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Electrophilic Halogenation−Reductive Elimination Chemistry of Organopalladium and -Platinum Complexes

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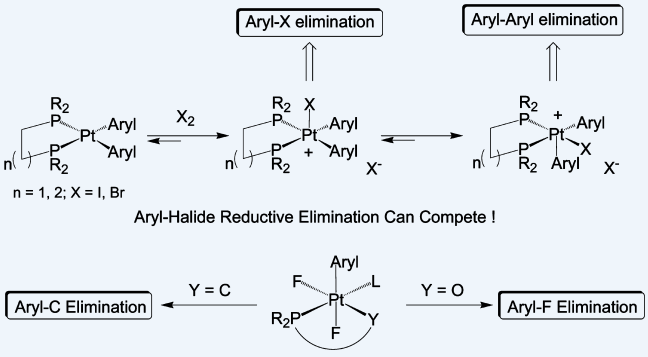
Supporting Information

CONSPECTUS: Transition metal-catalyzed organic transformations often reveal competing reaction pathways. Determining the factors that control the selectivity of such reactions is of extreme importance for the design of reliable synthetic protocols. Herein, we present the account of our studies over the past decade aimed at understanding the selectivity of reductive elimination chemistry of organotransition metal complexes under electrophilic halogenation conditions. Much of our effort has focused on finding the conditions for selective formation of carbon (aryl)−halogen bonds in the presence of competing C−C reductive elimination alternatives. In most cases, the latter was the thermodynamically preferred pathway; however, we found that the reactions could be diverted toward the formation of aryl−iodine and aryl−bromine bonds under kinetic conditions. Of particular importance was to maintain the complex geometry that prohibits C−C elimination while allowing for the elimination of carbon−halogen bonds. This was achieved by employing sterically rigid diphosphine ligands which prevented isomerization within a series of Pt(IV) complexes. It was also important to understand that the neutral M(IV) products often observed or isolated in the oxidative addition reactions are not necessarily the intermediates in the reductive elimination chemistry as it generally takes place from unsaturated species formed en route to relatively stable M(IV) complexes.



While aryl−halide reductive elimination for heavier halogens can be competitive with aryl−aryl coupling in diaryl M(IV) complexes, the latter reaction always prevails over aryl−fluoride bond formation. Even when one of the aryl groups is a part of a rigid cyclometalated ligand C−C coupling is still the dominant reaction pathway. However, when one of the aryl groups is replaced with a phenolate donor aryl−F bond formation becomes preferred over C−O bond elimination.

During our studies, other interesting reactions have been discovered. For example, the fluorination of the C(sp^3)−H bond can be very selective and compete favorably with C−C coupling. Also, in electron-poor complexes, metal oxidation can have higher energy than oxidation of the coordinated iodo ligand resulting in I−F elimination instead of the formation of aryl-I bond. Overall, electrophilic fluorination can lead to often very selective elimination reactions giving new C−C, C−I, C−F, or I−F bonds, with this selectivity dependent on the metal center, supporting ligands, complex geometry, and electrophilic fluorine source.

Together with the many reports on the halogenation of organometallic compounds that appeared in recent years, our results contribute to understanding the requirements for selective transformations under electrophilic conditions and design of new synthetic methods for making organohalogen compounds.

I. INTRODUCTION AND BACKGROUND

Considering the scarcity of the naturally occurring organofluorine compounds on one hand, and their omnipresence in drugs,[1] agrochemicals,[2] and advanced materials[3] on the other, there is a great interest in the development of new synthetic methodologies allowing the introduction of fluorine into organic molecules.[4] A myriad of potent fluorinating reagents have been prepared and used in fluorination of many classes of organic compounds.[5−7] Yet, by the beginning of the new century, it became evident that some important fluorination reactions could not be performed by simply picking the right fluorinating reagent. In particular, the selective introduction of fluorine into nonactivated aromatic rings remained a significant challenge.[8] Isolated efforts to expand the scope of fluorinating reagents to include late transition metal complexes, particularly palladium complexes, did not provide viable alternative fluorination methods despite their efficiency in the formation of C−C, C−N, and C−O bonds.[9] By the early 2000s, there were no experimental data on the formation of the C−F bond assisted by transition metal complexes, and all attempts to observe aryl−fluoride reductive elimination reaction have been unsuccessful.[10] Furthermore, very few late organotransition metal fluoro complexes were convincingly characterized, as the synthetic methods toward such complexes were insufficiently

Received: September 2, 2014
Published: January 20, 2015

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238−247

developed,[11−13] in particular with regard to metals in a high oxidation state.[14,15]

Although likely the most important, aryl−F elimination can be considered a particular case of a more general elimination of aryl−halogen bonds and can be influenced by the same factors. Surprisingly, only two literature reports described aryl−halide elimination from isolated transition metal complexes.[16,17] While the feasibility of such reaction was established, more synthetic and mechanistic information was necessary to make predictions regarding the most suitable systems for the formation of carbon−halogen bonds. It was important to perform detailed studies of aryl−halide reductive elimination reactions with regard to the nature of the metal and ligands, halogenation mechanism, complex geometry, solvent effect, and so forth. Deciphering the influence of these parameters could guide the development of strategies toward making new C−X bonds including in fluoroarenes. This Account presents our studies on the mechanism of electrophilic halogenation−reductive elimination transformations. Particular emphasis is placed on understanding the requirements for formation of carbon−halogen bonds usually in competition with other reductive elimination reactions.

