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# Platinum Carbon Bond Formation via Cu(I) Catalyzed Stille-Type Transmetallation: Reaction Scope and Spectroscopic Study of Platinum-Arylene Complexes†

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The preparation of Pt(II) complexes of the type *trans*-$L_2Pt(Ar)Cl$, $L_2Pt(Ar)_2$, and $L_2Pt(Ar)(Ar')$ (L = $PBu_3$, Ar = arylene) by CuI catalyzed reaction of *cis*-$(PBu_3)_2PtCl_2$ with aryl-stannanes is reported. The reactions proceed at 25 – 60 °C in moderate to good yields. The reaction is demonstrated to occur with phenyl- and 2-thienyl-stannanes that include a variety of functionality, and all of the resulting Pt-aryl complexes were been fully characterized by $^1H$, $^{13}C$, and $^{31}P$NMR spectroscopy, as well as mass spectroscopy. Photophysical properties of the $L_2Pt(Ar)_2$, and $L_2Pt(Ar)(Ar')$ complexes were measured, including steady-state absorption, photoluminescence, and photoluminescence quantum yields were investigated in order to understand how attachment of the platinum metal influences the excited state properties of the arylene ligands. This work affirms that CuI catalyzed coupling between Ar-$SnR_3$ and $L_2PtCl_2$ is a useful platinum-carbon bond formation reaction.

## Introduction

Bond formation between aromatic ligands and late transition metals such as Ni, Pd, and Pt is typically carried out by reaction between a metal halide and a corresponding aryl-organolithium or organomagnesium reagent.[1,2] A major disadvantage of this technique is that due to the strong nucleophilic and basic character of the organometallic reagents, the reactions do not tolerate a range of functionality. Oxidative addition is known to be one of the best approaches to create carbon-metal bonds.[3-7] However, this technique requires the use of air-sensitive zero-valent metal complexes, and therefore the reactions need to be carried out under inert conditions.

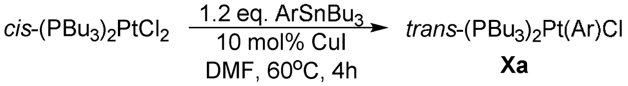
We have interest in the properties and applications of aryl-substituted Pt(II) complexes of the type, $L_2Pt^{II}Ar_2$, driven in part due to their useful linear and non-linear optical properties. One approach that has been used to form carbon-platinum bonds for these types of complexes relies on the room-temperature reaction between $(COD)PtCl_2$ and $ArSnR'_3$ where Ar represents an aromatic group and R' is either Me or Bu, and COD = 1,4-cyclooctadiene.[8-10] However, complexes of the type $L_2PtCl_2$, where L = $PR_3$, have not been demonstrated to react with aryl tin compounds. As comparisons are later made to analogous Pt(II) aryl-acetylide compounds, it is worth noting that mono- and disubstituted, via $ArCCSnR'_3$, as well as polymeric, via $R'_3SnCCArCCSnR'_3$, Pt(II) aryl-acetylides have been previously synthesized from $L_2PtCl_2$.[11,12] It has been shown that the Stille-coupling reaction can be accelerated 100-fold using Cu(I)-salts.[13-17] Following this lead, a similar strategy was considered, i.e., using a Cu(I) catalyst to facilitate the coupling reaction between $ArSnR_3$ and $L_2PtCl_2$ complexes. A recent paper by Gray and co-workers defines a Pd-catalyzed methodology to afford Au(III)-aryl complexes in a reaction that is conceptually similar to the ones reported in the present Article.[18]

Herein, the development of a facile and general route to synthesis of compounds of the type, *trans*-$(PBu_3)_2Pt(Ar)Cl$ and *trans*-$(PBu_3)_2PtAr_2$ by using Cu(I)-assisted transmetallation of aryl tin compounds with the phosphine bearing Pt-complexes is described. The scope of the reaction was explored by using variously substituted aryl tin derivatives, and a possible mechanism for the reaction is considered. Further, some of the resulting $(PR_3)_2PtAr_2$ complexes feature interesting photophysical properties, including ambient temperature phosphorescence arising from a long lived triplet excited state, and we have explored these effects using absorption, emission and time resolved absorption spectroscopy.

