Electrophilic functionalization of a cyclometallated ruthenium complex, an easy entry to new organometallic synthons

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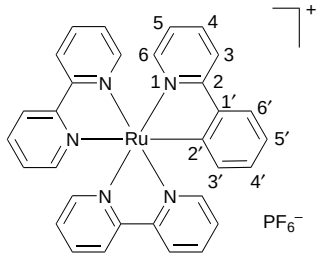
With the regiospecific halogenation of the complex [Ru(bpy)$_2$L^1]$^+$ (bpy = 2,2′-bipyridine, HL^1 = 2-phenylpyridine) new organometallic starting materials are now available.

Our long lasting interest into dinuclear mixed valence complexes originates from the fact that they are the best chemical models of molecular wires, the basic function of molecular electronics. Indeed, a simple spectroscopic study of the intervalence transition gives directly the ability of the bridging ligand to couple the two metallic centers.[1] Since it is usually achieved by a redox titration, the various species (reduced, mixed valence or oxidized) have to be stable for a long period of time, typically up to 1 h. Ruthenium cyclometallated complexes with a N_5C donor set were found to be among the best metallics ends for such purpose.[2]

In a recent report, the synthesis of such polynuclear complexes involved as 'building block' a brominated cyclometallated RuN_5C complex, which was prepared from a bromine containing ligand.[3] Such a synthesis could be advantageously shortened by a direct and regioselective halogenation of the metallated ligand *i.e.* after the complex is prepared.



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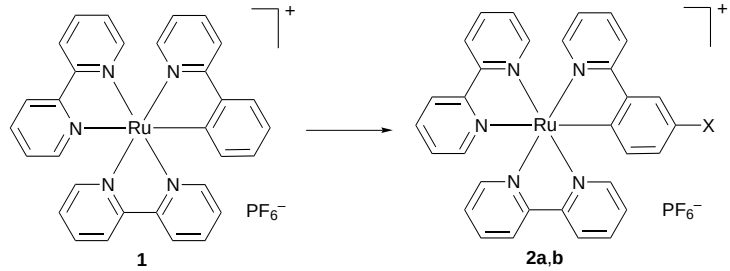
Apart from the typical cathodic shifts of all the redox potentials compared to the RuN_6 family,[4,5] few chemical properties of RuN_5C cyclometallated complexes have been reported. The presence of the C–Ru bond promotes oxidative dimerization,[5,6] but also nitration[3] or chlorination (albeit in low yield).[7] Since the cyclometallated analogue of [Ru(bpy)$_3$]$^{2+}$, *i.e.* [Ru(bpy)$_2$L^1]$^+$, was readily accessible from commercially available chemicals,[4] a systematic study of the electrophilic bromination and iodination of the complex [Ru(bpy)$_2$L^1]PF$_6$ **1** was undertaken on a preparative scale and the reactivity of the resulting complexes under Sonogashira alkynylation reaction was studied. We would like to report here our findings on these points.

Theoretical calculations using extended Hückel theory were first performed in an analogous manner as for [Ru(terpy)(dpb)]$^+$ [dpb = 1,3-bis(2-pyridyl)benzene].[8] As for this complex the HOMO was found to be not only mostly located on the metallated phenyl ring but also having an important coefficient on the C$^{5'}$.‡ Owing to its low oxidation potential (0.5 V *vs.* SCE) and rather high sensitivity to acidic medium, buffered, mildly oxidizing electrophilic conditions were selected.

Upon treatment of the complex with 1.1 equiv. of *N*-bromosuccinimide in MeCN at room temperature[9] and after a hydrazine quench, a single compound was isolated as a PF_6 salt by column chromatography (SiO_2/CH_2Cl_2). It was identified by FABMS as the expected bromo-substituted complex [Ru(bpy)$_2$L^2]PF$_6$ **2a**. Eventually the regioselectivity of the substitution was recognised by ^{1}H NMR spectroscopy since the pattern associated with the very shielded core hydrogen H$^{3'}$ was clearly simplifed. The bromination, easily scaled up, did not require anhydrous or anaerobic conditions to proceed and occurred within 4 to 6 h (Scheme 1).§

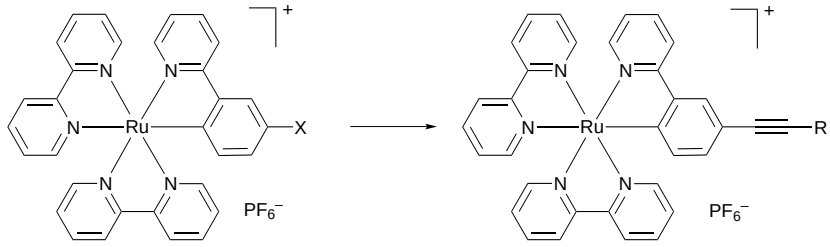
This result prompted us to prepare the iodo analogue, more interesting from a synthetic point of view. Surprisingly NIS[10] was found to be unreactive or lead to complex degradation in MeCN respectively at room or reflux temperature. We found that complex oxidation could be limited by using CH_2Cl_2 as solvent, the best iodinating agent being I_2/PhI(OAc)$_2$, at room temperature for 4 h.[11] Finally, column chromatography purification (SiO_2) after anion exchange using a 'basic eluent' $CHCl_3$–Et_3N–EtOH gave a reproducible isolated yield of *ca.* 50% of [Ru(bpy)$_2$L^3]PF$_6$ **3a**.