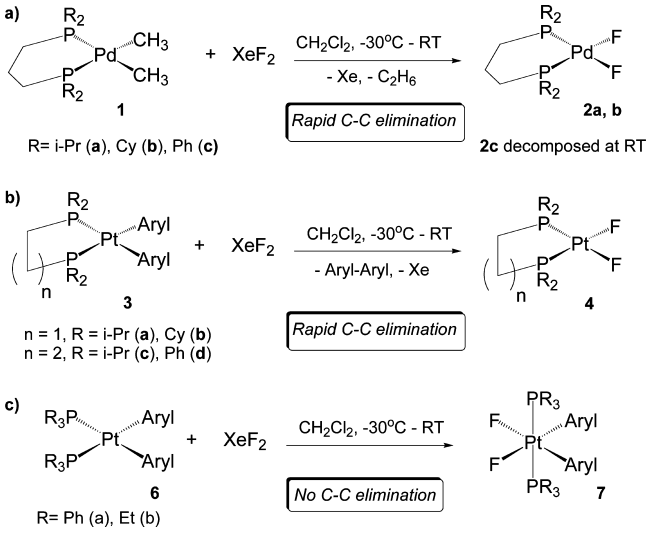
II. ELECTROPHILIC FLUORINATION−REDUCTIVE ELIMINATION CONCEPT

Because of the perceived inability of the low oxidation state aryl fluoro complexes to undergo the C−F reductive elimination reaction,[18] we hypothesized that transition metals in higher oxidation states would be more prone to undergo such a reaction. As common nucleophilic ligand exchange methods often led to undesired side reactions,[19] we decided to explore the possibility of making organotransition metal fluoro complexes via an electrophilic fluorination pathway which provides one or two fluoro ligands via a two-electron oxidation mechanism.[20] With two other groups already present in the metal coordination sphere, this oxidative addition reactions can trigger several competing reductive elimination pathways, with C−F elimination being only one of them.[21,22]

Due to their relevance to the formation of new carbon−carbon and carbon−heteroatom bonds, organopalladium(II) complexes were initially selected to study the reductive elimination from the anticipated organopalladium(IV) fluoro complexes. As a test reaction, several dimethyl Pd(II) complexes with various phosphine donors were prepared and treated with XeF_2, a solid commercially available source of electrophilic fluorine.[23] Interestingly, the first reaction between dipppPd$(CH_3)_2$ (**1a**) and XeF_2 gave a colorless solution that exhibited a complex ^{19}F NMR signal (and equally complex ^{31}P signal) at ca. −252 ppm.[24] The compound responsible for the signal turned out to be dipppPdF_2 (**2a**, Scheme 1a), the product of an extremely facile C−C elimination reaction and the first fully characterized difluoropalladium complex. In retrospect, using the chelating electron rich dippp ligand was important, as monodentate phosphine ligands or less electron-rich dppp analogues do not stabilize the difluoro palladium complex and give instead several decomposition products.

The heavier Pt analogues (**3**), which are expected to form more stable Pt(IV) intermediates, undergo similar transformations: only the C−C elimination products, biaryl and (P−P)PtF_2 complexes (**4**), are obtained upon reaction with XeF_2 (Scheme 1b). The difluoro platinum(II) complexes show a broader stability scope than their Pd analogues. Arylphosphine complexes ((dppp)PtF_2, **4d**) and complexes with

Scheme 1



monodentate phosphine ligands ($(Ph_3P)_2PtF_2$, **5**) can be isolated and fully characterized. Complex **5** must be prepared via the nucleophilic exchange reaction between $(Ph_3P)_2PtI_2$ and AgF because the reaction of the diaryl complexes $(R_3P)_2PtAr_2$ (**6**) with XeF_2 gives the Pt(IV) oxidative addition products **7** where the phosphines occupy mutually trans-positions (Scheme 1c).[25]

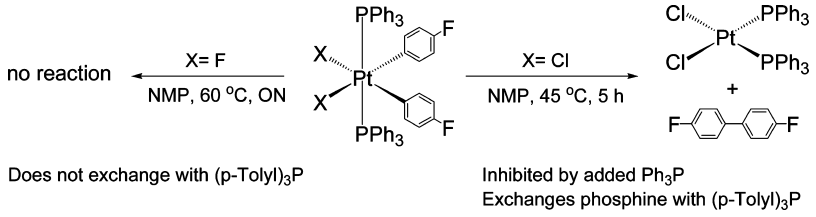
Although these results suggest that Pt(IV) fluoro complexes can be intermediates in C−C coupling reactions (Scheme 1b), complexes **7** are unexpectedly stable toward C−C reductive elimination even upon prolonged heating at 60 °C. This stability can be attributed to the necessity of generating an open coordination site, via ligand dissociation, prior to the reductive elimination step,[26] with the reaction being extremely slow for the difluoro Pt(IV) systems. In the analogous dichloro complexes, the dissociation of the phosphine ligand is significantly more facile, making these complexes prone to the aryl−aryl coupling under very mild conditions (Scheme 2).[25]

While the dependence of C−C elimination on a phosphine dissociation step is generally unsurprising,[27] such elimination under mild conditions in the reaction between complexes **3** and XeF_2 was unexpected. Diphosphine chelates are presumably more stable toward the dissociation and less likely to generate an open site required for C−C elimination. A possible factor in a higher reactivity of the proposed Pt(IV) chelates in comparison to **7** could be that the latter has an optimal geometry for an octahedral complex bearing pairs of aryl, phosphine and halide ligands. In chelates, one of the phosphines faces aryl ligand in the trans-position which can facilitate its dissociation. However, this hypothesis was invalid in the electrophilic fluorination of **7**, as complexes (P∼P)-$PtAr_2F_2$ (**8**) were independently prepared via the initial bromination of **3** with Br_2 followed by the exchange with AgF (Scheme 3),[28] and found to be sufficiently stable at room temperature.

