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 α-complex that is a suspected intermediate in C–C coupling. Herein we describe the isolation and characterization of an agostic5 species that can be considered an analog to a true C–C α-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-workers3,6 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,5,6,8 yet there is but one computational9 and one experimental10 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 orbitals6 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$_3$ signal (δ 0.50 ppm, $J_{PtH}$ = 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$_2$Cl$_2$ 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.

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 methyl protons appear as AB doublets, and two distinct triplets in the aliphatic region represent the methyl groups of the NE$_3$ moieties. These data demonstrate the reduction of molecular symmetry from C$_2$ to C$_1$. Finally, a Pt–CH$_3$ group is observed in the product and the $J_{PtH}$ 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.20

First, the increase of the $J_{PtH}$ 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–13C coupling constant of 636 (1) to 982 Hz (4) indicates a ligand trans to methyl roughly as donating as a trflate 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–H satellites, whereas that of 4 does not. Finally, the $^{195}$Pt–19F coupling constants to the 14 (1 Hz) and methyl (56 Hz) carbons of the agostic moiety indicate very little interaction.

The reaction of 1 and CH$_3$OTf at −40 °C in CD$_2$Cl$_2$ 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$_3$OTf, 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$_3$I and [CH$_3$I][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$_3$OTf to generate a five-coordinate intermediate [NCN]Pt/(CH$_3$)$_2$I (1) from which reductive elimination of ethane occurs.22,23 Three possible mechanisms were considered to explain the formation of 4 from 1 and CH$_3$OTf (Scheme 2). While nucleophilic attack by platinum on methyl triflate to form an intermediate, 1, on the...
pathway to both sp³→sp³ and sp²→sp³ coupling seemed plausible (mechanism A), that would imply that methyl—methyl and methyl—aryl coupling from 1 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 1.

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 1, 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 CD₃OTf (−40 °C, CD₂Cl₂). If mechanism B was followed, all of the Ar—Me in the resultant 4-d₃ would be Ar—CD₃. In mechanism A, since 1-d₃ is five-coordinate, its fluxionality would be expected to scramble the deuterium label between the Ar—Me and Pt—Me positions. When CD₃OTf was added to 1, 80% of the deuterium in 4-d₃ appears in the Ar—Me position and 20% of the deuterium appears in 4-d₃ 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.

A common intermediate to form 3 and 4 is consistent with the fact that the ratio of these reactions is the same for the CH₃OTf and CH₃I 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—CH₃ coupling from Pt at +40 °C. These results support the oft-cited but poorly documented more facile reductive elimination of sp² versus sp³ carbons, but show that the preference for sp² 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


(9) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. Organometallics 2005, 24, 715.


(14) See Supporting Information.


(16) The 13C NMR spectrum exhibits one-bond Pt—C coupling constants of the aryl carbons in 3 is 1014 Hz, indicative of the very weak triflate trans to the aryl group.

(17) When CD₃OTf was used, the resulting ethane was found to be ethane-d₄ via the Internet at http://pubs.acs.org.


(20) See Supporting Information for details.

(21) An alternate mechanism in which the Pt-bound CH₃ 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) Excepting, of course, the fraction of the CD₃OTf that became ethane-d₄ (the latter of which was observed by NMR and GC/MS).

(24) These percentages were observed by both ¹H and ²H NMR spectroscopies.

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