## Results and Discussion

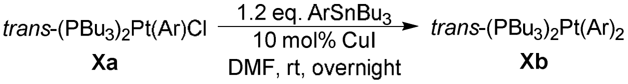
### Synthesis and Structure

Synthesis of aryl-platinum(II) complexes is achieved by mixing *cis*-$(PBu_3)_2PtCl_2$ and an aryl-stannane in dimethylformamide solvent (DMF) in the presence of 10 mol% CuI. Upon heating the reaction at 60°C for 4 hours only the monosubstituted complex (*trans*-$(PBu_3)_2Pt(Ar)Cl$, **Xa**) is formed (Scheme 1, Table 1). This reaction also goes at room temperature; however, under these conditions longer reaction times are required to achieve the same yield. Interestingly, after isolation the monosubstituted complex **Xa** can be reacted in a separate pot, again with catalytic CuI in DMF, but this time at room temperature, to afford the disubstituted complex (*trans*-(PBu$_3$)$_2$PtAr$_2$, **Xb**) (Scheme 2). Isolation of **Xa** is necessary for generation of **Xb**, as adding another portion of CuI after completion of the initial monosubstitution reaction mixture did not afford further reaction. Yields for all mono- and homodisubstituted complexes under their respective conditions are given in Table 1.



$$cis\text{-}(PBu_3)_2PtCl_2 \xrightarrow[\text{DMF, 60}^{o}\text{C, 4h}]{\text{1.2 eq. ArSnBu}_3 \text{ / 10 mol\% CuI}} trans\text{-}(PBu_3)_2Pt(Ar)Cl \ \ \mathbf{Xa}$$

**Scheme 1**. Synthesis of Monosubstituted Aryl-Planium Complexes.

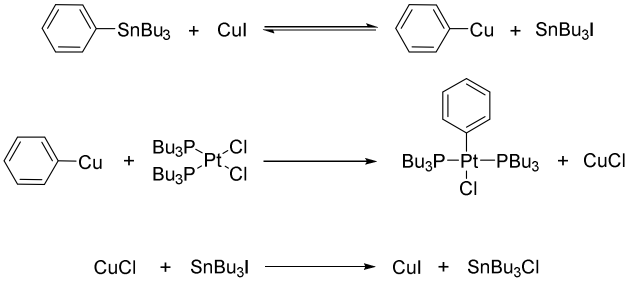


$$trans\text{-}(PBu_3)_2Pt(Ar)Cl \ \mathbf{Xa} \xrightarrow[\text{DMF, rt, overnight}]{\text{1.2 eq. ArSnBu}_3 \text{ / 10 mol\% CuI}} trans\text{-}(PBu_3)_2Pt(Ar)_2 \ \ \mathbf{Xb}$$

**Scheme 2**. Synthesis of Disubstituted Aryl-Planium Complexes.

A surprising finding is that when the aryl-stannane is thiophene based the substitution reaction has a different outcome (**8** and **9**, Table 1). In this case, the reaction time is reduced (~0.5 hours at room temperature), and the reaction directly affords the disubstituted product, with the monosubstited product not observed. This result holds even when equimolar amounts of aryl-stannane and *cis*-(PBu$_3$)$_2$PtCl$_2$ are mixed in the presence of 10 mol% CuI. Employing two equivalents of the thiophene based stannanes directly affords the *trans*-disubstituted complexes, in greater than 65% yield (Table 1). This unexpected behavior may be explained by the mono-substituted complexes **8a** and **9a** having greater reactivity than the *cis*-(PBu$_3$)$_2$PtCl$_2$, probably due to the minimal steric effects of the thiophene based rings.