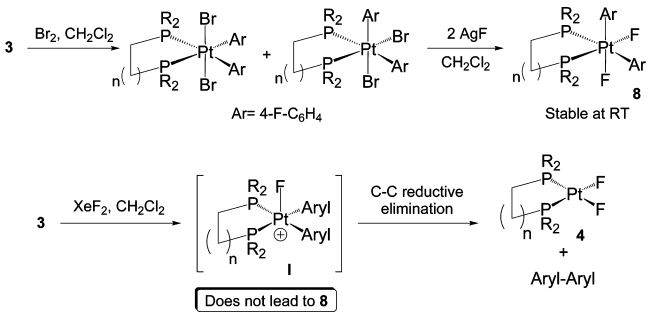
An alternative explanation of the facile aryl−aryl coupling under electrophilic fluorination conditions is that this reaction occurs *prior* to the formation of the neutral **8**. As the reactions likely proceed via the initial formation of a cationic unsaturated Pt(IV) intermediate (**I**, Scheme 3), the formation of the C−C bond from such intermediate or, more likely, its isomer can be

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238−247

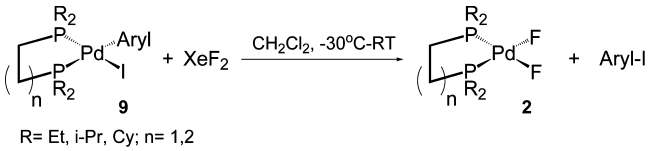
Scheme 2



Scheme 3



Scheme 4

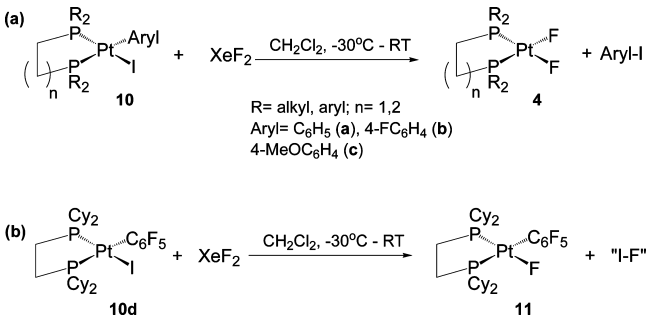


conceived. The potential role of such intermediates in determining the outcome of the reductive elimination step will be discussed below.

The electrophilic fluorination−reductive elimination chemistry can be successfully extended to aryl halide metal complexes. Clean elimination of an aryl−iodide product and formation of complexes **2** was observed in the reactions between (P∼P)Pd(Aryl)I (**9**) and XeF_2 (Scheme 4).[29] The reactions are very general and even the strongly bound C_6F_5 group in **9** (aryl = C_6F_5) undergoes smooth reductive elimination to give C_6F_5−I. Replacement of XeF_2 with *N*-fluoro-2,4,6-collidinium tetrafluoroborate as the fluorine source gives similar results, but about 10% of the corresponding aryl−fluorides is also observed in addition to the C−I reductive elimination products. Thus, the presence of a noncoordinating BF_4^- counterion creates a competition between C−I and C−F bond formation.

Similarly, complexes **4** and free aryl−I form instantaneously upon the addition of XeF_2 to solutions of the corresponding (P∼P)Pt(Aryl)I complexes (**10**, Scheme 5a). However, the reaction between (P∼P)Pt(C_6F_5)I (**10d**) and XeF_2 does not produce C_6F_5−I. Instead the fluoro complex (P∼P)Pt(C_6F_5)F (**11**) is formed in a quantitative yield (Scheme 5b, only the dcpe complex is shown).[30] The reaction stoichiometry suggests the formation of I−F, a transient compound highly unstable at room temperature. Evidence in support of this notion was obtained by addition of $Ph_2C{=}NNH_2$ to the reaction mixture at −78 °C. Hydrazones react with I−F to give Ph_2CF_2 along with N_2 and HI,[31] which was verified independently by preparing an authentic sample of iodine monofluoride.[32] Further studies have shown that the formation of the

Scheme 5



platinum(II) aryl fluoride and IF is not limited to the pentafluorophenyl derivative. 2,4,6-Trifluoro- and 2,6-difluorophenyl complexes (**10e**,**f**) also give these products, albeit in competition with the expected aryl−I reductive elimination reaction. It is essential to have both ortho positions occupied by fluorine substituents as 2,4-difluorophenyl Pt(II) complex (**10g**) gives exclusively the products of C−I reductive elimination (Scheme 6).[33]

Density functional theory (DFT) analysis of the reaction between **10** and XeF_2 showed that, with **10d**, the reactions at the metal center and coordinated iodide have essentially the same activation barriers (Figure 1). With the less-electron poor aryl ligands, including the partially fluorinated aryls, the metal center becomes more susceptible to the reaction with XeF_2.

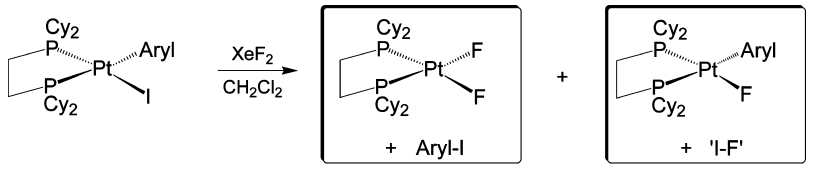
The observed rapid oxidation of the coordinated iodide ligand by an electrophilic fluorine source suggests that this reaction cannot be discounted in aryl−iodide reductive elimination. The initially formed IF molecule can also serve as the oxidant for Pt(II) aryl complexes. For example, IF, either freshly prepared or formed in the reaction between **10d** and XeF_2, immediately converts (dcpe)Pt(4-FC_6H_4)F to 4-FC_6H_4I and **4** (Scheme 7).

