EDGE ARTICLE

Suzuki–Miyaura coupling of arylboronic acids to gold(III)†

Ayan Maity,[a] Amanda N. Sulicz,[a] Nihal Deligonul,[a] Matthias Zeller,[b] Allen D. Hunter[b] and Thomas G. Gray*[a]

Gold(III) is prominent in catalysis, but its organometallic chemistry continues to be restricted by synthesis. Metal–carbon bond formation often relies on organometallic complexes of electropositive elements, including lithium and magnesium. The redox potential of gold(III) interferes with reactions of these classic reagents. Resort to toxic metals is common, including reagents based on mercury and thallium. We report that the palladium-catalyzed Suzuki–Miyaura coupling of arylboronic acids extends to cyclometalated gold(III) chlorides. Both monoarylation and diarylation are achieved. We propose a mechanism where oxidative addition to palladium with rearrangement at gold(III) fixes the stereochemistry of monoarylated intermediates. Singly arylated species form as thermodynamic isomers. These entities then go on to form diarylated complexes. Reactions proceed at room temperature, and the products are stable to air, moisture, and chromatography.

Introduction

Organometallic gold chemistry continues its broad advance, and gold(I) catalysis draws preponderant attention.[1–3] Gold(I) is typically redox-neutral. Its catalytic pathways differ fundamentally from those of other transition elements, where sequences of oxidative addition and reductive elimination predominate. Gold is often called the relativistic element. Its heavy-atom character[4–7] transforms the excited-state properties of luminescent gold species.[8–13] Relativistic effects may also modulate the thermal reactivity of gold; this remains a topic of active inquiry.[14] Gold(III) is less investigated, and is fast gaining scrutiny.[15–19]

Contemporary studies find that gold(III) aryl complexes are luminescent, with excited states that are often ligand-localized.[20] Limited syntheses hinder the emergence of organogold(III) chemistry. The major reactions that afford gold(III) complexes having three Au–C σ-bonds are transmetalation reactions from Grignard,[21] organolithium,[22,23] tin,[24–26] or mercury(II) reagents,[27] and oxidative aryl transfer from thallium(III) to gold(I).[28] All of these reagents are hazardous, organolithium and magnesium reagents being pyrophoric, and tin, mercury, thallium complexes being toxic. Substrate scopes are narrow. Gold(III) is oxidizing: $E°(Au^{III}/Au^0) = +1.51$ V in aqueous acid.[29]

[a]Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, USA. E-mail: tgray@case.edu

[b]Department of Chemistry, Youngstown State University, 1 University Plaza, Youngstown, Ohio 44555, USA

Its redox character interferes in reactions with formal carbanion sources. There is a clear need for wider-ranging nonredox transformations that yield organogold(III) species.

Gold–carbon σ-bonds are covalent and modestly polar. The Pauling electronegativities of gold (2.5) and carbon (2.55) are nearly equal. We therefore hypothesized that catalytic carbon–carbon bond-forming reactions might extend to carbon–gold bond formation. Among the most powerful are cross-coupling protocols, such as the Suzuki–Miyaura coupling of organoboron species with organic halides and pseudohalides.[30–40] This reaction is palladium-catalyzed, and a supporting base is normally required. Remarkably, cross-coupling reactions where the desired product is an organometallic complex are little explored.[41–44] Hence, gold(III)–carbon bond formation under palladium catalysis was sought.

Results and discussion

Gold(III) dichloro complex **1** [(tpy)AuCl₂] was chosen as representative. No reaction is observed between **1** and boronic acids without additives. Reactions were screened with a variety of palladium sources, phosphine ligands, and supporting bases; diaryl complexes are targeted. Table 1 summarizes outcomes. All reactions proceeded at room temperature, in contrast to the high-temperature (150 °C) transmetalations of Nevado and coworkers.[45] They contrast also with boron transmetalation to gold(I), for which palladium additives are needless.[46–49] We note that Mankad and Toste have reported carbon–carbon coupling in yields ranging from 0–68% in reactions of fluorogold(III) species with arylboronic acids.[50] Reaction between **1** and *p*-fluorophenylboronic acid in the presence of Pd(PPh₃)₄ and Cs₂CO₃

