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Stability of metal–metal interactions in transmetallation intermediates based on electronics of bridging arene ligands determined through pyridine titrations†

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In this contribution, we prepare the dinuclear complex [(CNC^F)(PPh$_3$)Pt–Au(PPh$_3$)]$^+$ (2-F) supported by an electron deficient derivative of 2,6-diphenylpyridine (CNC), 2,6-di(4-fluorophenyl)pyridine (CNC^F). Solution state spectroscopic data and solid-state structural data reveals formation of the desired dinuclear complex occurs and that it remains intact in solution. The solid state structure of 2-F, compared to [(CNC)(PPh$_3$)Pt–Au(PPh$_3$)]$^+$ (2), reveals a substantial change in the C–Au–P bond angle. We postulated that this change in bond angle arises due to a weaker interaction between [(PPh$_3$)Au]$^+$ and (CNC^F)Pt(PPh$_3$) (1-F) *vs*. (CNC)Pt(PPh$_3$) (1). Through pyridine titration experiments, we demonstrate that the interaction is indeed weaker between [(PPh$_3$)Au]$^+$ and 1-F *vs*. 1. Cyclic voltammetry (CV) experiments confirm that 1-F is less electron rich than 1. DFT calculations demonstrate that the HOMO of 1 and 1-F is not d$_{z^2}$, helping explain the differences in electrochemical behavior of 1 and 1-F and bonding between 1 and 1-F with [(PPh$_3$)Au]$^+$.

Transmetallation, the exchange of ligands between two metal centers, is a critical step in both catalysis and organometallic synthesis.[1] The role of transmetallation in catalytic cross coupling has made understanding the mechanism of transmetallation particularly important.[2] Mechanistic studies of transmetallation have focused on reactions between Sn- and B-based reagents with Pd- and Pt-complexes because of their relevance to the Stille and Suzuki–Miyaura coupling reactions respectively.[3,4] Hartwig and coworkers found an open coordination site is necessary for efficient transmetallation using certain Pd-complexes and Sn-reagents.[5] Transmetallation between Pd-complexes and boronic acids are accelerated with a Pd–OH *vs*. Pd–halide.[3,6]

By contrast, comparatively little is understood about the mechanism and thermodynamic driving force for transmetal-

lation between two transition metal complexes,[7] though it is known in the Sonogashira reaction[8] and has been proposed in other cooperative catalytic reactions.[9–13] Stahl and coworkers convincingly demonstrate transmetallation of an aryl group between two palladium species upon C–H activation *via* kinetic isotope effect (KIE) studies.[14] Other research groups have explored stoichiometric transmetallation between two organometallic complexes.[15–20] However, one of the challenges in developing a deeper understanding of transmetallation is the stability of the proposed intermediate along the pathway of transmetallation. Often, the proposed intermediate in transmetallation has a low kinetic barrier to formation of the final exchange product making it challenging to detect and directly probe its structure.[20] Despite this challenge, several research groups have examined dinuclear complexes that may play a role in understanding transmetallation reactions.[21–36]

Martin and coworkers used the CNC ligand (CNC = 2,6-diphenylpyridine) bound to Pt (1) to study transmetallation intermediates.[37] One such intermediate is generated by reaction of 1 with [(PPh$_3$)Au]$^+$ to yield 2 where the Au binds to the Pt and the *ipso* carbon of the phenyl ring. While metallophilic interactions between Pt and Au likely play a role in the stability of this complex, the simultaneous binding to the Pt–phenyl ring suggests that the electronics of the arene ring also play a role in stabilizing such a dinuclear complex.

We chose to study a fluorinated derivative of the CNC ligand (CNC^F) to establish the role of electron withdrawing groups in the stability of dinuclear Pt/Au complexes. For efficient cooperative catalysis with transmetallation as the key step, a delicate interplay of kinetic barriers between and thermodynamic stabilities of reaction intermediates is at work (Fig. 1). If the intermediate of transmetallation (*e.g.* 2 or 2-F) is highly stable, this will decrease the concentration of active catalyst in a cooperative catalytic reaction. An analogy can be drawn to the use of chain transfer reagents in alkene polymerization where highly stable bimetallic complexes between the polymerization catalyst and chain transfer reagent inhibit propagation as intermediate formation decreases the concentration of the propagating catalyst species.[38–44] Thus, under-