III. ELECTROPHILIC HALOGENATION−REDUCTIVE ELIMINATION OF CARBON−HALOGEN BONDS

The formation of the aryl−iodine bonds from the Pd or Pt complexes in the reaction with XeF_2 was an encouraging step in understanding the mechanism of this and similar C−X elimination reactions. Very few examples of an aryl−halogen coupling were reported in the literature,[16,17,34] and it was important to learn about the factors that lead to formation of a carbon−halogen bond in the presence of other groups capable of the reductive elimination. In M(II) phosphine complexes, the XeF_2-triggered oxidative addition-reductive elimination sequence proceeds extremely rapidly thus not allowing characterization of reaction intermediates and obtaining kinetic data. In contrast, oxidative addition of heavy dihalogen molecules to the diaryl complexes of Pt(II) is easier to monitor often revealing distinct Pt(IV) products prior to the reductive

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238−247

Scheme 6



	Complex	Products ratio	
Aryl=	C_6F_5 (**10d**)	0	100
	2,4,6-$F_3C_6H_2$ (**10e**)	42	58
	2,6-$F_2C_6H_3$ (**10f**)	70	30
	2,4-$F_2C_6H_3$ (**10g**)	100	0

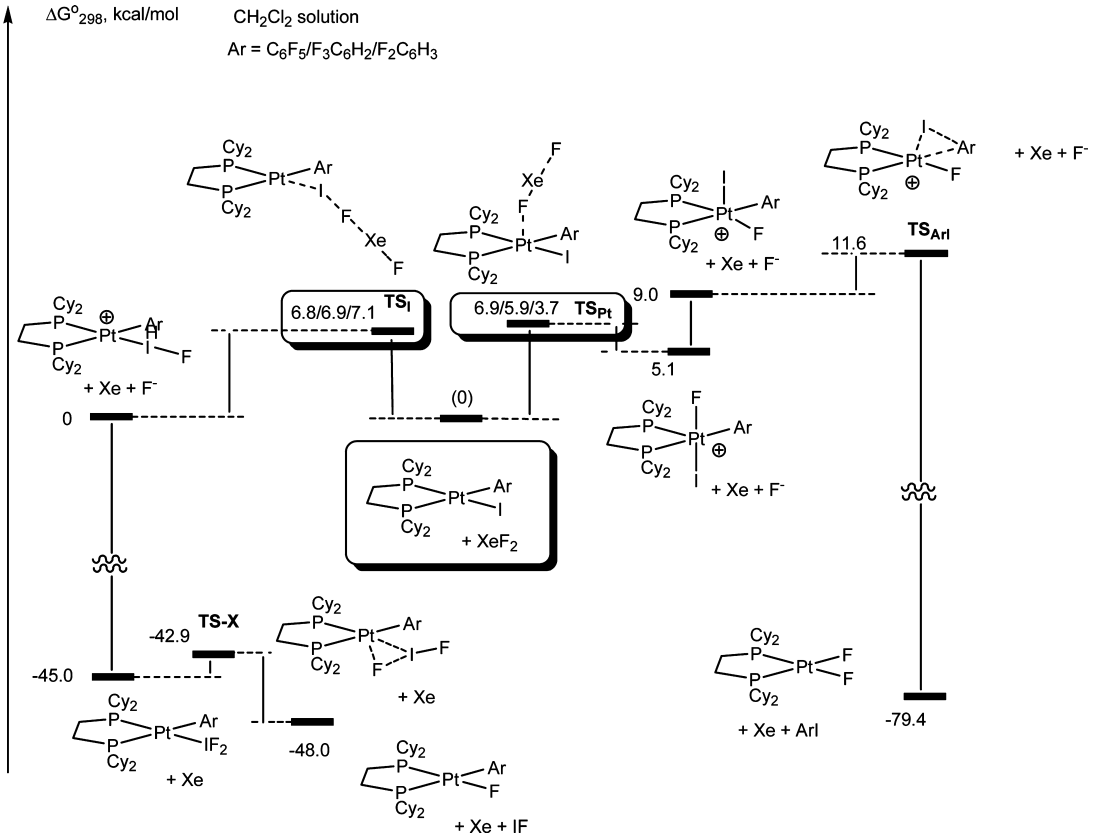
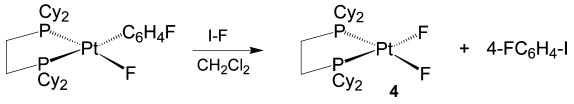
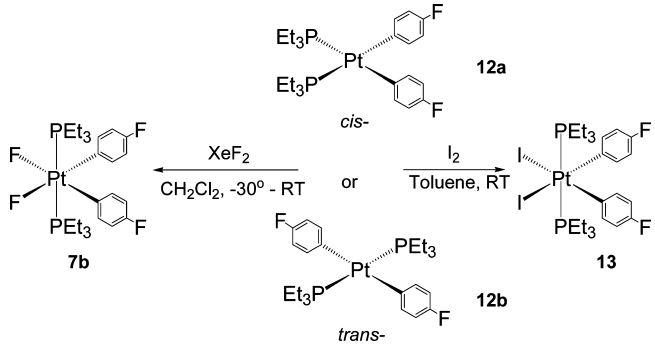


Figure 1. Calculated energy profile for the competing aryl–I and I–F elimination from **10d–f**.

