Metathesis reactions between heavy d8 fluorides and I(III)-pyridine complexes

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ABSTRACT

The reaction between *trans*- [AuF2(pyridine)2]+ and [PhI(pyridine)2]2+ results in the formation of PhIF2 and [Au(pyridine)4]3+. Investigation of the reaction pathway using model Pd and Pt analogues of the gold complex indicate the most likely mechanism is attack by the Au-F onto the I(III), rather than a redox process. This demonstrates that the Au(III)-F fragment can behave in a nucleophilic manner even in a relatively electron poor cationic complex.

INTRODUCTION

The chemistry of organometallic/coordination complexes of Au(III) fluorides is an under developed area. It has only been within the last decade that complexes of Au(III)-F compounds have been reported, and the number of structurally characterized examples remains around a dozen (e.g. **1**-**4**).1-7 In recent work led by Toste and Nevado in organometallic compounds such as **1**-**3**, it has been shown that the Au(III)-F bond may be displaced by boronic acids, leading to reductive elimination and bond formation reactions, indicating potential utility for the Au-F bond.1, 2 In addition to the structurally characterized examples, Riedel and co-workers have studied the solution phase chemistry of pyridine-AuF3 mixtures.8 Our own entry into the area involved the synthesis of pyridine ligated trans bis-fluorides **7Au**, from either Au(I) **5** or Au(III) **6Au\_CN** starting materials,9 the second trans examples reported shortly after the work of Orduna and co-workers on the synthesis of **4**.4 Our work added the feature that the complexes could be made from Au(III) and simple KF rather than the XeF2 most often used in previous work. XeF2 can also be used to access the compounds from Au(I) precursors in our system (Scheme 1). **7Au** features the shortest Au-F bonds in a coordination or organometallic complex structurally characterized to date at 1.90 Å. The [AuF4]- anion as tetra alkyl ammonium salts have been crystalographically characterized to have Au-F bonds of 1.899-1.901 Å.8 Gas phase AuF3 also features slightly shorter bonds, measured at 1.88-1.89 Å.10 Previously reported coordination complexes feature a shortest bond of 1.95 Å with a more typical range of 2-2.2 Å.1-3, 11





Scheme 1. Synthesis of Au(III)-F complex **7Au**.

Fluoride ligands are often utilized or required for the stabilization of ultra-high oxidation state metal centres. Given the stability of our Au(III)-F system, we wondered if it was possible to generate a Au(V) coordination complex from **7Au**, using the pyridine ligated I(III) oxidant **8** (Weiss’ reagent, [PhI(pyridine)2][OTf]2). Iodine (III) oxidant **8** is used to generate Au(III) complexes **6Au**, and our group has shown that they can be used to generate d-8 Pt(IV) and (transiently) Pd(IV) pyridine coordination complexes.12, 13 Ritter and co-workers were able to isolate Pd(IV) complexes using [PhI(4-cyanopyridine)2][OTf]2 and a chelating pyrazine borate ligand.14 In the attempt described here we discovered a new fluoride-pyridine metathesis reaction between Au(III) and I(III), as well as for the d-8 Pd(II) and Pt(II) analogues.

RESULTS AND DISCUSSION

Treatment of **7Au** with one equivalent of **8** in CD3CN resulted in an instant color change from pale to deep yellow (Scheme 2). The 19F NMR signal arising from Au(III)-F in **7** disappeared and a new signal appeared at -176 ppm. This chemical shift is consistent with PhIF2.14,15 The solvent was removed *in vacuo* followed by the addition of CDCl3giving a white solid which was filtered and re-dissolved in CD3CN. The 1H NMR spectrum of the solid redissolved in CD3CN contained signals consistent with compound **6Au** previously reported by our lab15 while the 1H and 19F NMR spectra of the filtrate contained signals consistent with PhIF2.16, 17 Analysis of the *in situ* 1H NMR spectrum of the reaction mixture in CD3CN showed a 1:0.75 ratio of **6Au** to PhIF2.

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Scheme 2. Reaction of **7Au** with **8**.