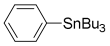
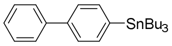
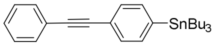
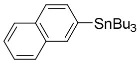
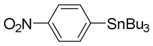
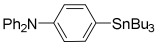
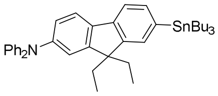
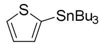
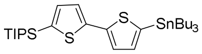
The mechanism for this transformation is believed to be of an analogous nature to that of the Cu-aided Stille coupling (Scheme 3).[15] In the first step, copper replaces tin on the aryl moiety, generating an arylcuprate complex as well as tributyltin iodide.[17] The arylcuprate then undergoes transmetallation with platinum, giving **Xa** and CuCl. Finally, tributyltin iodide and copper chloride undergo halogen metathesis to regenerate the CuI catalyst.



**Scheme 3**. Proposed Mechanism for the Cu(I)-mediated Transmetallation.

Upon further investigation into the products of the monosubstitution reaction, it was discovered that a structurally similar platinum complex forms under the reaction conditions. This complex has a nearly identical $^1$H NMR (with respect to both chemical shift and integration ratios) to that of the desired monosubstituted product *trans*-(PBu$_3$)$_2$Pt(Ar)Cl; however, the $^{31}$P NMR exhibits an ~5.5 ppm upfield shift. On the basis of the $^{31}$P NMR the product was tentatively assigned to *trans*-(PBu$_3$)$_2$Pt(Ar)I. Subsequent experiments showed that the Pt-iodo complex is formed when *trans*-(PBu$_3$)$_2$Pt(Ar)Cl (**Xa**) is treated with one equivalent of CuI at ambient temperature, as evidenced by observation of the upfield shift in the $^{31}$P NMR spectrum. Furthermore, it was found that the reaction of *trans*-(PBu$_3$)$_2$Pt(Ar)I with the corresponding aryl-stannane at room temperature with 10% CuI did not afford the disubstituted product. It was also found that reaction of **Xa** with CuCl and the corresponding aryl-stannane did not give rise to further substitution. Taken together, these results suggest that for the aryl-stannanes the reason the reaction stops at monosubsitution stems from several factors, including lack of reactivity of the *trans*-(PBu$_3$)$_2$Pt(Ar)I complex and CuCl as a catalyst. By contrast, when Ar is thiophene-based the stannanes apparently react much more quickly, alleviating these issues, giving rise to high yields of the disubstituted product directly.

**Table 1.** Yields of Mono- and Homodisubstituted Aryl-Platinum Products.

| | **Ar-SnBu$_3$** | ***trans*-(PBu$_3$)$_2$Pt(Ar)Cl** [a]<br>**Xa** | ***trans*-(PBu$_3$)$_2$Pt(Ar)$_2$** [b]<br>**Xb** |
|---|---|---|---|
| **1** |  | **1a: 75%** | **1b: 55%** |
| **2** |  | **2a: 63%** | **2b: 40%** |
| **3** |  | **3a: 60%** | **3b: 45%** |
| **4** |  | **4a: 65%** | **4b: 52%** |
| **5** |  | **5a: 45%** | **5b: 60%** |
| **6** |  | **6a: 53%** | **6b: 10%** |
| **7** |  | **7a: 30%** | **7b: 5%** |
| **8** |  | **8a: -** [c] | **8b: 65%** [d] |
| **9** |  | **9a: -** [c] | **9b: 72%** [d] |

[a] Outcome from reaction conditions presented in Scheme 1. [b] Outcome from reaction conditions presented in Scheme 2. [c] No product was observed. [d] The yields of the reaction between either **8** or **9** with 0.5 equivalents of *cis*-(PBu$_3$)$_2$PtCl$_2$. All yields reported are isolated yields.

