Inorganic Chemistry

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Strategy for Selective C_{sp2}–F and C_{sp2}–C_{sp2} Formations from Organoplatinum Complexes

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Cite This: *Inorg. Chem.* 2021, 60, 1016–1020 Read Online

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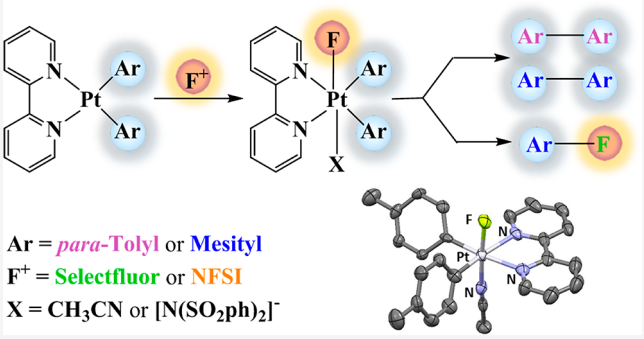
ABSTRACT: By changing the parameters of fluorination reaction of bisaryl-platinum(II) complexes, each possible competitive pathway of Ar–Ar and Ar–F formation can be selectively controlled. It was discovered that steric hindrance, type of fluorinating reagent, and temperature of reaction are determinants for Ar–F vs Ar–Ar bond formation pathway from bisaryl-fluoro-platinum(IV) complexes. The combination of bulky ligands such as mesityl with Selectfluor at RT leads to Ar–F bond formation in the presence of possible Ar–Ar formation.



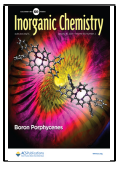
1. INTRODUCTION

The organofluorine compounds have been extensively used in the pharmaceutical industries, such as 29% of the top 200 Small Molecule Pharmaceuticals by Retail Sales in 2018[1] which have a C–F bond. Also, they have desirable properties for agrochemicals, materials,[2] and PET imaging.[3] Therefore, study on suitable synthetic pathways for carbon–fluorine bond formation and the effects of various parameters in this reaction is critical.[4] With few exceptions,[5] most catalytic aromatic fluorination reactions in recent decades involve Ar–F reductive elimination reaction from high-valent late transition metal-fluoro intermediate such as Pd,[6] Ni,[7] and Cu.[8]

On the other hand, Ar–F bond formation is one of the least kinetically competitive elimination reactions, and the Ar–F bond will not be formed in competition with the C–O,[9] C–X (X = Cl, Br, I),[10] alkyl–F,[11] or various C–C bond formation reactions.[12] Therefore, in the previously reported reactions, it was vital that the metal complex had none of these possible elimination pathways in parallel with C–F bond formation to have a successful fluorination reaction.