The results obtained from this reaction raise a question as to whether the observed products were being mediated by oxidation of Au(III) to a Au(V), as the chemistry of **8** with transition metals is dominated by oxidative processes.18 A possible mechanism based on the products is oxidation to a d-6 intermediate (**9Au**), followed by oxidative fluorination of PhI generated in the oxidation to give the final products (Scheme 3). **8** is known to be able to oxidize d-8 Pd(II) or Pt(II) compounds to give d-6, +4 oxidation state products or intermediates.13, 14

 Given the extremely high reduction potential for Au(V) it would be also possible for the pyridine ligands to become oxidized.



Scheme 3. Potential Au(V) intermediated pathway for the generation of **6Au** and PhIF2.

To provide a further insight into the possible pathway of this outcome analogous Pd(II) and Pt(II) complexes were examined (compounds **7Pd** and 7**Pt**) as isoelectronic models for Au(III) with accessible d-6 oxidation states to be reacted with **8**. Compound **7Pd** was synthesized according to literature procedure,19 while **7Pt** was not previously reported and was synthesized mimicking the synthetic protocol used to access **7Pd**. Isolation and X-Ray characterization of **7Pt** revealed a *cis-*geometry for the respective pyridine and fluoride ligands as shown in Figure 1. Surprisingly, there is only one structurally characterized Pt(II)-F complex with a similar structural motif, with PPh3 ligands rather than pyridine.20



Figure 1. Solid-state structure of **7Pt**. Thermal ellipsoids are depicted at 50% probability level. Selected bond distances (Å): Pt1–F1 1.986(4), Pt1–N1 1.996(7).

Pd(II) compound **7Pd** was stirred with I(III) reagent **8** in CDCl3 for two hours. Proton and 19F NMR spectra of the reaction mixture indicated the presence of PhIF2**.** Compound **6Pd**was also detected in 1H NMR and mass spectrometry ([m/z]+ = 211) which was confirmed by comparison with reported spectroscopic details (Scheme 4).21 The ratio of **6Pd** and PhIF2 in the reaction mixture was 1:1 as determined by integration of the 1H NMR spectrum.



Scheme 4. Reaction of **7Pd** with **8**.

The reaction of Pt(II) compound **7Pt** with **8** was attempted in CDCl3 and led to a yellow solid (Scheme 5) which was isolated and washed with CH2Cl2. The 19F NMR spectrum of the isolated solid in CD3CN contained a singlet at -267 ppm (JPt-F(satellite) = 1745 Hz for the 195Pt satellites) consistent with the reported compound **9Pt,**22 which was also confirmed by proton NMR and mass spectrometry analysis. 19F NMR spectrum of the filtrate in CDCl3 contained a singlet at -178 ppm (consistent with PhIF2) andproton NMR spectrum of the filtrate contained signals consistent with **6Pt,** PhIF2 and PhIwhich were confirmed by comparison with the reported spectroscopic details of **6Pt**,22, 23 or genuine samples for PhI and PhIF2. This result indicates that a d-6 compound (**9Pt**) can be accessed from **7Pt** and **8R**, and is therefore a potential intermediate for the Pd and Au systems. The reaction was re-run in CD3CN to ensure solubility of **9Pt** to determine *in situ* product ratios, which were found to be 1:0.75 for **6Pt:9Pt** based on integration of the 1H NMR spectrum. One other species that could not be identified was apparent in the aromatic region containing a phenyl group of the *in situ* experiment.



Scheme 5. Reaction of **7Pt** with **8**.

As the critical control experiment, to investigate if these outcomes are mediated via oxidative addition and then oxidative fluorination of PhI or direct exchange, Pt(IV) compound **9Pt** was synthesized independently according to literature procedures22 and reacted with iodobenzene in CH3CN, which resulted in no reaction. Reflux of the reaction mixture for 3 hours also resulted in no observable reaction based on 19F NMR spectroscopy.

Based on this we propose that the products observed in the reaction of Au(III) and Pd(II) with I(III) reagents are generated via a direct metathesis reaction, rather than reductive elimination from a d-6 intermediate. In the case of Pt(II) reaction with I(III), the observed product distribution is generated due to two competing reactions, oxidation of Pt(II) to Pt(IV) to give **9Pt** allowed for by the greater accessibility of Pt(IV) as compared to Pd(IV)/Au(V), and metathesis between Pt(II) and I(III) to give PhIF2 and **6Pt**.