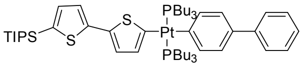
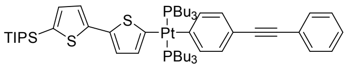
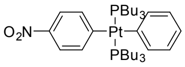
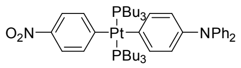
As noted above, preparation of the symmetrical *trans*-disubstituted complexes can be accomplished when the isolated *trans*-monosubstituted complexes (**1a-7a**) are subjected to a second transmetallation reaction using an equimolar amount of aryl-stannane and 10 mol% CuI at room temperature. Temperature was also found to be a key factor in allowing formation of the disubstituted complexes **1b-7b**. In particular, if the reaction is carried out with heating (T > 50°C) the halogen metathesis pathway is favored (giving rise to the corresponding *trans*-(PBu$_3$)$_2$Pt(Ar)I species) and the disubstituted product is not formed. The remaining *trans*-(PBu$_3$)$_2$Pt(Ar)Cl starting complex remains unreacted. This allows assignment of *trans*-

$(PBu_3)_2Pt(Ar)I$ as the thermodynamic product, and the desired disubstituted platinum complexes **1b-7b** as kinetic products.

Regardless of the details concerning the reaction mechanism, the ability to control the reaction to afford mono-substituted complexes **Xa** (when Ar is not thiophene based) offers the opportunity to subject the complexes to reaction with a second aryl stannane to afford platinum aryl complexes with mixed aryl ligands. Thus, as shown in Table 2, we demonstrated this reaction by preparing four mixed ligand complexes, **10-13.** The synthesis of **13** offers additional evidence supplementary to the notion that copper-tin transmetallation step is rate limiting. Specifically, in principle the unsymmetrical bis-aryl complex **13** could be prepared from either **5a** or **6a**. However, it was found that reaction of **5a** with the electron donor substituted aryl stannane **6** does not produce **13** at any reaction temperature. By contrast, complex **6a** reacts smoothly with electron poor aryl stannane **5** at room temperature affording **13** in 45% yield.

**Table 2.** Yields and Structures of Heterodisubstituted Aryl-Platinum Products.

$$\underset{\textbf{Xa}}{trans\text{-}(PBu_3)_2Pt(Ar)Cl} \xrightarrow[\text{DMF, RT, overnight}]{\text{1.2 eq. ArSnBu}_3} \underset{\textbf{10-13}}{trans\text{-}(PBu_3)_2Pt(Ar)(Ar')}$$

| Precursors | | | Platinum Products |
|---|---|---|---|
| **2a** | **9** | **10: 60%** |  |
| **3a** | **9** | **11: 65%** |  |
| **1a** | **5** | **12: 60%** |  |
| **6a** | **5** | **13: 45%** |  |

## Photophysical Properties

During the past two decades, there has been considerable interest in the photophysics of platinum(II) aryl acetylide complexes of the type *trans*-$(PBu_3)_2Pt(CC\text{-}Ar)_2$ due to the strong propensity of the heavy metal center to induce spin-orbit coupling and rapid intersystem crossing to the triplet state.[19-21] Many platinum(II) aryl acetylides undergo intersystem crossing with nearly unit quantum yield and give rise to efficient room temperature phosphorescence from triplet states that are mainly of ligand based $\pi,\pi^*$ character. There is also interest in application of platinum acetylides in non-linear absorption materials and organic electronic devices.[22-26] While there have been a handful of studies on the structurally-related platinum aryl complexes,[9,10] this area has been stymied mainly due to the difficulty of synthesizing these complexes via the aryl-lithium or –magnesium reagents. One of the goals of the present synthetic effort was to expand the range of platinum(II) aryls that are available for photophysical study and in optoelectronic materials application. Thus, in the present study we provide a preliminary survey of the photophysical properties of the complexes that were synthesized in order to provide insight regarding the effect of the platinum center on the excited state properties of the arylene chromophores.