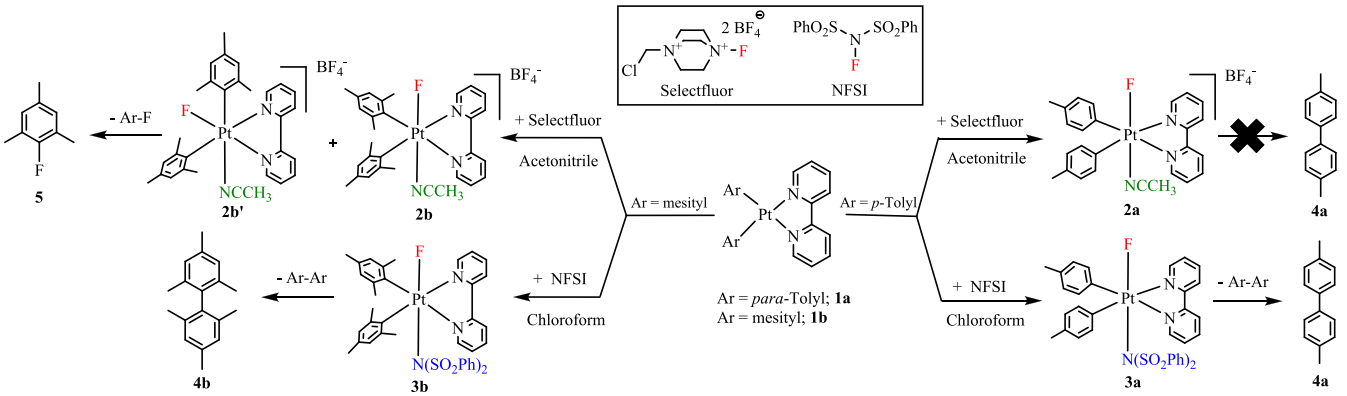
In general, investigation on platinum compounds as more inert analogues for similar palladium catalysts and study on effective parameters on kinetic, selectivity, and mechanism of reaction are common pathways for designing more effective catalysts. In this regard, there are only two platinum compounds reported for successful Ar–F bond formation. The first report was the Ar–F bond formation from monoaryl-platinum complex with a tridentate phosphine ligand by Gagne and co-workers[13] in which there is only one possible pathway for C–F bond formation without any other possible competitive pathways for the reductive elimination reaction. In the second report, Vigalok, Vedernikov, and co-workers[14] described the fluorination of monoaryl-platinum(II) complex with a very bulky anionic P^O chelating ligand to obtain bisfluoro-monoaryl-platinum(IV), in which the resulting six coordinate complex is not a usual suitable species for reductive elimination. Nevertheless, the Ar–F bond was formed in competition with C–O bond formation that could be favored by the steric bulk of the chelating ligand over their C–O elimination in that complex. Also, in the latter, the only suitable fluorinating source was XeF_2 as the strongest electrophilic fluorinating reagent (based on the reduction potential), and the similar result was not repeated by other milder reagents such as Selectfluor and N-fluoro-2,4,6-collidinium. However, XeF_2 is not a convenient reagent for usual experimental conditions. (Note: XeF_2 is a moisture-sensitive compound that has low vapor pressure[22] with nauseating odor and decomposes in contact with light.[23] It has limited lifetime in various common organic solvents and different type of vessels.[24] Also, it is a hazardous compound in a way that it is corrosive to exposed tissues and releases toxic compounds in contact with moisture (MSDS: xenon difluoride). So, all these limitations and precautions for using this compound even in lab scale make it an inappropriate candidate for usual reagent in common chemical transformation.)

Received: October 21, 2020
Published: January 5, 2021



https://dx.doi.org/10.1021/acs.inorgchem.0c03122
Inorg. Chem. 2021, 60, 1016–1020

Scheme 1. Reaction of [(bipy)Pt(Ar)$_2$], 1, with Electrophilic Fluorinating Reagents at RT



To study the Ar−F bond formation in more detail, we decided to study the reactivity of bisaryl-platinum(II) complexes with electrophilic fluorinating reagents to obtain bisaryl-fluoro-platinum(IV) complexes which are in a dilemma between Ar−Ar and Ar−F bond formation reaction and investigate the impact of various parameters such as the type and amount of fluorinating source, steric hindrance of aryl groups, time and temperature of reactions, on these two competitive pathways. Also, the milder electrophilic fluorinating reagents, NFSI (*N*-fluorobenzenesulfonimide) and Selectfluor (*N*-chloromethyl-*N*′-fluorotriethylenediammonium bis(tetrafluoroborate)) were chosen instead of XeF_2. Both of them do not attack glass vessels like most fluoride-containing reagents, and their use does not involve any special techniques or equipment in storing and handling. So, they have simpler reaction conditions and provide more suitable results for future practical fluorination transformations. However, in all our experiments, the fluorinating reagents were used under air, and dry solvents were not used.

2. RESULTS AND DISCUSSION

As represented in Scheme 1, the bis(*para*-Tolyl)platinum(II) complex [(bipy)Pt(4-CH_3−C_6H_4)$_2$], **1a**, was reacted with 1 equiv of Selectfluor in acetonitrile to generate the fluoro-Pt(IV) complex, **2a**. The signal of coordinated fluoro ligand appears at δ = −295.3 ppm with $^1J_{Pt-F}$ = 1592 Hz in ^{19}F NMR. The crystal **2a** was obtained by slow diffusion of *n*-hexane into its dichloromethane solution. The X-ray crystal structure **2a** (Figure 1) shows the platinum center is located in an almost perfect octahedral environment with coordinated acetonitrile solvent *trans* to fluoro ligand. The N(2)−Pt(1)−F(1) bond angle being 175.9° and the Pt(1)−F(1) bond length of 1.94 Å, is within the typical range of fluoro-Pt(IV) complexes.[14,15] This complex was stable at RT and did not have any tendency for either Ar−Ar or Ar−F bond formation even after about 1 month in solution and solid state. Also, by the reaction of **1a** with 2 equiv of Selectfluor, **2a** was stable after a week at RT. After heating at 80°C for 12 days, 4,4′-dimethylbiphenyl signals are observed in ≈35% yield (based on ^{1}H NMR). No 4-fluorotoluene was observed by GC-MS, ^{1}H NMR, or ^{19}F NMR, indicating that no Ar−F bond formation occurred (Figures S2−S6).