Results from electrochemistry experiments are in line with the synthetic results. In DMSO solution, **7Pt** undergoes an irreversible oxidation at +0.85 V (vs. Fc/Fc+). For the corresponding Au compound no oxidation is seen to the solvent limit. Repeating the experiment in MeCN for the Au compound to use a wider potential window, no oxidation is observed out to the solvent limit of +2.75 V (vs. Fc/Fc+) .

Theoretical calculations at the MP2/LANL2DZ level of theory using an CH3CN solvent forcefield show that the observed reaction for Au has a ΔG of -57 kJ/mol. Oxidation to an Au(V) analogue of **9Pt** is unfavourable by 90 kJ/mol. A transition state to an Au(V) could not be found, but must be higher than the 90 kJ/mol increase in energy. The observed rapid room temperature reaction rules out a barrier of this magnitude on the way to such a potential intermediate. For Pt the ΔG to **9Pt** is -292 kJ/mol, and conversion to **6Pt** from starting material is less favourable at -164 kJ/mol. The observed distribution of products thus suggests the two processes are kinetically similar. For Pd the oxidation is also thermodynamically favourable at -171 kJ/mol, consistent with the known ability of I(III) reagents to oxidize Pd(II) complexes.24 The observed reaction leading to **6Pd** is also favourable, but less so at -102 kJ/mol, indicating that oxidation for Pd is kinetically supressed.

Ruling out an oxidation event at the Au atom, this leaves the most likely mechanism for the reaction to be nucleophilic attack on the I(III) centre by the Au-F moiety. To investigate whether **8** could potentially react with nucleophilic fluoride to give PhIF2, reactions with KF were carried out.

To a solution of **8** in CH3CN was added 2 equivalents of KF and 6 equivalents of 18-crown-6. After 30 minutes, an aliquot was removed for 19F NMR spectroscopy which showed clean formation of PhIF2 (Scheme 6). The solvent was removed in vacuo and the residue was washed with Et2Oyielding a white solid. A sample of the solid re-dissolved in CD3CN gave resonances in the 1H NMR and 19F NMR consistent with PhIF2 which was isolated in 67% yield.



Scheme 6. Direct reaction of **8** with fluoride.

This reaction is interesting from two perspectives, one as a route to PhIF2 that does not involve HF or an exogenous oxidant,25, 26 and secondly as a rare example of chemistry at the iodine atom in Weiss’ reagent that does not involve a redox process. The only other example of a non-redox reaction at iodine in this class of reagent is ligand exchange from one type of pyridine to another reported by our group in 2012.27 The iodine atom can also act as an electrophile in Electrophilic Aromatic Substitution reactions, but becomes 2-coordinate.28, 29

In the context of the group 10 chemistry described above, the results of this reaction indicate that free fluoride contaminant is an unlikely cause of the reaction, as exogenous 18-crown-6 must be added. Also, identical results are obtained using **7Au** synthesized from XeF2 rather than KF, making contamination from excess fluoride unlikely, especially given the quantitative nature of the transformation. Compound **7Au** has been shown not to react with free pyridine, making labile pyridine from **8** in solution implausible as the agent to initiate the transformation, as well as the I(III) centre losing pyridine in a non-reductive process being highly unfavourable. This leaves nucleophilic attack by the Au-F on I(III) as the most likely, albeit surprising, mechanism given the highly electrophilic nature of cationic Au(III).

CONCLUSIONS

Here we have demonstrated that although being bound to a charged Au(III), the fluoride in **7Au** is sufficiently nucleophilic to replace pyridine on a coordinatively saturated I(III), and despite the apparent good stability of **7Au** it is reactive enough to generate a relatively high energy compound in PhIF2. It is also shown that this reactivity is common to the Pd(II) and Pt(II) analogous M-F complexes, albeit with oxidation to Pt(IV) a competing reaction for that metal. From the iodine angle, this work is a rare example of non-redox chemistry occurring at the iodine centre in Weiss’ reagent.

ASSOCIATED CONTENT

**Supporting Information**.

Experimental procedures, NMR spectra of reaction mixtures and isolated compounds. Cartersian coordinates and electronic energies of calculated species. Electrochemical experimental details.

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TOC Figure and Synopsis



Reaction of Au(III) difluorides and analogous Pd/Pt complexes with pyridine ligated I(III) cations results in nucleophilic attack of the M-F bonds onto I(III).