Scheme 7



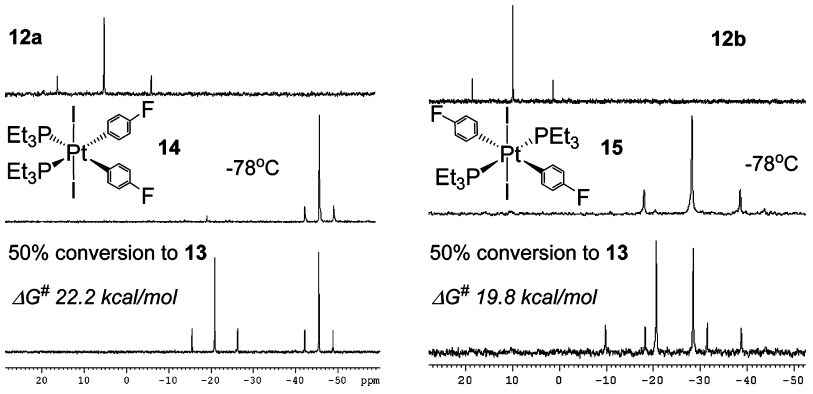
Scheme 8



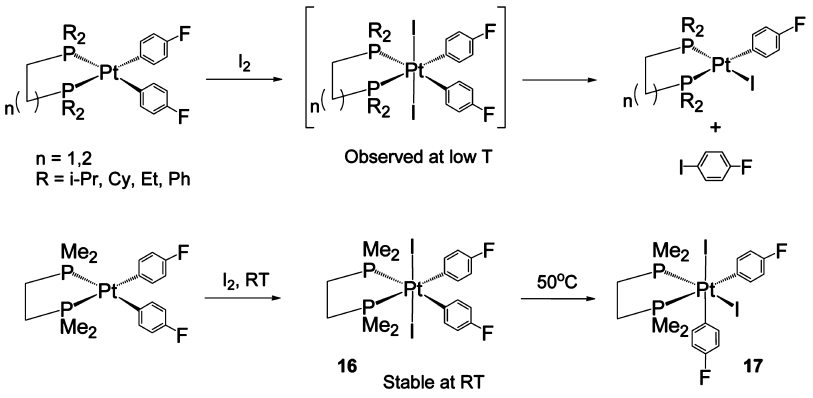
elimination step. For example, both *cis*- and *trans*-$(Et_3P)_2Pt(Ar)_2$ (**12**) react with XeF_2 or I_2, giving the *trans*-$(Et_3P)_2Pt(Ar)_2X_2$ (X = F, **7b**, or I, **13**) as the only product (Scheme 8).[35] However, while the reaction with XeF_2 is too fast even at −78 °C to provide relevant mechanistic details, the addition of I_2 can be followed up at this temperature by $^{31}P\{^1H\}$ NMR spectroscopy. The initially formed trans oxidative addition products **14** and **15** were characterized in solution, and their isomerization to **13** studied kinetically (Scheme 9).[36,37] Solvent plays an important role in this reaction; the isomerization of **14** in toluene is about 20 times faster than that in acetone and has a large negative activation entropy value of ca. −40 e.u. Together with additional experiments, these data suggest that

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238–247

Scheme 9



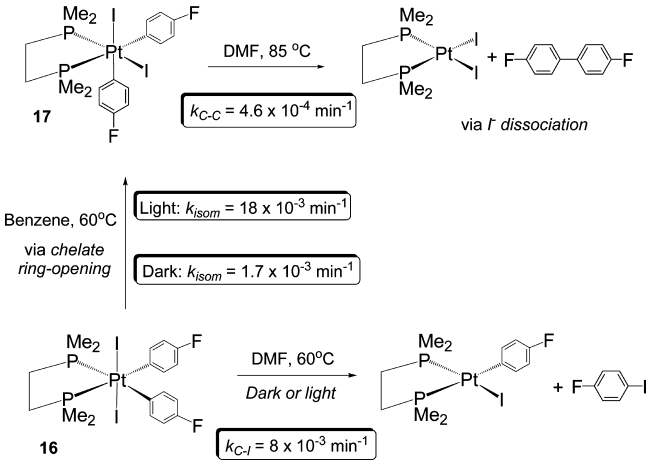
Scheme 10



partial (an ion-pair mechanism) or complete iodide dissociation precedes the isomerization, with coordinating solvent stabilizing the unsaturated intermediate.

As with XeF_2, complexes **3** bearing *bidentate* diphosphine ligands form significantly less stable adducts with I_2 but the elimination of aryl iodides rather than diaryls takes place in this case (Scheme 10).[38] At low temperatures, signals attributed to unstable Pt(IV) intermediates could be observed in the ^{31}P and ^{1}H NMR spectra. With the sterically unencumbered (dmpe)-$PtAr_2$ complex (**3e**), oxidative addition products were isolated at room temperature (Scheme 10) and this system was chosen to study the electrophilic iodination−reductive elimination chemistry. As expected, the kinetic product of this iodination reaction is the *trans*-(dmpe)$Pt(Ar)_2I_2$, **16**, which upon warming in benzene above 50 °C is quantitatively converted to the thermodynamically favorable *cis*-(dmpe)$Pt(Ar)_2I_2$, **17**.[39] Less expectedly, in the dark, the isomerization reaction at the same temperature is considerably slower and significant amounts of the aryl iodide reductive elimination products are observed. In more polar DMF, in the dark, the aryl−I elimination is the dominant reaction path (ca. 90%, Scheme 11). This reductive elimination reaction only takes place from **16**, as **17** gives exclusively C−C bond formation at a much higher temperature (>80 °C). In the latter reaction, clear inhibition by the external I^- is observed. In contrast, aryl iodide reductive elimination from **16** is insensitive to the presence of I^- or light conditions. DFT calculations suggest that while aryl−I elimination proceeds via an ion-pair type transition state (Figure 2a), the competing **16**-to-**17** isomerization requires ligand predissociation with light-assisted diphosphine chelate opening being the most favorable pathway. By using the rigid dmpbz ligand, this

Scheme 11



ring-opening and consequent isomerization reaction can be completely shut down leaving aryl−I reductive elimination the only available reactivity path for the *trans*-Pt(IV) complex **19** (Scheme 12a). Remarkably, this path is significantly less thermodynamically favorable (~26 kcal/mol) than the C−C elimination, demonstrating that the reactions are under kinetic control.

Thus, maintaining the halide ligand in the axial position and the aryl group in the equatorial position appears to be crucial for the aryl−halide elimination. This requirement was later verified in the reductive elimination of aryl−Br from Pt(IV) (Scheme 12b).