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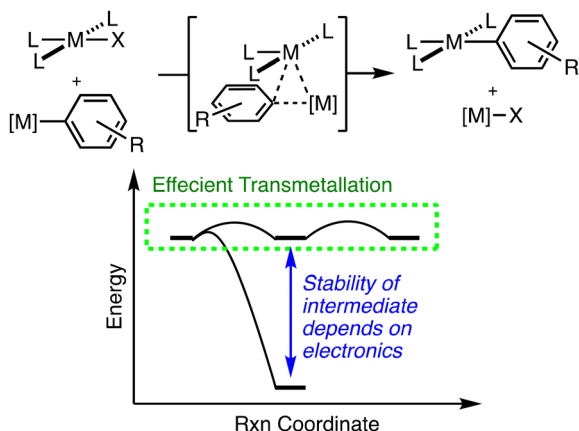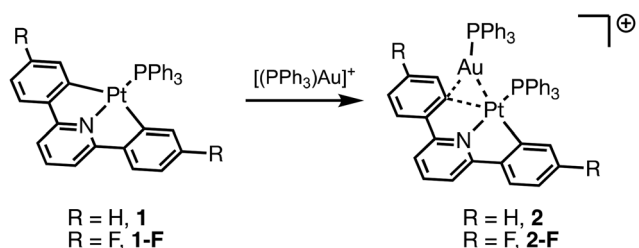
Fig. 1 (Top) Transmetallation of an arene group between two organometallic complexes. (Bottom) Hypothetic free energy surface for transmetallation. The stability of the transmetallation intermediate is dependent on the electronics of the arene ring.

standing the strength of such dinuclear complexes as a function of metal identity (as Martin and coworkers have previously described)[31,37,45,46] as well as electronics of the bridging arene ligand (reported here) are vital to the development of cooperative catalytic reactions.

Herein, we describe the synthesis of **2-F** and compare its structure and stability to the known complex **2**. First, we describe the differences between the solid-state structure of **2** and **2-F**. Then, we use pyridine titration experiments to probe the thermodynamic stability of these two complexes. We also use cyclic voltammetry (CV) to determine the anodic peak potential of both (CNC^R)Pt(PPh$_3$), when R = H and F. We correlate the oxidation potential determined by CV experiments to the thermodynamic stability of the dinuclear [(CNC^R)(PPh$_3$)Pt–Au(PPh$_3$)]$^+$ complexes.

First, we set out to synthesize **2-F** by reaction of the known **1-F** complex with the *in situ* generated [(PPh$_3$)Au]$^+$ (Scheme 1).[47] We observed two peaks in the ^{31}P NMR spectrum of this new complex at 33.8 ppm with Pt satellites ($^2J_{P–Pt}$ = 267 Hz) and 21.5 ppm with Pt satellites ($^1J_{P–Pt}$ = 3568 Hz) corresponding to the PPh$_3$ ligands bound to Au and Pt respectively. Similar to complex **2**, the $^2J_{P–Pt}$ of the PPh$_3$ ligated to Au supports that a dinuclear complex remains intact in solution as a two bond coupling between Pt and the P of PPh$_3$ bound to Au is observed. The ^{1}H NMR spectrum of **2-F** reveals an expected

upfield shift of the *ortho* C–H (relative to Pt) of 0.18 ppm upon coordination of the cationic Au species. A similar shift upfield was observed for **2** of 0.21 ppm upon coordination of [(PPh$_3$)Au]$^+$.[37]

The solid-state structure of **2-F** (Fig. 2), obtained by single crystal X-ray diffraction, revealed differences between **1-F** and **1** upon binding the [(PPh$_3$)Au]$^+$.[37] Most prominently, the bond angles between the P–Au–C for the two complexes are substantially different; for **2-F**, P–Au–C = 173.5°, whereas for **2**, P–Au–C = 153.2°. Interestingly, despite this change in the P–Au–C bond angle, the degree of arene group transfer (as indicated by the C$_{para}$–C$_{ipso}$–Au angle) does not change substantially between **2** and **2-F**. For **2-F**, C$_{para}$–C$_{ipso}$–Au = 120.9° whereas for **2** C$_{para}$–C$_{ipso}$–Au = 120.1°. If the arene fully transferred to Au, the C$_{para}$–C$_{ipso}$–Au would reach ~180°, with no arene Au interaction C$_{para}$–C$_{ipso}$–Au would be ~90°.[46] Other bond metrics change minimally between the proteo and fluoro substituted arenes including the Pt–Au distances, 2.7430(5) Å for **2-F** and 2.7222(2) Å for **2**. The Pd derivative of **2** (**2-Pd**) has been previously characterized by single crystal X-ray diffraction.[46]