The absorption and emission maxima, molar absorptivity, and fluorescence quantum yields for all of the complexes prepared in this study are listed in Table 3. The UV-visible absorption and emission spectra for selected complexes are illustrated in Figure 1, and the supplementary information contains the remaining spectra of previously unreported complexes. In general, the absorption spectra of the complexes are dominated by intraligand $\pi,\pi^*$ transitions, and the absorption of the disubstituted complexes (**Xb**) is red-shifted slightly relative to the mono-substituted analogs (**Xa**). For example, this trend is easily seen in the spectra for **3a**/**3b** and **7a**/**7b** shown in Figure 1. This red-shift is also observed in families of platinum aryl-acetylide complexes, where it has been attributed to the effect of p$\pi$-d$\pi$ conjugation through the platinum center, with possible contribution from excitonic (J-type) coupling of the transition dipoles on the adjacent conjugated ligands.[27,28] In general, the disubstituted complexes have higher molar absorptivity than their monosubstituted analogues (Table 3) as expected given that the transitions are ligand localized.

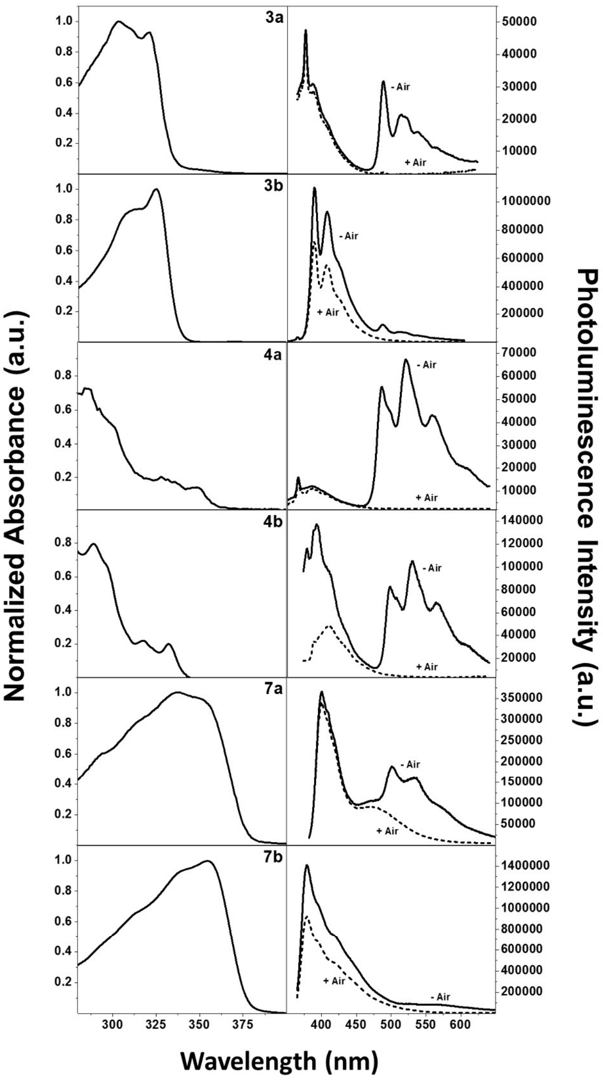


**Figure 1**. Absorption and photoluminescence spectra of complexes **3a,b**, **4a,b**, **and 7a,b** in THF solution; -air is vacuum degassed solutions.

**Table 3.** Summary of Photophysical Properties.

| Complex | Absorption $\lambda_{max}$ (nm)[a] | ε ($M^{-1}cm^{-1}$) | Emission $\lambda_{max}$ (nm) | Flr. QY Φ[b] |
|---|---|---|---|---|
| **1a** | 232 | 62200 | 315 | [c] |
| **1b** | 237 | 51800 | 325 | [c] |
| **2a** | 281 | 32200 | 350 | 0.0075 |
| **2b** | 293 | 87800 | 352, 368 | 0.031 |
| **3a** | 303 | 54300 | 340 | 0.0054 |
| **3b** | 325 | 119000 | 385, 392 | 0.081 |
| **4a** | 240 | 73400 | 380 | 0.0054 |
| **4b** | 247 | 140000 | 379, 392 | 0.023 |
| **5a** | 337 | 19000 | 404 | [c] |
| **5b** | 342 | 32800 | 419 | [c] |
| **6a** | 300 | 29000 | 414 | 0.043 |
| **6b** | 303 | 66600 | 400 | 0.05 |
| **7a** | 337 | 20000 | 380 | 0.013 |
| **7b** | 335 | 95000 | 378 | 0.05 |
| **8a** | - | - | - | - |
| **8b** | 262 | 23700 | 352 | 0.04 |
| **9a** | 350 | 118000 | 412 | 0.089 |
| **9b** | 358 | 77700 | 407 | 0.36 |
| **10** | 353 | 65000 | 415 | 0.054 |
| **11** | 326 | 52300 | 415 | 0.030 |
| **12** | 341 | 19000 | 385 | 0.021 |
| **13** | 306 | 48500 | 360 | 0.013 |