DOI: 10.1021/ar500325x
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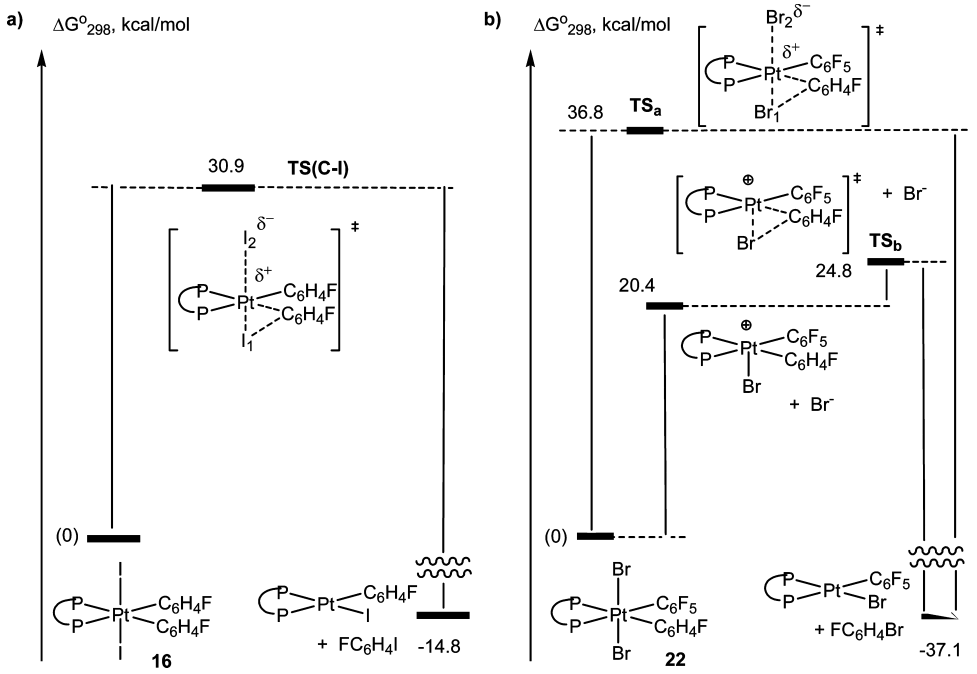
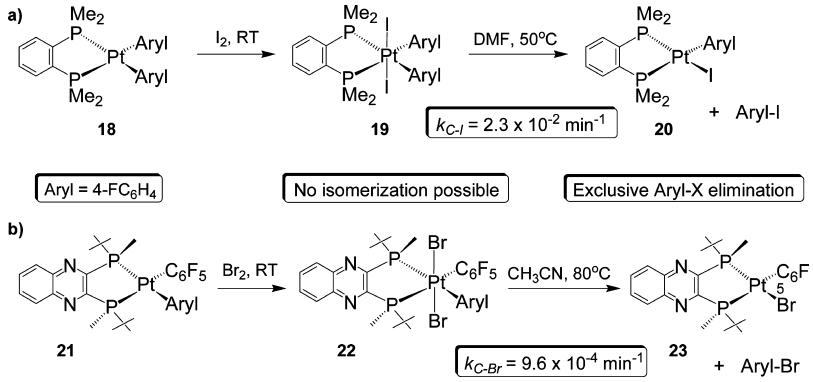


Figure 2. Calculated energy profiles and transition states for the 4-FC_6H_4–I (a) and 4-FC_6H_4–Br (b) reductive elimination from Pt(IV) complexes.

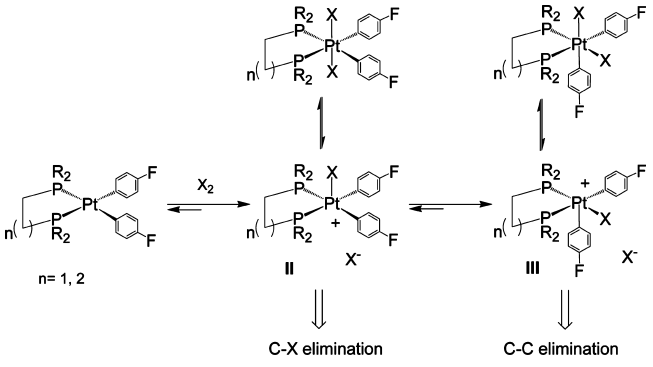
Scheme 12



Only the trans oxidative addition product **22** is obtained in the reaction between the electron-poor quinoxaline-based Pt(II) complex **21** and Br_2. Upon heating in acetonitrile, complex **22** undergoes the aryl–Br reductive elimination reaction giving bromo complex **23** and 4-FC_6H_4Br. Similar to **19**, the rigidity of ligand's backbone prevents the isomerization reaction and allows observation of aryl–Br reductive elimination under relatively mild conditions.[40] The reaction path involves dissociation of one of the bromo ligands giving cationic pentacoordinate Pt(IV) intermediate. Unlike in **16**, the activation barrier for concerted aryl–Br elimination from a hexacoordinate ion-pair type transition state was found to be prohibitively high in energy (Figure 2b). Another interesting point is that in very polar solvents, DMF or NMP, Br_2 reductive elimination from **22** takes place. This reaction proceeds as a microscopic reverse of the Br_2 oxidative addition to **21** via the same cationic Pt(IV) intermediate.

The above findings allowed us to draw the proposed mechanistic paths (Scheme 13) for the competing aryl–aryl and aryl–halide elimination reactions. The initially formed pentacoordinate Pt(IV) cation (**II**) can undergo aryl–halide reductive elimination. It can also be trapped by the halide ligand present in the system giving the kinetic trans-oxidative addition product. The isomerization to **III** can lead to the thermodynamic product having the halogen atoms in the mutual cis-position, with only aryl–aryl reductive elimination possible from the cation **III**.