Interestingly, **2-Pd** shows some structural features related to both **2** and **2-F**; for example, Pd–Au = 2.7422(3) Å, similar to the Pt–Au distances in **2** and **2-F**. In **2-Pd**, the P–Au–C = 173.8°, which is quite similar to that of **2-F** (P–Au–C = 173.5°). However, the degree of arene transfer in **2-Pd** is much higher than **2** and **2-F** as indicated by C$_{para}$–C$_{ipso}$–Au = 143.1° *vs.* 120.1° and 120.9° for **2** and **2-F** respectively. The higher degree of arene transfer in **2-Pd** is reflective of generally stronger Pt–C bonds relative to Pd–C bonds. Clearly, there are multiple struc-

Scheme 1 Synthesis of dinuclear complexes **2** and **2-F**.
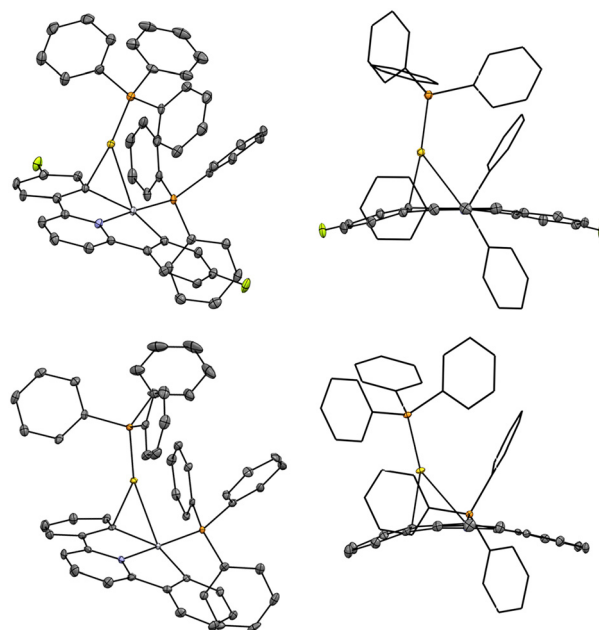
Fig. 2 (Top) Molecular structure of the cation portion of complex **2-F**. Hydrogens, DCM solvent, and triflate anion omitted for clarity. (Bottom) Molecular structure of the cation portion of complex **2**.[37] Hydrogens and perchlorate anion omitted for clarity. For both complexes, thermal ellipsoids are shown at the 50% probability level.

tural factors to consider when trying to understand the bonding interactions between such dinuclear, frustrated trans-metallation complexes.

Previously, Martin and coworkers have used Energy Decomposition Analysis (EDA) to understand the strength of the interactions in dinuclear complexes such as **2**, **2-Pd**, and other related complexes.[37,45] Herein, we chose to use experimental data to qualitatively determine the relative stabilities of **2** *vs.* **2-F**. We postulated that the C–Au–P bond angle difference between **2** and **2-F** (with similar degrees of arene group transfer) may arise from an overall decrease in stability of the interaction between the $[(PPh_3)Au]^+$ and **1-F** relative to **1**. We chose to evaluate the thermodynamic strength of these interactions using pyridine titrations. We dissolved $[(CNC^R)(PPh_3)Pt–Au(PPh_3)]^+$ in dcm–*d2* and added various equivalents of pyridine or 2-fluoropyridine. In these titration experiments, an equilibrium may be established between the dinuclear complex plus pyridine and the monometallic Pt complex and a pyridine ligated $[(PPh_3)Au]^+$ (Fig. 3).