Table 1 Optimization of reaction conditions for diarylation of dichlorogold(III) complexes[a]
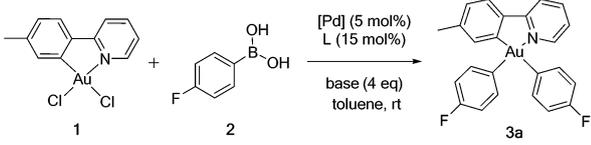
Entry	Catalyst	Ligand (L)	Base	Time (h)	Yield[b] (%) Mono	Di
1	Pd(PPh$_3$)$_4$	None	Cs$_2$CO$_3$	24	60	30
2	Pd(PPh$_3$)$_4$	None	Cs$_2$CO$_3$	48	0	85
3	Pd(PPh$_3$)$_4$	None	K$_2$CO$_3$	16	51	0
4	Pd(OAc)$_2$	None	K$_2$CO$_3$	16	90	0
5	Pd(OAc)$_2$	PPh$_3$	K$_2$CO$_3$	16	38	0
6	Pd(OAc)$_2$	P^{t}Bu$_3$	K$_2$CO$_3$	16	40	60
7	Pd$_2$dba$_3$	Xphos[c]	K$_2$CO$_3$	16	50	44
8	Pd(dppf)Cl$_2$	dppf[c]	K$_2$CO$_3$	16	27	0
9	Pd(OAc)$_2$	dcpe[c]	K$_2$CO$_3$	16	34	0
10	PdCl$_2$	P^{t}Bu$_3$	K$_2$CO$_3$	16	31	0
11	Pd(OAc)$_2$	PCy$_3$	K$_2$CO$_3$	16	49	0
12	Pd(OAc)$_2$	P^{t}Bu$_3$	NaOMe	16	12	47
13	Pd(OAc)$_2$	P^{t}Bu$_3$	KOH	16	25	25
14	Pd(OAc)$_2$	P^{t}Bu$_3$	^{n}Bu$_4$NF	16	0	0
15	Pd(OAc)$_2$	P^{t}Bu$_3$	K$_3$PO$_4$	16	0	88
16	Pd$_2$dba$_3$	PCy$_3$	K$_3$PO$_4$	16	5	86
17	Pd(OAc)$_2$	[HP(^{t}Bu)$_3$]BF$_4$	K$_3$PO$_4$	16	0	90
18	None	[HP(^{t}Bu)$_3$]BF$_4$	K$_3$PO$_4$	16	0	0

[a] Conditions: experiments were performed with **1** (0.05 mmol), **2** (0.125 mmol), Pd catalyst (0.002 mmol), ligand (0.007 mmol), base (0.2 mmol), toluene (5 mL), rt. [b] Yields are based on ^{19}F NMR relative to C$_6$H$_5$F as an internal standard. [c] Xphos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl; dppf = 1,1′-bis(diphenylphosphino)ferrocene; dcpe = 1,2-bis(dicyclohexylphosphino)ethane.

in toluene led, after 24 h, to a mixture of mono- (60%) and di(p-fluorophenyl) complexes (30%), as estimated by ^{19}F NMR spectroscopy, Table 1, entry 1. The diaryl analogue is the exclusive product after 48 h, and shows ^{19}F singlets at δ −120.4 and −119.4 ppm, Table 1, entry 2. A similar reaction using K$_2$CO$_3$ as base led to 51% monoaryl product, Table 1, entry 3. The monoaryl product is recovered in 90% yield without added ligand, showing that L is not obligatory for the first coupling; Table 1, entry 4. A reaction with Pd(OAc)$_2$, tri-(t-butylphosphine), and K$_2$CO$_3$ gave mono- and diaryl products in 40% and 60% yields, respectively, Table 1, entry 6. Changing the supporting base to K$_3$PO$_4$ afforded diaryl product in 88% yield after 16 h; no monoaryl product was observed; Table 1, entry 15.

