J. C.; Weller, A. S. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6921.
(3) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870 and references therein.
(4) Siegbahn, P. E. M.; Blomberg, M. R. A. *J. Am. Chem. Soc.* **1992**, *114*, 10548.
(5) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6909.
(6) Gandelman, M.; Shimon, L. J.; Milstein, D. *Chem.*−*Eur. J.* **2003**, *9*, 4295.
(7) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250.
(8) (a) Suzuki, A.; Brown, H. C. *Organic Synthesis Via Boranes: Suzuki Coupling*; Aldrich Chemical Co.: Milwaukee, WI, 2003; Vol. 3. (b) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z. Q. *Chem. Commun.* **1996**, 1.
(9) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Organometallics* **2005**, *24*, 715.
(10) Gatard, S.; Celenligil-Cetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808.
(11) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431.
(12) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.
(13) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.
(14) See Supporting Information.
(15) Pregosin, P. S.; Kunz, R. W. *NMR 16: Basic Principles and Progress, Grundlagen und Fortschrifte*; Diehl, P., Fluck, E., Eds.; Springer-Verlag: New York, 1979.
(16) The ^{13}C NMR spectrum exhibits one-bond Pt−C couplings also consistent with mutually strong *trans* donors ($^1J_{PtMe}$ = 624 Hz, $^1J_{PtAr}$ = 636 Hz).
(17) The ^{195}Pt−^{13}C coupling constant of the aryl carbon in **3** is 1014 Hz, indicative of the very weak triflate *trans* to the aryl group.
(18) When CD_3OTf was used, the resulting ethane was found to be ethane-d_3 by GC/MS.
(19) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233.
(20) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798 and references therein.
(21) See Supporting Information for details.
(22) An alternate mechanism in which the Pt-bound CH_3 group itself acts as the nucleophile cannot be conclusively ruled out, though it lacks the precedent of an oxidative addition-type pathway (ref 23 and references therein).
(23) (a) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423. (b) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442.
(24) Excepting, of course, the fraction of the CD_3OTf that became ethane-d_3 (the latter of which was observed by NMR and GC/MS).
(25) These percentages were observed by both ^{1}H and ^{2}H NMR spectroscopies.

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