As expected, the electron-withdrawing nature of the substituent induced an anodic shift with respect to parent complex **1** for the Ru^{III}–Ru^{II} redox couple of complexes **2a** and **2b** (Table 1). Reactivity of complexes **2a** and **2b** towards Sonogashira's alkynylation [Pd(PPh$_3$)$_4$, CuI, Et_3N, DMF] was then investigated with protected acetylene, *i.e.* trimethylsilylacetylene and 3-methylbut-3-yn-2-ol, as substrates (Scheme 2). In all cases, compounds were isolated as PF_6 salts by column chromatography. A marked difference between **2a** and **2b** was observed



1 **2a**,**b**

Scheme 1 *Reagents and conditions*: X = Br: NBS, MeCN, room temp., 6 h, 95%, **2a**; X = I: PhI(OAc)$_2$, I_2, CH_2Cl_2, room temp., 6 h, 50%, **2b**



Scheme 2 *Reagents and conditions*: i, **2a**, DMF, Et_3N, CuI, $Pd(PPh_3)_4$, 80 °C, 18 h, 80%; ii, **2b**, DMF, Et_3N, CuI, $Pd(PPh_3)_4$, 20 °C, 18 h, 80%

Table 1 Ru^{III}–Ru^{II} redox couples *vs.* SCE (MeCN, 0.1 M $NBu^n_4PF_6$, Pt)

Complex	E^0 (Ru^{III}–Ru^{II})/mV
$[Ru(bpy)_2(L^1)]PF_6$ **1**	464
$[Ru(bpy)_2(L^2)]PF_6$ **2a**	520
$[Ru(bpy)_2(L^3)]PF_6$ **2b**	498

since the iodo complex reacted at room temperature with both alkynes, while the bromo complex required at least heating to 80 °C. Furthermore **2a** did not react with silylated acetylene ($SiMe_3$ or $SiEt_3$). These results, in sharp contrast with a RuN_6 analogue developed by Tzalis and Tor,[12] might indicate that the limiting step is the oxidative addition of the C–Br bond on the Pd^0 complex.

Hence we have shown that, despite the possibility of over-oxidation of the metal center, the presence of the C–Ru bond not only activates the metallated aromatic ring towards electrophilic substitution but also controls its regioselectivity. This *a posteriori* functionalization provides a simple and unique entry to synthetically interesting synthons which would have been difficult to prepare otherwise, especially for the iodo complex **2b**. We are currently studying their reactivity as building blocks in the preparation of more sophisticated architectures such as molecular wires or switches.

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Notes and References

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‡ Since the HOMO is very close in energy to the two other orbitals belonging to the t_{2g} set of low-spin d^6 Ru^{II}, more complete information is given by the examination of net charges borne by carbon atoms, because they are determined by all occupied orbitals. Thus for carbon atoms *para* to pyridine nitrogens, values near +0.06 are found, while the carbon atom *para* to the C–Ru bond exhibits a −0.09 charge, confirming its better reactivity towards electrophiles. Calculations were performed with the CACAO program (CACAO PC Version 4.0, July 1994. C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399 using −12.0 eV for Ru 4d energy). A related calculation by the Fenske Hall method has been reported (E. C. Constable and C. E. Housecroft, *Polyhedron*, 1990, **9**, 1939).

§ *Selected analytical data* for **2a**: ^{1}H NMR (CD_3CN, 250 MHz, $SiMe_4$): δ 6.36 (d, 1 H, 8.0 Hz), 6.93 (dd, 1 H, 8.0, 2.1 Hz), 6.97 (td, 1 H, 6.5, 1.4 Hz), 7.22 (td, 3 H, 6.6, 1.3 Hz), 7.41 (td, 1 H, 7.0, 1.2 Hz), 7.60 (dd, 1 H, 5.7, 1.3 Hz), 7.66–7.88 (m, 7 H), 7.94–8.10 (m, 4 H), 8.30 (dd, 2 H, 8.0, 3.4 Hz), 8.39 (d, 1 H, 8.0 Hz), 8.46 (d, 1 H, 8.2 Hz). Anal. Calc. for $C_{31}H_{23}BrF_6N_5RuP$, C, 47.04; H, 2.93; N, 8.85. Found: C, 46.94; H, 3.25; N, 8.66%. FABMS (NBA matrix) *m*/*z*: 648 $(M - PF_6)^+$, calc. 646.5.

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