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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

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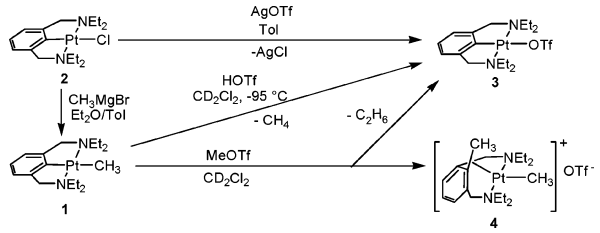
The formation and cleavage of C−H and C−C bonds by metal complexes is presently an area that stimulates great interest because these fundamental reaction types possess numerous current and potential applications, yet our understanding of them remains limited. C−H bond activation, particularly of alkanes, 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 ^{1}H 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−^{1}H 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 ^{1}H 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 ^{1}H 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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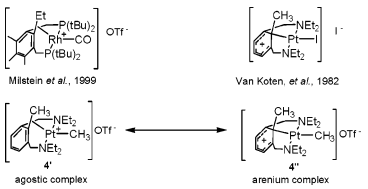
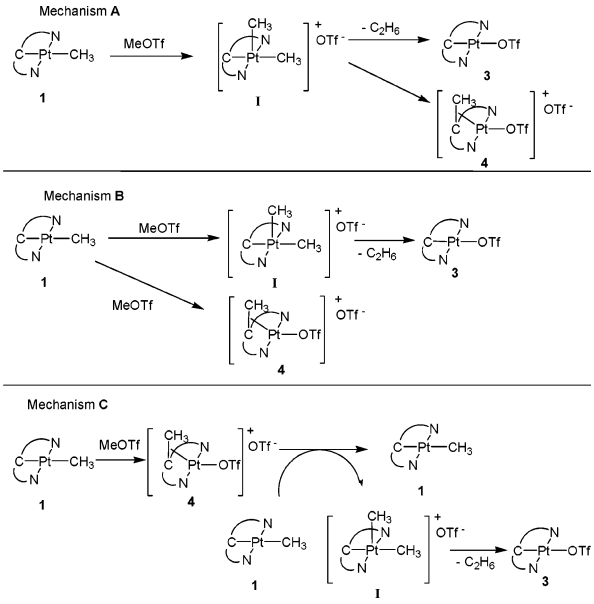
Chart 1



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.

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(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.
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(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).
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(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 ^1H and ^2H NMR spectroscopies.

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