Use of the air- and moisture-stable phosphonium salt [HP(^{t}Bu)$_3$]BF$_4$ gave the diarylated gold(III) complex in unimpaired yields, Table 1 entry 17; and allowed reaction components to be weighed in open air. (However, reactions proceeded under an argon atmosphere.) Use of the stronger bases NaOMe and KOH gave diminished yields of both products, Table 1 entries 12 and 13. No reaction was observed in the presence of anhydrous ^{n}Bu$_4$NF, Table 1 entry 14.

The reaction accelerated with addition of 2-propanol. With K$_2$CO$_3$ as supporting base, the reaction was complete in 10 h, Table 2 entry 10. With K$_3$PO$_4$, the reaction was completed in 4 h, Table 2, entry 9. The reaction conditions described in Table 2, entry 10, involving K$_2$CO$_3$ were chosen for subsequent work for its higher yield across a variety of boronic acid substrates.

The standardized protocol was applied to the synthesis of a range of gold(III) aryls, Table 3. Aryl groups with electron-withdrawing (**3a–f**), electron-neutral (**3g–l**) and electron-releasing substituents (**3m–o**) were bound to gold. Isolated yields range from 42–78%. Efficiencies are comparable for boronic acids with electron-withdrawing or releasing substituents. Organogold complexes are readily prepared having oxidized substituents that, like gold(III) itself, degrade on treatment with lithium reagents or other formal carbanion sources. The products are purified by column chromatography on basic alumina. They are stable as solids to air and water.

The reaction is specific for auration at borylated carbons. Complexes **3a**, **3c**, **3d**, **3j**, **3l**, and **3n** were characterized by X-ray diffraction crystallography. Thermal ellipsoid diagrams are deposited as ESI.† In each structure, p-tolylpyridyl chelates as a bidentate ligand. Geometric parameters about the metal are within ranges typical of Au(III).[51] Trans-influences of carbon and nitrogen are evident in gold–aryl carbon bond distances. In all instances, the Au–C bond trans to carbon is significantly longer[52] than that trans to nitrogen.

While surveying reaction parameters for diarylation, mono-arylated products were isolated. Complexes **4a** and **4b** were isolated as products of incomplete aryl transfer. ^{1}H NMR experiments show that both products form as a single isomer. The crystal structure of **4a** appears as Fig. 1(a); that of **4b** is provided as ESI.† The p-fluorophenyl ligand binds trans to the pyridyl nitrogen despite the kinetic trans effect. Nevertheless, the observed structure of **4a** is expected to be more stable than diastereomer **4a′** where p-fluorophenyl binds opposite carbon, Fig. 2.

Table 2 Screening of bases and solvents for diarylation of dichlorogold(III) complexes[a]

Entry	Base	Solvent	Time (h)	Yield[b] (%) Mono	Di
1	K$_3$PO$_4$	1,4-Dioxane	16	0	0
2	K$_3$PO$_4$	DMF	16	0	0
3	K$_3$PO$_4$	1% ^{i}PrOH in toluene	16	10	70
4	K$_3$PO$_4$	1% EtOH in toluene	16	30	60
5	K$_3$PO$_4$	THF	16	50	50
6	Li$_3$PO$_4$	Toluene	16	0	0
7	KOH	Toluene	16	30	10
8	K$_2$CO$_3$	10% H$_2$O in THF	16	0	0
9	K$_3$PO$_4$	1 : 1 toluene–^{i}PrOH	4	0	82
10	K$_2$CO$_3$	1 : 1 toluene–^{i}PrOH	10	0	85

[a] Conditions: experiments were performed with **1** (0.05 mmol), **2** (0.125 mmol), Pd(OAc)$_2$ (0.002 mmol), [HP(^{t}Bu)$_3$]BF$_4$ (0.007 mmol), base (0.2 mmol), indicated solvent-solvent mixture (5 mL), rt. [b] Yields are based on ^{19}F NMR relative to C$_6$H$_5$F as internal standard.