While the Selectfluor has a higher reduction potential,[16] it has a greater N−F bond dissociation energy than NFSI[17] does. In addition, the suitable solvents for the reactions with Selectfluor are limited to high polar solvents which have a high coordinating ability such as MeCN, DMF, and H_2O.[18]

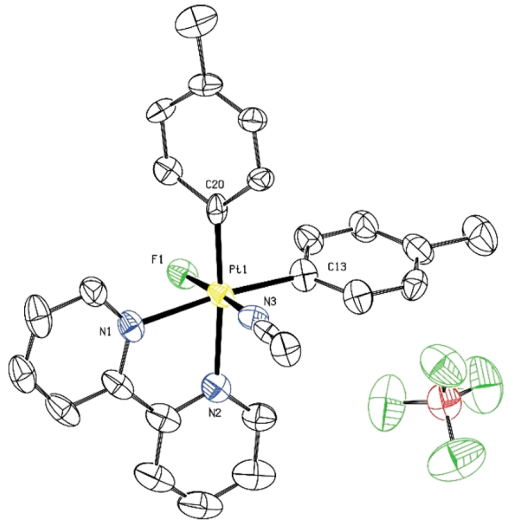


Figure 1. X-ray crystal structure of [(bipy)Pt(4-CH_3−C_6H_4)$_2$F(NCCH_3)]BF_4, **2a**. The H atoms were omitted for clarity.

However, the NFSI could be used in various organic solvents especially inert and noncoordinating solvents such as $CHCl_3$, CH_2Cl_2, and toluene.[19] Moreover, the NFSI contains a bulky anionic residue [dibenzenesulfonimide]$^-$ having a coordinating ability that could be another distinct parameter to have a different reactivity in comparison with Selectfluor.

To modify the rate and yield of the Ar−Ar bond formation, the fluorinating reagent was changed to NFSI. By the reaction of **1a** with 1 equiv of NFSI in chloroform, the biaryl product signals were observed with ≈35% yield (based on ^{1}H NMR) after about 1 month at RT. The signal of plausible resulted fluoro-Pt(IV), **3a**, was observed as a singlet at δ = −263.7 ppm with $^1J_{Pt-F}$ = 1111 Hz in ^{19}F NMR. Increasing the temperature of this reaction to 60 °C was successful in acquiring even more yield (>95%) of this product. Also, the amount of biaryl formation increased to 45% by the reaction of **1a** with 2 equiv of NFSI in 2 weeks (Figures S7−S10). Thus, it is obvious that NFSI has a higher reactivity to induce the Ar−Ar formation, but none of them was successful to form the Ar−F bond from **1a**.

It is worth noting that the reaction of XeF_2 with a complex similar to **1a** in dichloromethane, as a usual solvent for reactions with XeF_2, did not lead to any Ar−Ar formation, and only [Pt(bipy)F(Ar)$_2$Cl] was formed and decomposed to unknown products after a day at RT (Figure S11). XeF_2 has an

https://dx.doi.org/10.1021/acs.inorgchem.0c03122
Inorg. Chem. 2021, 60, 1016−1020

