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Palladium-catalysed direct arylation of a tris-cyclometallated Ir(III) complex bearing 2,2′-thienylpyridine ligands: a powerful tool for the tuning of luminescence properties†

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Palladium-catalysed direct 5-arylation of metallated thiophenes of *fac*-Ir(N^$C^{3'}$-thpy)$_3$ with aryl bromides *via* C–H bond functionalisation allows the synthesis of a variety of new Ir complexes in only one step (thpyH = 2,2′-thienylpyridine). The method offers simple modification of the nature of the ligand and hence of the photophysical properties of such complexes.

Palladium-catalysed C–H bond activation/functionalisation is a powerful tool to access fine chemicals. However, it has apparently never been applied to metallated ligands as a strategy to access new luminescent materials. Charge-neutral, tris-cyclometallated iridium(III) complexes of the form Ir(N^C)$_3$ bearing 2-(hetero)-arylpyridines, including 2,2′-thienyl-pyridine (thpy), exhibit long lifetimes and high emission quantum yields,[1–3] making them efficient phosphorescent components for OLEDs and other applications (Fig. 1).[4]

Normally, the tuning of the absorption and emission properties of such complexes requires the preparation of a variety of substituted ligands before complexation, and no straightforward general route is available. Such ligands can be synthesized using Stille,[5] Negishi,[6] or Suzuki[7] cross-coupling reactions as the key step before coordination to iridium(III). However, subsequent access to the tris-cyclometalated complexes usually requires drastic reaction conditions (~200 °C), which are incompatible with ligands bearing thermally unstable functional groups.[2] Therefore, to overcome these limitations, a straightforward and selective method for the *in situ* functionalisation of iridium complexes is highly desirable.

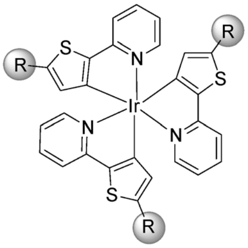
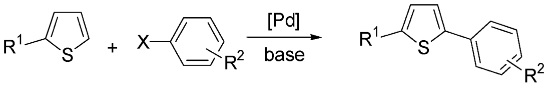


Fig. 1 Generic structure of an Ir(N^C)$_3$ complex incorporating 2,2′-thienylpyridine-based ligands.



Scheme 1 Arylation of thiophenes by C–H bond activation.

One possible strategy would be the so-called "direct arylation", involving regioselective C–H bond functionalisation of thiophenes.[8,9] In 1990, Ohta *et al.* reported the arylation of thiophenes or furans with aryl halides, *via* a direct C–H bond activation, in moderate to good yields using 5 mol% Pd(PPh$_3$)$_4$ as the catalyst (Scheme 1).[10]

Since these results, the palladium-catalysed direct arylation of heteroaryl derivatives with aryl halides or triflates has proved to be a powerful method for the synthesis of arylated heterocycles.[11] This reaction appears to be more attractive than palladium catalysed Suzuki, Stille or Negishi cross-couplings,[12] as no prior preparation of an organometallic derivative and its transmetallation product using B(OR)$_3$, XSnR$_3$, or ZnX$_2$ is required. In this context, Ir(N^$C^{3'}$-thpy)$_3$, **1**,[3] should represent an attractive building block for accessing—in only one step—a wide variety of new complexes which might display useful luminescent properties (Scheme 2).

We report here that this approach offers straightforward access to luminescent tris-cyclometallated iridium complexes bearing 5-aryl-2-pyridylthiophene ligands. A substantial modulation of the excited-state properties of the family of new complexes **2c–9c** has been achieved through the introduction of the aryl groups.

First, we attempted to promote the coupling of complex **1** with 4-bromobenzonitrile in the presence of Pd(OAc)$_2$ as the catalyst and KOAc as the base (Scheme 2).

We selected a phosphine-free catalyst for such reactions in order to avoid a possible decomposition of the iridium complexes by ligand exchange with phosphines. We observed that such phosphine-free reaction conditions, previously operative

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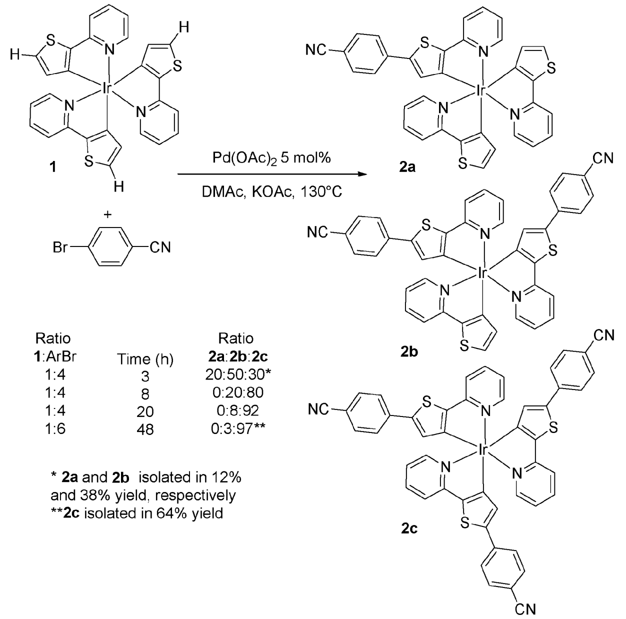