Table 3 Gold(III) products and isolated yields. Carbon–gold bonds formed are indicated in red. Et = ethyl; Ph = phenyl
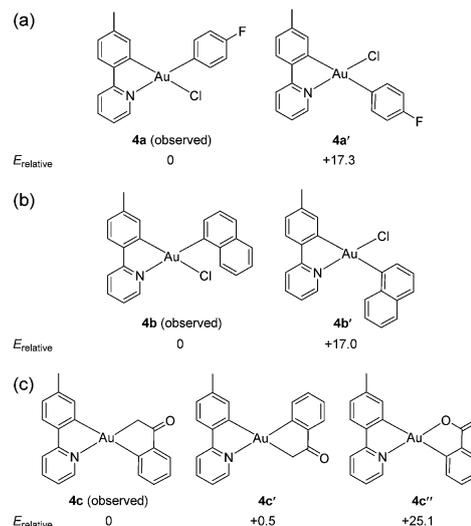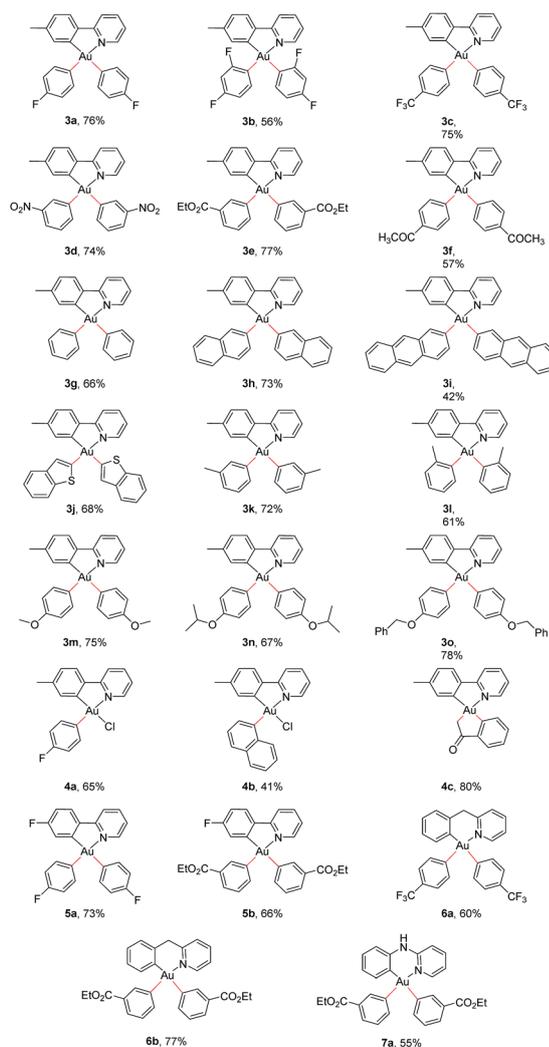
3a, 76% 3b, 56% 3c, 75%
3d, 74% 3e, 77% 3f, 57%
3g, 66% 3h, 73% 3i, 42%
3j, 68% 3k, 72% 3l, 61%
3m, 75% 3n, 67% 3o, 78%
4a, 65% 4b, 41% 4c, 80%
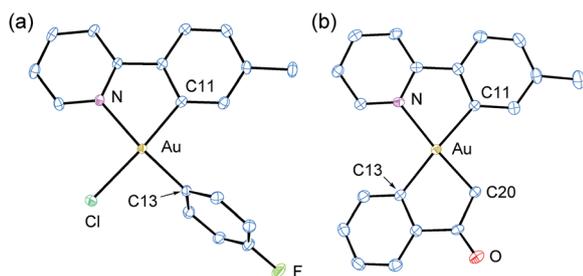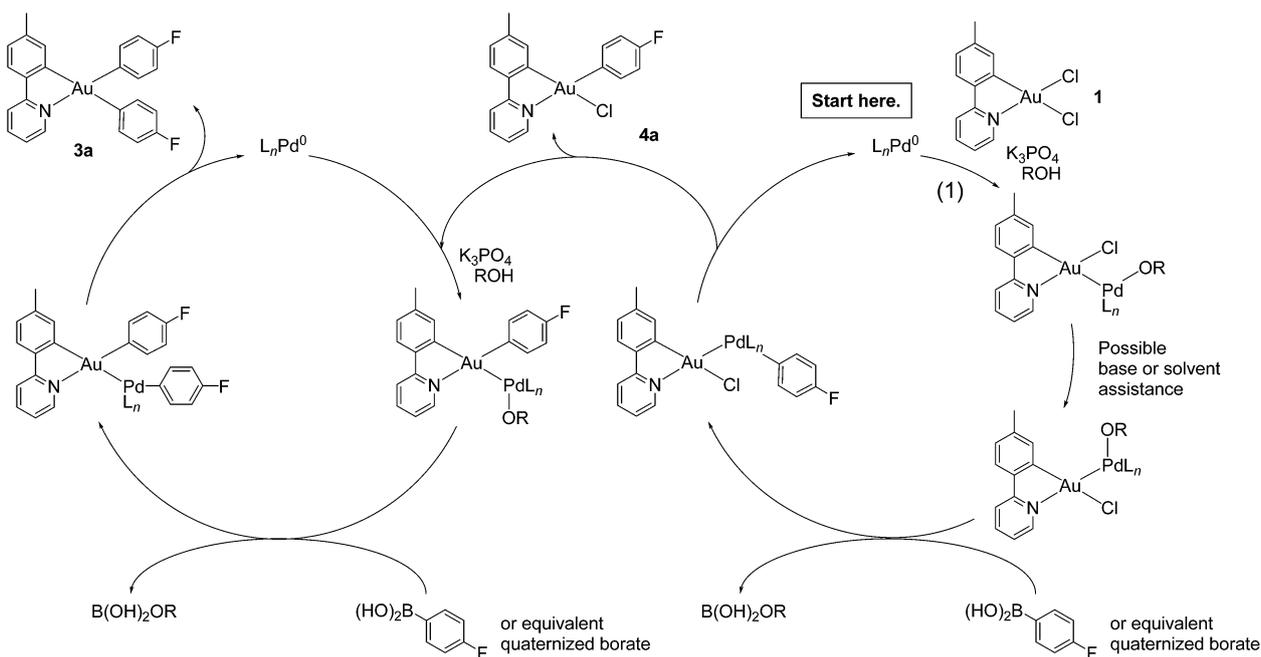5a, 73% 5b, 66% 6a, 60%
6b, 77% 7a, 55%