[a] $\lambda_{max}$ may not correspond to the red-most absorption band. [b] In air-saturated THF. [c] $\Phi < 0.001$.

Many of the platinum aryl complexes are luminescent, again from states that are largely intraligand π,π* in nature. In most cases the emission is dominated by fluorescence; however, in some cases phosphorescence is observed from deaerated solutions. For example, as shown in Figure 1, complexes **3a**/**3b**, **4a**/**4b** and **7a**/**7b** exhibit fluorescence that has only a small Stokes shift from the lowest absorption band, and in deaerated solution phosphorescence is observed at longer wavelength. In most cases, the fluorescence quantum efficiency is quite low (< 0.05, Table 3), suggesting that singlet-triplet intersystem crossing is very efficient. The 0-0 energy of the phosphorescence emission corresponds closely with those of the parent aryl systems, suggesting that the triplet states are localized on a single arylene unit, as has been suggested in the platinum acetylide systems.[22,23]

Close inspection of the emission data for the corresponding mono- and di-substituted pairs (**Xa/Xb**) reveals an interesting trend. In particular, the monosubstituted complexes, **1a-9a**, exhibit lower fluorescence quantum yields compared to the disubstituted counterparts, **1b-9b**. In addition, in general for the complexes that display phosphorescence, the phosphorescence emission is more efficient for the mono-substituted complexes (e.g. see **7a/7b**, Figure 1). These trends strongly suggest that spin-orbit coupling is *stronger* in the mono-substituted complexes, which gives rise to more efficient singlet-triplet and triplet-singlet transitions.

In order to provide more insight into the structural basis for this effect, DFT calculations were carried out, and the results provide a possible explanation for these effects as arising from systematic differences in the Pt-C bond lengths in the mono- and di-substituted pairs of complexes. Specifically, the DFT calculations show that in the mono-substituted complexes (**Xa)** the Pt-C bonds are markedly shorter than in the di-substituted complexes (average values 2.036 Å for **Xa** vs. 2.118 Å for **Xb**, see Table 4 for details). The shorter Pt-C bond in the mono-substituted series is presumably due to the different trans effects of the chloride and aryl ligands. In particular, the weaker trans effect of the chloride ligand allows for stronger Pt-C bonding in the mono-substituted complexes.[29,30] When two aryl ligands oppose each with respect to the platinum center, this effect is cancelled out, resulting in a longer Pt-C bond for both aryl ligands and reduced intersystem crossing, as shown by the increased fluorescence quantum yields.

**Table 4.** Pt-C Bond Lengths Calculated by using DFT

| Complex | Bond length (Å) |
|---|---|
| **3a** | 2.0335 |
| **4a** | 2.0363 |
| **7a** | 2.0387 |
| **3b** | 2.1151 |
| **4b** | 2.1178 |
| **7b** | 2.1213 |

Finally, in order to provide further evidence for intersystem crossing in the platinum aryl complexes, nanosecond-microsecond transient absorption (TA) spectroscopy was carried out on the four homoleptic complexes that exhibit ground state absorption at 355 nm (laser excitation wavelength). In each case, the complexes exhibit moderate to intense transient absorption, with lifetimes in the range of 1 – 5 μs, which can be assigned to the triplet excited state (see supplementary information for spectra of **7a**, **7b**, **9a** and **9b**). Where comparison is possible, the triplet absorption spectra of the platinum aryls are nearly the same as those of the corresponding platinum acetylide complexes that contain the same arylene chromophore.[22,23] This highlights the notion that the triplet excited states are localized on a single arylene unit in these complexes. Interestingly, the triplet lifetimes of the platinum aryls are significantly shorter than the in the corresponding platinum acetylides, suggesting that spin-orbit coupling is stronger in the former.