Ratio 1:ArBr	Time (h)	Ratio 2a:2b:2c
1:4	3	20:50:30*
1:4	8	0:20:80
1:4	20	0:8:92
1:6	48	0:3:97**

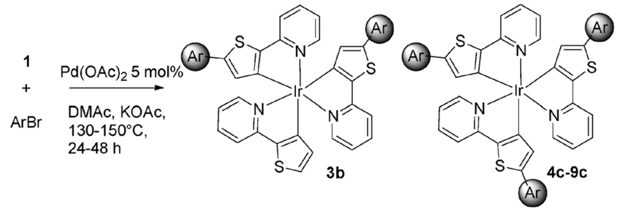
* **2a** and **2b** isolated in 12% and 38% yield, respectively
****2c** isolated in 64% yield

Scheme 2 Arylation of the thiophene unit of *fac*-Ir(thpy)$_3$ by C–H bond activation, leading to hetero- and homoleptic complexes.

on various thiophene derivatives,[11g] can be directly applied to the metallated (double l) thiophene of *fac*-Ir(thpy)$_3$ **1**. The reaction of 4-bromobenzonitrile with **1** afforded the expected tris-heteroarylated product **2c**. Interestingly, both the reaction time and ratio of reactants were found to have a dramatic influence on the product distribution. The highest selectivity and yield in favour of the formation of **2c** were observed at 150 °C after 48 h. When we employed shorter reaction times (3 or 8 h) and a lower reaction temperature (130 °C), complexes **2a** and **2b** could be obtained.

Then, the scope of this reaction was examined using a variety of other aryl bromides and heteroaryl bromides (Table 1). Electron-deficient *para*-substituted aryl bromides, 4-(trifluoromethyl)-bromobenzene and 3,5-bis(trifluoromethyl)bromobenzene, gave the desired 5-arylated thiophene complexes **4c** and **5c** in 48% and 63% yield, respectively (Table 1, entries 2 and 3). On the other hand, complex **3c** from 4-bromonitrobenzene could not be easily isolated in pure form owing to its very low solubility. Only complex **3b** could be purified by column chromatography. To optimise the yield of this diarylated complex, the reaction was stopped after 24 h instead of 48 h, giving **3b** in 50% yield (Table 1, entry 1). With 1- or 2-bromonaphthalene as the coupling partners, the desired tris-arylated complexes **6c** and **7c** were obtained, albeit in relatively low yields (Table 1, entries 4 and 5). The procedure thus seems to be more efficient when electron-deficient aryl bromides are employed. This might be the result of easier oxidative addition of such aryl bromides to palladium. Finally, we examined the reaction with the two heteroaryl bromides, 3-bromopyridine and 5-bromopyrimidine. In both cases, the desired tris-heteroarylated complexes **8c** and **9c** were obtained in relatively good yields of 52% and 56% respectively (Table 1, entries 6 and 7).

Table 1 Direct arylation of **1** with aryl bromides



Entry	Aryl bromide	Product	Yield (%)
1	4-Bromonitrobenzene	**3b**	50[a]
2	4-(Trifluoromethyl)bromobenzene	**4c**	48
3	3,5-Bis(trifluoromethyl)bromobenzene	**5c**	63[b]
4	2-Bromonaphthalene	**6c**	20
5	1-Bromonaphthalene	**7c**	26
6	3-Bromopyridine	**8c**	52[b]
7	5-Bromopyrimidine	**9c**	56

Conditions: catalyst: Pd(OAc)$_2$ (0.05 mmol), aryl bromide (6 mmol), **1** (1 mmol), KOAc (6 mmol), DMAc, 130 °C, 48 h, under argon, isolated yields. [a] 24 h. [b] 150 °C.

The photophysical properties of selected complexes **2a–c**, **4c**, **5c**, and **8c** were investigated by means of absorption and emission spectroscopy in CH_2Cl_2 solution (Table 2). The absorption spectra of the four new homoleptic complexes **2c**, **4c**, **5c** and **8c** are shown in Fig. 2, together with that of **1** for comparison. It can be seen that the aryl-functionalised complexes have similar absorption profiles to one another, but they differ from **1** in that they display stronger, well defined bands in the long-wavelength portion of the spectrum, one at around 420 nm and a second at around 480 nm. The extinction coefficients, ε, of these bands increase with increasing electron-withdrawing ability of the aryl *para*-substituent (*viz.* $p\text{-}C_6H_4\text{–}CF_3 < p\text{-}C_6H_4\text{–}CN$). Moreover, by comparison of the trio of complexes **2a–c**, the increase in extinction coefficients of the new bands is seen to correlate with the number of aryl groups introduced (overlaid absorption spectra for these three complexes—with one, two and three cyanophenyls—are shown in Fig. S1, ESI†). Notably, complex **2a** shows *two* bands in the 300–350 nm region, of which the higher-energy is evidently associated with the non-functionalised thpy ligands and the lower with the aryl-appended ligand.†