Fig. 1 (a) Crystal structure of p-fluorophenyl complex **4a**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Unlabeled atoms are carbon. Selected interatomic distances (Å): C11–Au, 2.023(4); Au–N, 2.116(3); C13–Au, 2.018(4); Au–Cl, 2.3707(9). Selected angles (°): N–Au–C11, 81.05(14); C13–Au–Cl: 91.07(10). (b) Crystal structure of C-enolate **4c**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Unlabeled atoms are carbon. Selected interatomic distances (Å): C11–Au, 2.058(5); Au–N, 2.134(4); C13–Au, 2.080(5); C20–Au, 2.041(6). Selected angles (°): N–Au–C11, 79.62(18); C13–Au–C20, 80.8(2).

Fig. 2 Relative energies in kcal mol^{-1} calculated for (a) mono-p-fluorophenyl isomers **4a** and **4a'**; (b) mono-1-naphthyl isomers **4b** and **4b'**; and (c) enolate complexes **4c**, **4c'**, and **4c''**. Energies are calculated from sums of electronic and thermal free energies.

Density-functional theory (DFT) calculations using the parameter-free hybrid functional of Perdew, Burke, and Ernzerhof[53] were used to evaluate the relative thermochemistry of isomers. The calculations indicate that **4a** is 17.3 kcal mol^{-1} more stable than **4a'** with *trans*-disposed carbons, Fig. 2. Results are similar for 1-naphthyl complex **4b** (Table S1, ESI†). Hence, binding of the first aryl ligand selects for the thermodynamic product.