## Summary and Conclusions

In summary, a method for generating organometallic systems of the type $L_2Pt(Ar)Cl$, $L_2PtAr_2$, and $L_2Pt(Ar)(Ar')$ ($L = PBu_3$) starting from *cis*-$(PBu_3)_2PtCl_2$ and an aryl-stannane has been developed, and the basic photophysical properties of a series of these complexes measured. This synthetic method offers the ability to stop at the monosubstituted product under mild reaction conditions, which previous methods have been lacking. The ability to stop the reaction at the monosubstituted product opens a pathway to synthesis of heteroleptic complexes of the type $L_2Pt(Ar)(Ar')$. Despite these advantages, a deactivation pathway exists in which halogen metathesis occurs at the platinum center, deactivating both the copper catalyst and the platinum center to further reaction. Fortunately, this process occurs slowly enough at the described conditions, to give moderate to good yields of a monosubstituted aryl-platinum species. This species can then undergo a homo or heteroligation with a second equivalent of aryl-stannane and fresh CuI catalyst. However, electron donor substituted phenyl stannanes afford low yields under disubstitution conditions.

The photophysical properties of these systems are quite similar to those of their aryl-actylide congeners. Low fluorescence quantum yields are seen for all complexes, indicating that the platinum center efficiently induces intersystem crossing to the triplet state. Interestingly, this effect is weaker in the disubstituted complexes, presumably due to longer platinum-carbon bonds, as shown by DFT calculations. Room temperature phosphorescence was observed for compounds containing ligands with more than a single phenyl unit (**3a,b**, **4a,b**, **7a,b**).

This work once again shows the usefulness of copper in transmetallation pathways, as it has activated a stannane for subsequent transmetallation on a platinum center with monodentate ligands. This results in fewer synthetic steps as well as increased control of stereochemistry about the platinum center. Homo and heteroligated aryl-platinum(II) species can be synthesized via the reaction, including ligands that may not tolerate the harsher conditions found in previous methods, which may give rise to products for use in material applications.

## Experimental

### General Remarks

All reactions were carried out under argon atmosphere. All starting chemicals used for the synthesis of the platinum complexes were purchased from commercial suppliers, and used without additional purification. $K_2PtCl_4$ was purchased from Strem Chemicals. *cis*-$Pt(PBu_3)_2Cl_2$[31], tributyl(phenyl)stannane, [1,1'-biphenyl]-4-yltributylstannane[32], tributyl(4-(phenylethynyl)phenyl)stannane[33], tributyl(naphthalene-2-yl)stannane[34], tributyl(4-nitrophenyl)stannane[14], N,N-diphenyl-4-(tributylstannyl)-aniline[35], 9,9-diethyl-N,N-diphenyl-7-(tributylstannyl)-9-fluoren-2-amine[36], triisopropyl(5'-(tributylstannyl)-[2,2-bithiophene]-5-yl)silane[37] were synthesized according to literature procedures. Solvents were of reagent grade unless otherwise noted. Silica gel (230-400 mesh, 60 Å, Silicycle Inc.) was used for column chromatography. $^1H$ (500, 300 MHz), $^{13}C$ (125, 75 MHz), NMR spectra were recorded on a Varian Inova or Varian Mercury spectrometer, respectively. $^{31}P$ (121 MHz) NMR spectra were recorded only on the Varian Mercury spectrometer. The chemical shifts for $^1H$ and $^{13}C$ were reported in ppm relative to tetramethylsilane (TMS) or residual protonated solvent peaks. 85% $H_3PO_4$ was used as an external reference for $^{31}P$ NMR. Mass spectrometry and elemental analysis were performed by Mass Spectrometry Services and CHN Elemental Analysis Services respectively, both of which are located in house at the University of Florida.