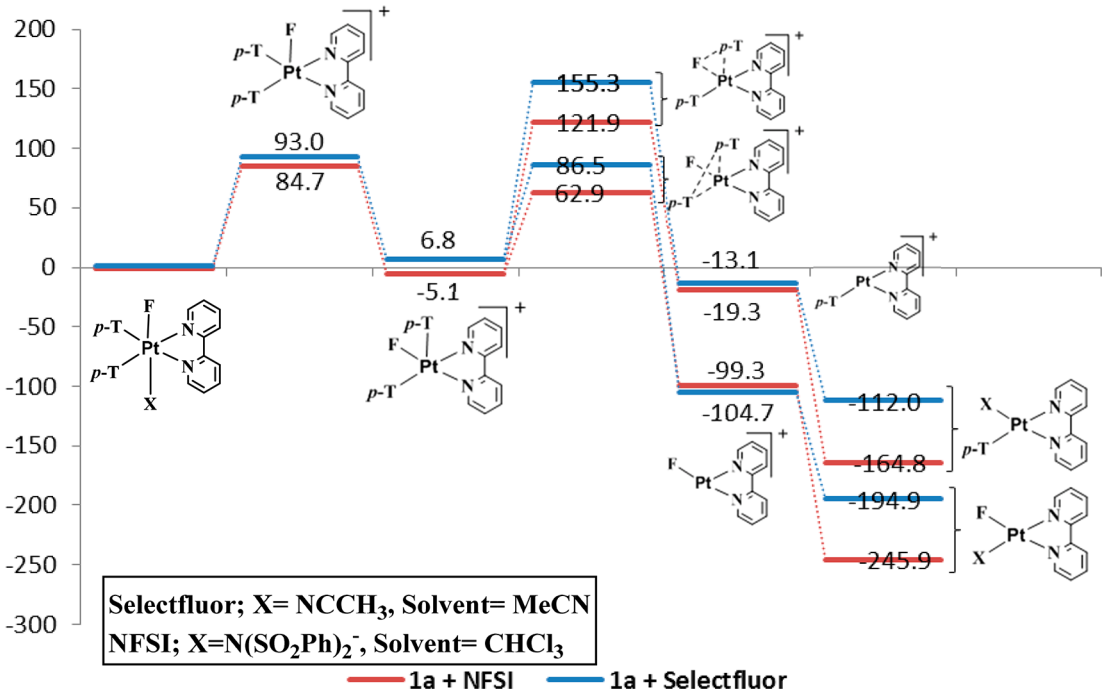


Figure 2. Calculated energy (kJ/mol) profile for the fluorination reaction of **1a**.

entirely different reactivity than Selectfluor and NFSI, although this product was consistent with the previously reported results by Puddephatt[15] et al., and they suggested that Cl was abstracted from dichloromethane.

The mechanism pathway and influence of fluorinating reagents on each step could be investigated by density functional theory (DFT) calculations. As it is shown in Figure 2, the mechanism pathway of possible reductive elimination reactions from **2a** and **3a** goes through a concerted three-centered transition state (TS), and the most important energy barrier steps are (1) dissociation of the anionic residue of NFSI in **3a** and coordinated acetonitrile in the presence of acetonitrile solvent molecules in solution in the reaction of **2a** with Selectfluor to form a suitable 5-coordinate intermediate for reductive elimination and (2) the concerted 3-centered TS for Ar−Ar and Ar−F reductive elimination step. In the former, a small difference (~8 kJ/mol) exists between Selectfluor and NFSI, but in the latter, the energy barrier for Ar−Ar reductive elimination with NFSI is much smaller (~20 kJ/mol) than Selectfluor that is consistent with obtained experimental results. The difference between activation barriers of 5-coordinate intermediates could be due to counterion effects (BF_4^- for the reaction with Selectfluor and $N(SO_2Ph)_2^-$ for the reaction with NFSI), and the impacts of two solvents (MeCN and $CHCl_3$) used in the DFT calculations of these two reactions. It is worth noting that the parallel Ar−F formation pathway has a higher energy TS (~64 kJ/mol) compared with Ar−Ar formation. This is consistent with our results and the previously reported results by Vigalok that Ar−F formation usually does not occur when Ar−Ar formation is possible.[20]

To study the effect of increasing the steric hindrance, the bis(mesityl)platinum(II) complex, [(bipy)Pt(1,3,5-$(CH_3)_3$-$C_6H_2)_2$], **1b**, was reacted with 1 equiv of Selectfluor in acetonitrile, and two isomers of related plausible fluoro-Pt(IV) complex, **2b** and **2b′**, were formed immediately. Suitable crystals for X-ray structural determination were not obtained, but the signals of these complexes were observed as two singlet at $\delta = -311.1$ ppm with $^1J_{Pt-F} = 1160$ Hz and $\delta = -325.1$ ppm with $^1J_{Pt-F} = 1405$ Hz in ^{19}F NMR which are consistent with the previously reported Pt(IV)-fluoro complexes having similar structures.[14,15] The former isomer decomposed at RT, and mesitylene as the major product of this decomposition was confirmed by GC-MS and ^1H NMR, but the latter isomer was stable for more than 2 months in acetonitrile (Figures S12, S13).