All of the complexes are luminescent in solution at room temperature (Fig. 3). Compared to the starting species **1**, the complexes show a strong bathochromic shift of the well-resolved 0–0 band, up to 125 nm for **2c**. The quantum yields are substantially lower than for **1** and the lifetimes somewhat shorter. Increased non-radiative decay would be anticipated for the lower-energy excited states, but an estimate of the radiative (k_r) and non-radiative (Σk_{nr}) decay constants from the quantum yield and lifetime data suggests that not only is there an increase in Σk_{nr}, but also a decrease in k_r upon arylation (Table S1, ESI†). This effect can be attributed to the more extended conjugated system in the new complexes, such that the influence of the metal in promoting intersystem crossing through the spin–orbit coupling effect is reduced.[13] A predominantly ligand-centred $^3\pi\text{–}\pi^*$ assignment seems appropriate, supported by the lack of significant influence of temperature on the emission maxima; spectra at 77 K are shown in Fig. S2 (ESI†). The heteroleptic complexes **2a** and **2b** show identical spectra to **2c**, indicating that the lowest-energy state (*i.e.* the emissive state) is associated with the functionalised ligand, consistent with the difference in emission energy between **2c** and **1**.

In summary, we have demonstrated that 2,2′-thienylpyridine ligands coordinated to iridium(III) can be directly arylated with a

Table 2 Photophysical data of selected Ir complexes in CH_2Cl_2 at 298 K

Complex	Absorption λ_{max}/nm (ε/M^{-1} cm^{-1})	Emission λ_{max}/nm	τ/μs	$\Phi_{lum} \times 10^2$
1	300 (35 500), 343 (15 900), 398 sh (11 900)	548, 592, 643 sh	7.1	40
2a	303 (35 600), 346 (40 500), 416 (19 500), 485 sh (5290)	677, 742, 812 sh	1.1	0.84
2b	344 (57 400), 425 (27 000), 484 sh (9150)	676, 740, 813 sh	1.3	0.81
2c	340 (75 700), 426 (36 800), 486 sh (13 200)	673, 738	1.5	1.1
4c	322 (69 900), 411 (30 500), 476 sh (11 700)	652, 712, 795 sh	2.4	2.0
5c	322 (53 400), 411 (23 300), 477 sh (8700)	654, 714, 798 sh	2.1	1.7
8c	326 (42 900), 408 (19 100), 472 sh (8020)	645, 703, 784 sh	2.8	1.9

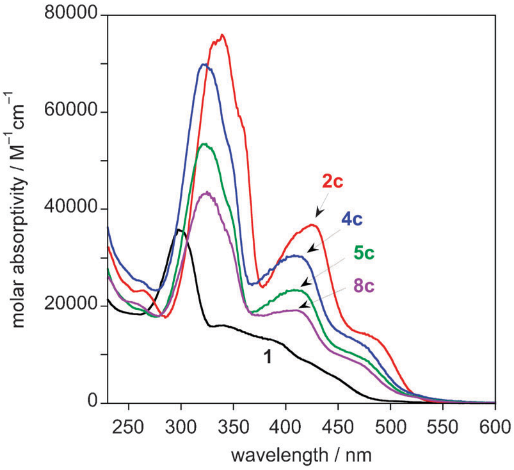


Fig. 2 UV-visible absorption spectra of complexes **1**, **2c**, **4c**, **5c** and **8c** in CH_2Cl_2 solution at 298 K.

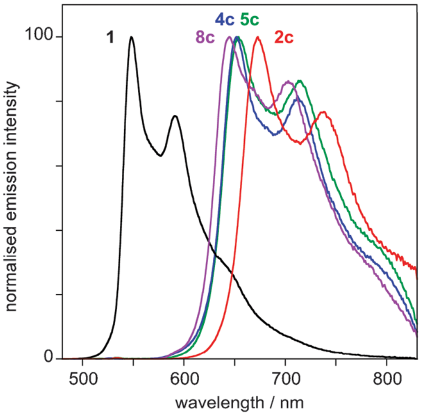


Fig. 3 Emission spectra of complexes **1**, **2c**, **4c**, **5c** and **8c** in CH_2Cl_2 solution at 298 K.

variety of aryl bromides using a $Pd(OAc)_2$ catalyst. The thiophene ring was regioselectively arylated at the C^5 position. This method provides facile access to arylated Ir complexes under mild reaction conditions. Moreover, it should be noted that a range of functionalities such as nitrile, nitro or trifluoromethyl on the aryl bromide are tolerated. Such functional group tolerance allows the easy modification of the electronic structures and, as a consequence, the photophysical properties of the molecules. We anticipate that these Pd-catalysed syntheses will provide a powerful new tool for the preparation of novel light-emitting materials.

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