Scheme 13

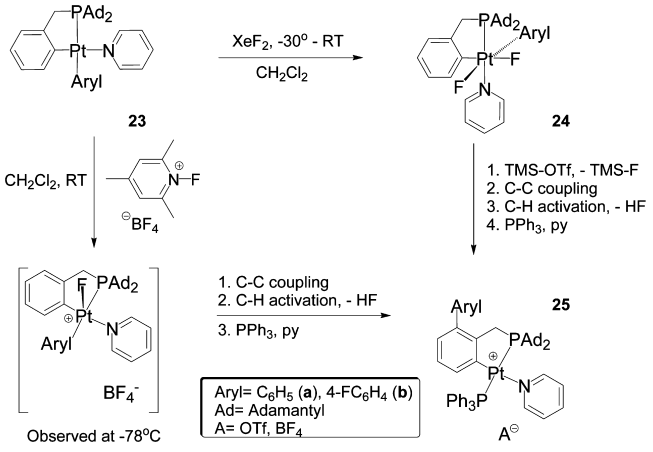


DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238–247

IV. ELECTROPHILIC FLUORINATION–REDUCTIVE ELIMINATION IN CYCLOMETALATED SYSTEMS

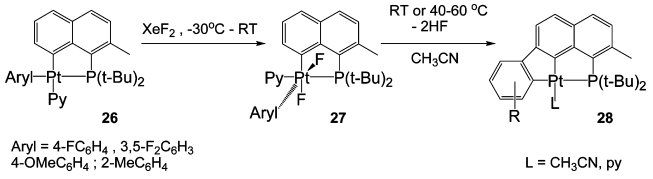
Although the aryl–iodide and aryl–bromide eliminations from M(IV) are highly competitive with the thermodynamically more favorable C–C elimination, this is not the case for the fluoro complexes. When a source of the electrophilic fluorine is used, the high barrier for C–F elimination from the cation **I** (Scheme 3) favors isomerization and consequent C–C elimination reactions. To slow down these two steps, a series of chelated Pt(II) analogues (**23**) was prepared by cyclometalation of the phosphine ligand with $(COD)PtCl_2$ followed by reaction with an aryl Grignard reagent. Unlike **3**, complexes **23** react with XeF_2, giving isolable and thermally stable Pt(IV) difluoro complexes (**24**, Scheme 14).[41] Yet, these complexes

Scheme 14



undergo exclusive C–C bond elimination upon heating or activation with a Lewis acid, suggesting that this reaction is preferable over the C–F bond elimination even in cyclometalated systems. A further increase in the rigidity of the chelate was attempted by using a naphthalene-based ligand system (Scheme 15), but here also formation of the C–C bond

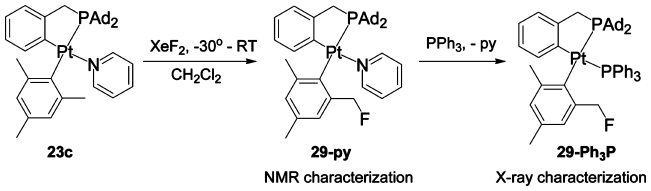
Scheme 15



was observed upon heating of the isolated Pt(IV) difluoro intermediates (**27**). The reactions proceeded further giving products (**28**) of an unprecedented aryl migration to the *β*-position of the naphthalene ring.[42]

Interestingly, with bulky mesityl as the aryl group (**23c**), the reaction with XeF_2 leads to the selective monofluorination of one of the ortho-methyl groups to give **29**, the first example of the C–H fluorination with a Pt complex (Scheme 16).[41,43] The X-ray structure of the *o*-tolyl Pt(IV) difluoro complex (**30**, Figure 3)[44] shows one of the fluoro ligands in proximity to the *o*-methyl group. It is conceivable that, with the two methyl groups in the mesityl ligand, fluorine-assisted C–H activation can occur. Alternatively, the C–H activation can take place in an unsaturated Pt(IV) intermediate. The formation of the C–F

Scheme 16



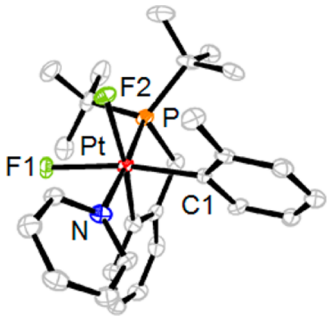
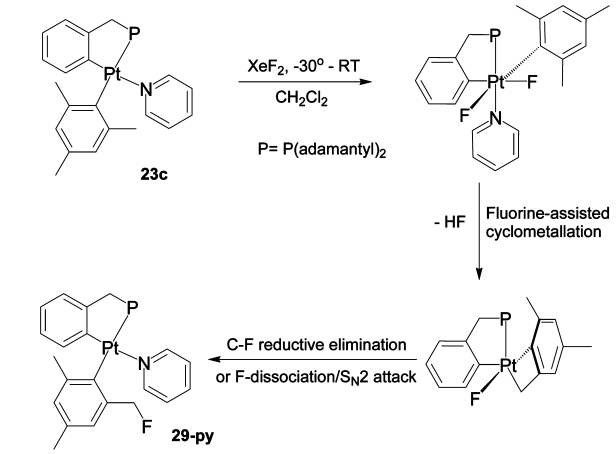


Figure 3. X-ray structure of the *o*-tolyl Pt(IV) difluoro complex **30**.

bond proceeds either via the concerted reductive elimination reaction or S_N2 attack at the benzylic carbon in the presumed strained platinacycle (Scheme 17). Recent studies on related

Scheme 17



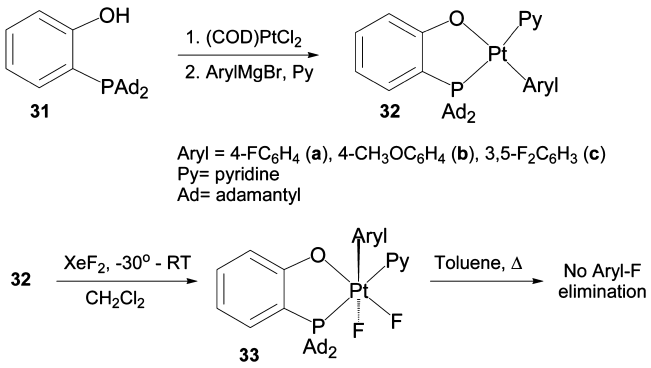
systems provided evidence for both pathways in $C(sp^3)$–F coupling.[45,46] No benzylic fluorination with **23c** takes place when N-fluoropyridinium derivatives are used as the source of the electrophilic fluorine. Instead, C–C reductive elimination products are formed, similar to what was observed with other aromatic ligands.