By repeating this reaction at 80 °C for 4 days, both isomers decomposed, and mesitylene was formed as the major product, similar to its RT reaction (Figure S14). Surprisingly, by the reaction of complex **1b** with 2 equiv of Selectfluor, 2-Fluoro-1,3,5-trimethylbenzene was confirmed as the product of Ar−F formation pathway with 78% yield by GC-MS (Table 1), ^1H NMR and ^{19}F NMR (Figures S15, S16). One of the proposed mechanism pathways for Ar−F bond formation could be the reductive elimination reaction, which is corroborated by the DFT calculations that Ar−F elimination has less energy TS than Ar−Ar elimination (Figure S21). By increasing the amount of Selectfluor to 3 equiv, the yield of Ar−F formation

Table 1. Yield of Fluorination Reactions in Various Conditions[a]

	fluorinating reagent	temperature	Ar−H	Ar−Ar	Ar−F
1a	Selectfluor/1 equiv	RT	0%	0%	0%
1a	NFSI/1 equiv	RT	0%	35% (90%)[b]	0%
1b[c]	Selectfluor/1 equiv	80 °C	55%	2.6%	0%
1b	Selectfluor/2 equiv	RT	22%	0%	78%
1b	Selectfluor/3 equiv	RT	12%	0%	87%
1b	NFSI/1 equiv	60 °C	46%	49%	4.4%
1b[c]	NFSI/2 equiv	RT	3.6%	13.7%	0%

[a]All yields were obtained by GC-MS except the reactions of **1a** which were determined by ^1H NMR. [b]Heated at 60 °C. [c]Accompanied by various unknown organic compounds.

https://dx.doi.org/10.1021/acs.inorgchem.0c03122
Inorg. Chem. 2021, 60, 1016−1020

increased to 87% by GC-MS analysis (Table 1). It should be mentioned that the amount of dimesityl as Ar−Ar product of competitive pathway is >3% in all reaction conditions of **1b** with Selectfluor that is completely contrary to the reactivity of **1a**. To the best of our knowledge, it is the first Ar−F bond formation in the presence of possible Ar−Ar formation. Similarly, the increase of C−F bond formation from palladium complexes by increasing the amount of XeF_2 was reported previously.[21]

When **1b** was reacted with NFSI instead of Selectfluor, it showed different tendency for bond formation pathway. By the reaction of **1b** with 1 equiv of NFSI, the plausible fluoro-Pt(IV) complex, **3b**, was formed with ^{19}F NMR resonance at δ = −308.5 ppm with $^{1}J_{Pt-F}$ = 1090 Hz. This complex decomposed after 3 days at RT, and the main detectable products were mesitylene and dimesityl in ^{1}H NMR (Figures S17, S18). By increasing the temperature, the same products were formed with small changes in their ratio (Figure S20); however, by increasing the amount of NFSI, these products were determined accompanied by various unknown organic compounds (Figure S19). No evidence was found by ^{1}H NMR, ^{19}F NMR, and GC-MS for the formation of Ar−F product. Interestingly, the product of the reaction of **1b** with NFSI in the mixture of $CDCl_3/CD_3CN$ (50:50), is the same as the product of the reaction of **1b** with Selectfluor in CD_3CN. Therefore, it is clear that acetonitrile has a higher coordinating ability than $N(SO_2Ph)_2^-$.

Also, another possible reaction of **1b** with fluorinating reagents is the fluorination of ortho methyl groups of mesityl, similar to the previous reports.[12c,14] However, in our reactions of **1b** with Selectfluor and NFSI in various conditions, no C_{sp^3}−F formation in ortho methyls of mesityl was detected by GC-MS, ^{1}H NMR, and ^{19}F NMR.

3. CONCLUSIONS

In summary, we reported the first example of Ar−F bond formation in competition with possible Ar−Ar formation. Parameters such as the type and amount of fluorinating reagents, temperature, and steric hindrance determine the selectivity for Ar−F vs Ar−Ar bond formation from platinum(IV) aryl fluoride complexes. Moreover, by computational studies, the influence of ligand steric properties and fluorinating reagents were investigated on the transition states of Ar−Ar and Ar−F probable reductive elimination reaction. These results could be a valuable guide to have better prediction on the reactivity of fluorinating reagents and designing more efficient catalytic fluorinating systems that are currently underway. Also, we are investigating the effects of the ancillary bipyridine ligands in fluorination reactions in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03122.

Synthetic details, NMR studies, X-ray data, and theoretical data (PDF)

Cartesian coordinates (ZIP)

Accession Codes

CCDC 1984303 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.G.H. is thankful for financial support from the Iran National Science Foundation (INSF Grant No. 98007952), Iranian Science Elites Federation (ISEF Grant No. 98225) and the Shahid Beheshti University Research Councils. Technical support of the Chemistry Computational Center at Shahid Beheshti University and X-ray Crystallography by Dr. Behrouz Notash is gratefully acknowledged.

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