Based upon a qualitative comparison of these two complexes, it is clear that $[(PPh_3)Au]^+$ binds less strongly to the more electron deficient **1-F** than **1**. While one equivalent of pyridine completely displaces $[(PPh_3)Au]^+$ from **2-F**, nearly 10 equivalents of pyridine are required to completely displace $[(PPh_3)Au]^+$ from **2** based upon ^1H NMR spectroscopic analysis. Using 2-fluoropyridine as the titrant, **2** is only minimally affected; however, an equilibrium is established where $[(PPh_3)Au]^+$ is partially displaced from **2-F** by 2-fluoropyridine. It is worth noting that 2-fluoropyridine is a weaker base than pyridine by several orders of magnitude revealing how weak of an interaction exists between $[(PPh_3)Au]^+$ and **1-F**. Importantly, control reactions (see ESI† for details) demonstrate that pyridine and 2-fluoropyridine do not react with **1** or **1-F** and appear to bind readily to $[(PPh_3)Au]^+$. Based on the ppm shift change upon addition of pyridine and 2-fluoropyridine, we can calculate the K_{eq} for these titration experiments (see ESI† for details).[48,49] The affinity of pyridine and 2-fluoropyridine for the $[(PPh_3)Au]^+$ fragment of **2-F** is higher than for **2** by two orders of magnitude (Fig. 3).

Both titration results were initially surprising. We anticipated that pyridine would more easily displace $[(PPh_3)Au]^+$ from both **2** and **2-F**. The stability of **2**, however, suggests that the Pt–C bond of **1** serves as a reasonably good ligand for the cationic gold species as it competes with pyridine for ligation with $[(PPh_3)Au]^+$. While **2** has been studied computationally and through variable temperature NMR spectroscopy,[37] a more direct experimental measurement of the stability of **2** has not been reported previously. Based on the stability of **2**, it was surprising that **2-F** was readily displaced by pyridine and equilibrium established with 2-fluoropyridine (a substantially weaker base than pyridine) as the only difference between these complexes is the meta (relative to Pt) fluoro groups of **2-F**.

Based on the electron withdrawing nature of fluorine, we expect that the Pt–C bond of **1-F** is likely less electron rich than **1**, leading to a dinculear complex **2-F** with lower overall stability than **2**. Using CV, we established that **1-F** is less electron rich than **1** as judged by the relative oxidation potentials of these two complexes. The onset of oxidation of **1-F** occurs ~200 mV more anodic relative to **1**. However, neither **1** nor **1-F**
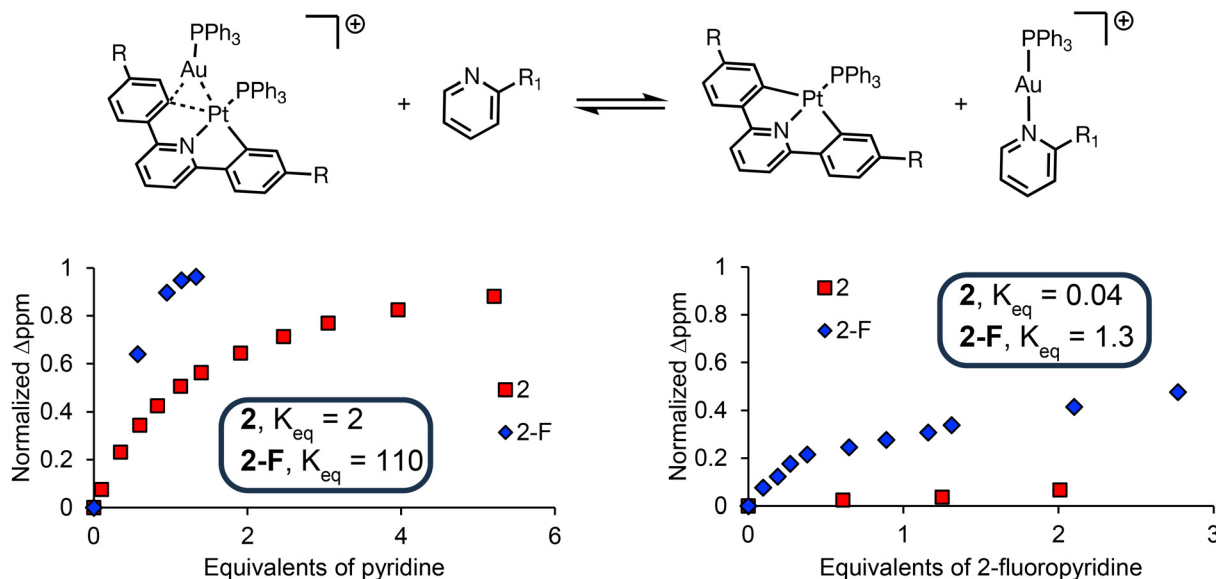
Fig. 3 (Top) Titrations of **2** (R = H) and **2-F** (R = F) with pyridine (R₁ = H) and 2-fluoropyridine (R₁ = F). Titrations were monitored by ^1H NMR spectroscopy (see ESI† for details). We used the peak associated with the proton alpha to Pt in **2** & **2-F** and monitored the change in ppm based on the equivalents of pyridine or 2-fluoropyridine added. We normalized the ppm change upon pyridine (or 2-fluoropyridine addition) plotting the normalized Δppm on the *y*-axis. Here, the value of zero on the *y*-axis corresponds to no change in the ppm shift (*i.e.* the chemical shift of the starting **2** or **2-F**). The value of one on the *y*-axis corresponds to complete dissociation of $[(PPh_3)Au]^+$ from the Pt (*i.e.* the chemical shift of **1** or **1-F**). (Bottom left) Titration of **2** or **2-F** with pyridine. (Bottom right) Titration of **2** or **2-F** with 2-fluoropyridine.