The stereochemistry of **4a** and **4b** is surprising in that the aryl ligand is *trans* to nitrogen. If arylation proceeds in a single step, then the *shorter* Au–Cl bond ostensibly breaks first. Attempts to grow single crystals of **1** failed. However, the structure of the related complex dichloro(2-(4-fluorophenyl)-pyridine)gold(III) was obtained. This complex differs from **1** in that fluorine substitutes for methyl in the C^N ligand. The structure (ESI†) shows a longer Au–Cl bond *trans* to carbon. Pertinent interatomic distances are 2.3750(15) Å for Au–Cl *trans* to C and 2.2721(17) Å for Au–Cl *trans* to N. Thus, the shorter Au–Cl bond opposite nitrogen is sacrificed in the first arylation.

Geometry optimization of [(tpy)Au^{III}Cl]$^+$ fragments tells against a limiting dissociative mechanism initiated by chloride loss. Energy minimization of [(tpy)Au^{III}Cl]$^+$ leads to a T-shaped structure where the space *trans* to carbon is empty. An incoming ligand is expected to attack this open site, leading to a stereochemistry unlike that observed. The aryl ligands in **4a** and **4b** are opposite nitrogen. We therefore propose transmetalation by an associative or associative interchange mechanism, possibly mediated by palladium, that avoids mutually *trans* carbon atoms and leads to the thermodynamic isomers **4a** and **4b**.

Reactions of **1** with (2-acetylphenyl)boronic acid yielded the singly arylated **4c**. ^{1}H and ^{13}C NMR spectra indicate a single species in solution. This complex is a C-bound enolate stabilized by chelation of the benzene ring. The pK_a of acetophenone is 24.7 in dimethyl sulfoxide.[54] Deprotonation of the α-carbon

Scheme 1 Proposed mechanism of gold(III) monoarylation (right cycle) and subsequent diarylation (left cycle).

atom may simply result from the action of base. Vapor diffusion of pentane into dichloromethane solution afforded diffraction-quality crystals. The structure of **4c** appears in Fig. 1(b). The sp³-hybridized carbon atom lies *trans* to the pyridyl nitrogen of the tpy ligand. A ν(CO) stretching frequency at 1666 cm^{-1} and a ^{13}C{^{1}H} NMR resonance at δ 209 ppm both indicate retention of the C-bound enolate geometry. It is noteworthy that gold(III) binds to the softer carbon, rather than oxygen, as is common for oxidized metals of the earlier d-block.[55,56]

DFT calculations find that the C-bound enolate is some 25.1 kcal mol^{-1} more stable than the O-bound tautomer. Observed **4c** is virtually isoenergetic with the –C-bound "flipped" enolate where sp³-hybridized carbon binds opposite the tpy tolyl carbon. Line drawings and relative energies appear as in Fig. 2(c). Experimentally, a single complex is recovered, not a mixture, suggesting that the reaction is specific for **4c**.

A potential mechanism for the formation of **3a–o** appears in Scheme 1. Oxidative addition of **1** to palladium(0) presumably occurs at the longer Au–Cl bond *trans* to carbon. Rearrangement follows, possibly through a five-coordinate intermediate that pseudorotates.[57,58] Formation of a palladium alkoxide or hydroxide intermediate precedes transmetalation from boron, in keeping with results from Hartwig, Amatore, Jutand, and their respective co-workers.[59–61] Reductive elimination[62] yields monosubstituted products with the stereochemistry established for **4a** and **4b**. Singly arylated products re-enter the catalytic process, undergo transmetalation and reductive elimination, and emerge as diaryls. Experiments that test this hypothesis are underway.

Conclusions

We report catalytic arylation of gold(III) through Suzuki–Miyaura couplings at room-temperature. The reaction is

palladium-mediated and requires an assisting base; the electrophilic reacting partner is a cyclometalated gold(III) dichloro complex. Screening experiments show that palladium(II) acetate is an effective catalyst precursor when combined with potassium phosphate and tri-(*t*-butylphosphine). The phosphine is conveniently delivered as an air- and moisture-stable phosphonium tetrafluoroborate salt. Variously substituted arylboronic acids couple to gold in similar yields. An *ortho*-substituted enolizable ketone leads to a C-bound enolate, without continuing to form a diaryl. Spectroscopic characterization of the enolate complex indicates that a single product forms. Crystal-structure determination shows that the sp³-hybridized carbon binds opposite the pyridyl nitrogen, and a phenyl carbon binds *trans* to the tolyl carbon of the C^N ligand. DFT calculations find the C-enolate to be more stable than an O-bound tautomer.