The above survey of various metal systems and reaction conditions suggests that, unlike other C–X reductive elimination reactions, the formation of an *aryl*–fluorine bond is not competitive with the more rapid elimination of a C–C bond even when one of the aryl groups is a part of a stable chelating ring. The analysis of limited literature examples of the aryl–fluorine reductive elimination reactions shows that they do not involve systems with alternative elimination pathways. For example, no formation of an *aryl*–F bond was observed by Sanford and co-workers in a very recently reported complex that simultaneously underwent alkyl–F, alkyl–N, and aryl–alkyl reductive elimination reactions.[47] Realizing this, we

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238–247

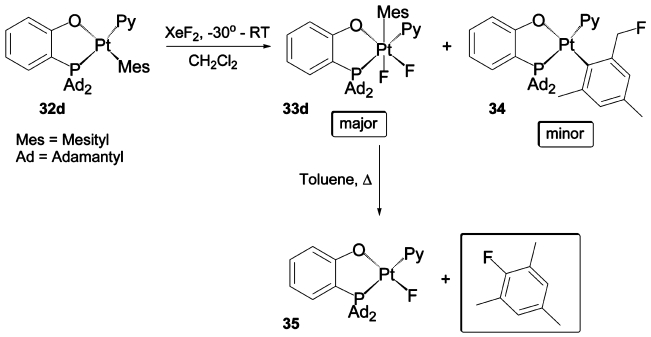
decided to study the competitive formation of the C−F and C−O bonds. As oxygen is the closest to fluorine both in size and electronegativity, the formation of the two bonds should be more competitive and can eventually be tilted toward the elimination of the C−F bond.[48,49] Toward this end, the phenol-based cyclometalated Pt(II) system (**32**, Scheme 18) was

Scheme 18



designed and tested in electrophilic fluorination reactions. Stable Pt(IV) difluoro complexes (**33**) are obtained upon the reaction with XeF_2, but heating or removal of one of the fluoro ligands with Lewis acid does not lead to the C−F elimination products in a mixture of compounds. Yet again, the reaction with the mesityl derivative proved to be pivotal for the observation of a new reactivity pattern in the phenolate-based platinum system. The reaction of complex **32d** with XeF_2 in CH_2Cl_2 gives the difluoro Pt(IV) complex **33d** as the major product along with several products of the benzylic C−H fluorination (**34**, Scheme 19). Solvent plays an important role

Scheme 19



in this reaction: in less polar chlorobenzene, **34** is obtained as a product of single C−H activation in about 1:1 ratio with **32d**, while in acetonitrile only **33d** is formed. Significantly, heating pure **33d** in toluene at 80 °C leads to selective conversion to the Pt(II) monofluoro complex **35** and free 1-fluoro-2,4,6-mesitylene which are products of aryl−fluorine reductive elimination (Scheme 18).[50] The reaction follows first-order kinetics with $\Delta G^{\#} \approx 24$ kcal/mol. Gagné and co-workers recently reported aryl−F bond formation in reactions between Pt(II) aryl complexes and Selectfluor, however the proposed Pt(IV) intermediates could not be isolated.[51] Interestingly, no fluorination of the C−H bonds takes place upon heating of **33d**, and this complex does not appear to be an intermediate in the benzylic fluorination which presumably proceeds from a catonic Pt(IV) intermediate en route to **33d**. The mechanisms of these reactions are presently under investigation. Overall, the conversion of **33d** to **35** and 1-fluoro-2,4,6-mesitylene establishes the feasibility of the selective aryl−F elimination from an M(IV) complex in the presence of other elimination alternatives and shows the way toward other competitive C−F reductive elimination reactions.

V. CONCLUSIONS

Electrophilic halogenation of organometallic Pd(II) and Pt(II) complexes creates reactive M(IV) products that can undergo reductive elimination. Although the reaction outcome depends on the nature of the halogen, metal, eliminating hydrocarbyl group and supporting ligands it is the geometry of the M(IV) complex that often plays a crucial role in determining the reductive elimination path as most of these reactions are kinetically controlled. In particular, aryl−halide coupling can compete favorably with thermodynamically preferred C−C elimination when the kinetic unsaturated intermediate cannot undergo isomerization because of steric constrains.

In the electrophilic fluorination, selective C−C, C−I, or I−F bond elimination can be achieved depending on the ligands and source of electrophilic fluorine. Aryl−fluoride elimination could not compete with these reactions; however, aryl−F elimination is preferred over aryl−O elimination in a closely related system. Finally, C(sp^3)−H benzylic fluorination is another viable path in electrophilic fluorination of Pt(II) aryl complexes that can be faster than aryl−aryl or aryl−F reductive elimination reactions.

While many research groups have become involved in the pursuit of making new carbon (aryl)−halogen bonds via metal assistance, there is still much work to do in this area. Given the importance of these compounds, there is no doubt that this pursuit will continue for many years. We hope that the results described in this Account contributed to understanding the reaction parameters that lead to selective formation of carbon−halogen bonds in a number of possible reductive elimination pathways. In turn, this understanding will contribute to the development of new synthetic methodologies toward halogenated aromatic compounds.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystal data for complex **30** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

Most of the research described in this Account has been supported by the US−Israel Binational Science Foundation.

Notes

The authors declare no competing financial interest.

Biography

Arkadi Vigalok received his M.Sc. degree from Kazan State University in 1992 and Ph.D. degree from the Weizmann Institute of Science (with Prof. David Milstein) in 1999. He then joined the group of Prof. Timothy Swager at MIT, as a Fulbright postdoctoral fellow, where he worked on metal-containing conducting polymers. In 2002, he joined the faculty of the School of Chemistry at Tel Aviv University where he is presently a professor of chemistry. His research interests include the

DOI: 10.1021/ar500325x
Acc. Chem. Res. 2015, 48, 238−247

formation of carbon−halogen bonds, particularly carbon−fluorine bonds, mediated by late transition metal complexes. He also has interests in supramolecular chemistry and organic synthesis in the aqueous media.

■ ACKNOWLEDGMENTS

I am indebted to the students who did all the experiments reported herein and whose names appear in the cited publications. I have also greatly benefited from the long-standing collaboration with Profs. Israel Goldberg (Tel Aviv University) and Andrei Vedernikov (University of Maryland) who are responsible for all the X-ray structures and DFT studies, respectively, reported in our work. I would also like to thank the reviewers for their helpful suggestions.

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