exhibit fully reversible electrochemical behavior as determined by scan rate dependent CV studies precluding a more detailed analysis. These electrochemical results support our hypothesis that the electron deficient nature of the CNC^F ligand plays a substantial role in the decreased stability of the dinuclear complex **2-F** *vs*. **2**.

Given that both **1** and **1-F** are d^8 complexes and nearly square planar in geometry, one might expect that the HOMO is the d$_{z^2}$ orbital. The d$_{z^2}$ should be minimally impacted by the electronics of the arene rings. The results from CV studies suggest, however, that the HOMO is impacted by the electronics of the arene ring. The expectation that the d$_{z^2}$ orbital is the HOMO arises from a sigma only view of bonding in transition metal complexes, whereas the extended π structures of CNC and CNC^F may alter the HOMO of complexes **1** and **1-F**. DFT calculations (see ESI† for details) performed at various levels of theory (B3LYP, PBE, PBE0, and M06, see ESI† for details) reveal that the HOMO is a d$_{\pi^*}$ orbital for both **1** and **1-F** with significant contributions from the ligand π orbitals, which likely explains why the oxidation potential of **1** and **1-F** are different by ~200 mV.

Conclusions

In this manuscript, we have synthesized the new dinuclear complex **2-F** and compared it to the previously studied **2**. Solution state NMR spectroscopic data support that the Pt–Au interaction remains intact for **2-F** similar to the previously studied **2**. However, the interaction between Au and Pt in **2-F** is much weaker than in **2** (based on pyridine titration experiments) while structural data suggests a similar degree of arene group transfer between Pt and Au in both complexes. CV experiments reveal that **1** is easier to oxidize than **1-F**, which helps explain the increased stability of **2** relative to **2-F**. DFT results reveal that the HOMO is the d$_{\pi^*}$ orbital of **1** and **1-F**. These computations help explain both the difference in oxidation potential between **1** and **1-F** and the stability of the interaction between [(PPh$_3$)Au]$^+$ and **1** *vs*. **1-F**.

Complex **2-F** and its comparison to **2**, help shed light on the proposed intermediates involved in transmetallation. Martin and coworkers have established that the metal identity in these dinuclear complexes plays a major role in their structure and stability. Here, we show that the electronics of the arene ring involved in this arrested transmetallation state impacts the stability of the dinuclear complex but not the degree of arene group transfer. As the development of cooperative catalytic reactions continues where transmetallation is the key step, it is important to not only consider the metals involved in transmetallation but also the steric and electronic parameters of the ligands that undergo exchange during transmetallation.

Author contributions

R.M. synthesized and characterized **2-F**, collected all titration data, collected CV data, and assisted in manuscript writing. E.

Data availability

The NMR spectroscopic data supporting the research in this article can be found in the ESI.† The CV chromatograms supporting the research in this article can also be found in the ESI.† Geometric coordinates used in the DFT calculations supporting this research are included with this submission. Crystallographic data for compound **2-F** has been deposited at the CCDC under 2364269 and can be obtained from https://www.ccdc.cam.ac.uk/structures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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