Compounds **4a** and **4b** are singly arylated products that were characterized structurally. Spectral data indicate a single isomer of each in solution. Both crystal structures show aryl substitution *trans* to the C^N *nitrogen* atom. This stereospecificity is counterintuitive given the *trans*-influence of carbon: the shorter Au–Cl bond disappears first. We propose that oxidative addition of an Au–Cl bond to palladium happens *trans* to the tolyl carbon of the C^N ligand. Rearrangement yields the more stable isomer, with a gold–carbon bond *trans* to nitrogen. Reductive elimination generates monoaryls of the observed stereochemistry and liberates palladium. The monoaryl product, if not isolated, can then re-enter the catalytic sequence to yield diaryls. The photophysical properties of gold(III) aryls are being investigated, as are extensions to other gold complexes and to other metals.

Experimental

Synthesis of [(tpy)Au(p-C₆H₅F)₂] (3a)

In a 100 mL Schlenk flask, Pd(OAc)₂ (2.6 mg, 0.011 mmol) was dissolved in 10 mL dry toluene under argon. [HP(ᵗBu)₃]BF₄ (9.9 mg, 0.034 mmol) and K₂CO₃ (128 mg, 0.917 mmol) were added, resulting in a pale yellow solution that was allowed to stir for 5 min at room temperature under argon. To this solution was added **1** (100 mg, 0.229 mmol) followed by 4-fluorophenylboronic acid (80.2 mg, 0.573 mmol) and 10 mL dry 2-propanol. The reaction mixture was degassed in three freeze-pump-thaw cycles. Finally the reaction mixture was sealed and left stirring for 10 h at room temperature. Reaction progress was monitored by TLC. After the reaction was complete, the volatiles were removed under reduced pressure. The resulting crude product was re-dissolved in 10 mL methylene chloride and was passed through a plug of Celite. The volume of solvent was reduced, and the crude mixture was then purified by a short basic-alumina column using variant polarity between hexanes and hexanes–diethyl ether (1 : 3, v/v). The desired product was eluted using hexanes–diethyl ether (1 : 2, v/v). Removal of solvent left a white solid, which was dried under vacuum for 6 h. Yield 96 mg (76%); TLC (hexanes–diethyl ether, 40 : 60 v/v): $R_f =$ 0.68; ^{1}H NMR (400 MHz, CD₂Cl₂): δ 8.06 (dt, $J =$ 5.9, 1.0 Hz, 1H), 7.95 (d, $J =$ 4.7 Hz, 2H), 7.71 (d, $J =$ 8.1 Hz, 1H), 7.45 (d, $J =$ 6.7 Hz, 1H), 7.43 (d, $J =$ 6.5 Hz, 1H), 7.40 (d, $J =$ 6.1 Hz, 1H), 7.37 (d, $J =$ 6.1 Hz, 1H), 7.18 (q, $J =$ 2.6 Hz, 1H), 7.09 (dd, $J =$ 8.1, 1.2 Hz, 1H), 7.02–6.90 (m, 4H), 6.78 (d, $J =$ 1.1 Hz, 1H), 2.22 (s, 3H); ^{19}F NMR (376.1 MHz, CD₂Cl₂): δ −119.4 (m, 1F), −120.4 (m, 1F); UV/Vis (methylene chloride): λ_{max}, nm (ε, M^{-1} cm^{-1}) 272 (sh, 31 000), 329 (12 000); emission (methylene chloride): λ_{em}, nm (int.) 467 (170), 494 (199); analysis (calcd, found for C₂₄H₁₈AuF₂N): C (51.90, 52.21), H (3.27, 3.31), N (2.52, 2.88).

Acknowledgements

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