### Absorption and Emission Spectroscopy

Steady–state absorption spectra were recorded on a Varian Cary 50 or a Cary 100 dual–beam spectrophotometer. Corrected steady–state emission measurements were performed on a Photon Technology International spectrophotometer (QuantaMaster). Absorption and fluorescence samples were run in aerated solution, while phosphorescence samples were deaerated with at least four freeze-pump-thaw cycles. Optically dilute samples with O.D. < 0.1 at the excitation wavelength were used. Fluorescence quantum yields were determined by relative actinometry, with quinine sulfate as an actinometer ($\Phi_{Fl} = 0.54$).[38]

### Nanosecond Transient Absorption (TA) Spectroscopy

Measurements were performed on an in–house apparatus that is described in detail elsewhere.[39] The third harmonic of a Continuum Surelite series Nd:YAG laser ($\lambda$ = 355 nm, 10 ns fwhm, 180 µJ–pulse$^{-1}$) was used as the excitation source. Probe light was produced by a xenon flash lamp and the transient absorption signal was detected with a gated–intensified CCD mounted on a 0.18 M spectrograph (Princeton PiMax/Acton Pro 180). Solutions had a matching optical density of 0.7 after a minimum of four freeze-pump-thaw cycles. An initial CCD image capture delay of 50 ns following the laser pulse was used to ensure full conversion to the triplet state before observation. An average of 100 images were acquired.

### Computational Details

DFT calculations were performed in the Gaussian 09, revision C.01[40] suite of programs at the B3LYP level with the 6-31G(d) basis set for C, H, N, 6-31G+(d) for P, S, and SDD for Pt. Phosphine butyl groups were replaced by methyl groups to improve computational efficiency. The ground state structures were optimized in the gas phase from idealized starting configurations without symmetry constraints. The optimized structures were confirmed to be minima by the lack of imaginary frequencies.

### General Procedure for the Formation of Monosubstituted Products (1-9a)

One equivalent of *cis*-$Pt(PBu_3)_2Cl_2$ was dissolved in 10 mL of dry DMF and degassed for 30 minutes. 1.2 equivalents of a corresponding tin compound was then added to the system along with CuI (10 mol% with respect to tin). The solution was then heated to 70°C and stirred for 4 hours. The solvent was then removed in vacuo. Column chromatography was employed to purify the monosubstituted products. Physical data for new monosubstituted complexes can be found in the supplementary information.

### General Procedure for Disubstituted Products (1-9b, 10-13)

One equivalent of *trans*-$PtAr(PBu_3)_2Cl$ was dissolved in 5 mL of dry DMF and degassed for 30 minutes, 1.2 equivalents of a corresponding tin compound was then added to the system along with CuI (10 mol% with respect to tin). The system was stirred at room temperature, overnight, and the precipitated product was filtered off, washed with DMF, and dried under vacuum. Physical data for new homodisubstituted complexes can be found in the supplementary information.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Text, figures, and tables giving experimental procedures and characterization data for all reported complexes. See DOI: 10.1039/b000000x/

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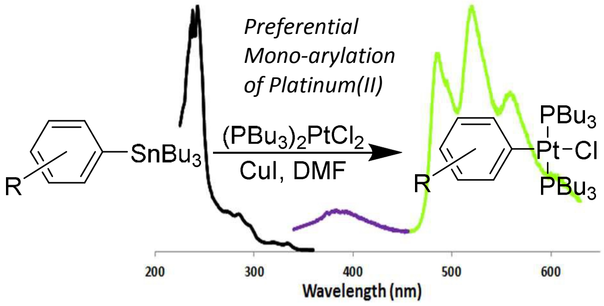
### TOC Graphic



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