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Synthesis of aromatic ruthenabenzothiophenes *via* C–H activation of thiophenes†

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The first ruthenabenzothiophenes have been achieved *via* the C–H activation of thiophene. These species feature high thermal stability and resistance of a moderate oxidant, which constitute valuable addition to the rare metallaaromatic containing second-row transition metals.

Metallaaromatics are organometallic compounds derived from the formal replacement of a (hydro)carbon unit in conventional aromatic hydrocarbons with a transition-metal fragment.[1] Since the seminal prediction of archetypal metallabenzenes by Thorn and Hoffmann in 1979,[2] the synthesis of monocyclic and polycyclic metallaaromatics has been achieved by various methodologies during the past decades. Metallaaromatics are now regarded as an attractive part of the much larger family of compounds classified as heteroaromatics, not only their special structural features but also interesting chemical and physical properties can be exhibited.[3] Although great efforts have been made to synthesize such aromatic complexes, only a limited number has been described in those with a metal of the first or the second transition series.[4–7] Most of such species feature the coordination of the aromatic metallacycle to another metal fragment.[4,5] Non-metal-coordinated metallaaromatics containing a first-row or second-row transition metal are quite rare, although examples of these species have been detected spectroscopically at low temperature in 1995.[6] We have made an entry into this category with the synthesis of the first ruthenabenzene bearing phosphonium substituents by the reaction of $RuCl_2(PPh_3)_3$ with HC≡CCH(OH)C≡CH.[7] The tethered ruthenabenzenes synthesized by Wright *et al.* constitute another addition to this category.[8]

Our efforts to expand the metallaaromatic family have led to the discovery of osmanaphthalene and osmanaphthalyne,[9] which have been synthesized by intramolecular C–H activation of benzene. Recently, a number of ruthenium complexes have been identified as efficient and powerful catalysts for sp^2 C–H activation processes involving metallacyclic ruthenium intermediates.[10] Inspired by these facts, we envisioned that analogous aromatic ruthenacycles might be accomplished *via* the C–H activation process. Herein, we report a new metallaaromatic species, *i.e.* ruthenabenzothiophenes, by the intramolecular C–H activation of thiophenes.

Treatment of a dark red solution of $RuCl_2(PPh_3)_3$ in tetrahydrofuran (THF) with excess thiophenyl propynol and PPh_3 over approximately 24 hours led to a color change of the reaction mixture to deep brown, and subsequent formation of a yellow precipitate. Filtration and washing of the precipitate with ether afforded the ruthenacyclic complex **1** as a yellow solid in 65% yield (Scheme 1). The complex has been characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopy, single-crystal X-ray diffraction analysis, high resolution mass spectrometry (HRMS) and elemental analysis.[11]

Notably, complex **1** is reactive at ambient temperature in the presence of an acid as verified by ^1H NMR spectroscopy. When excess HBF_4 was added to the solution of **1** in CH_2Cl_2, a number of unidentified species was formed within 3 hours. The transformation proceeded better when excess HCl was added instead. When a CH_2Cl_2 solution of **1** was stirred at room temperature in the presence of HCl, it was cleanly converted into complex **2** within 2 hours (Scheme 1). Following workup, a red solid assigned as bisruthenabenzothiophene (**2**) was isolated (74%). Analysis of **2** by ^1H NMR spectroscopy shows four signals, suggestive of the symmetry of the ruthenabenzothiophene dimer (Fig. S3†). The ^1H signals of ruthenabenzene rings were observed at 16.26 and 7.73 ppm, which are slightly up-field shifted compared with our previously reported ruthenabenzene (17.5 and 8.2 ppm).[7] The two ^1H signals of

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† Electronic supplementary information (ESI) available: Experimental procedures, characterization of new compounds, crystallographic details for compounds **1**, **4**, and **5**, cyclic voltammogram for compounds **2** and **4** and theoretical calculations. CCDC 1048063, 1048066 and 1048067. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04557f

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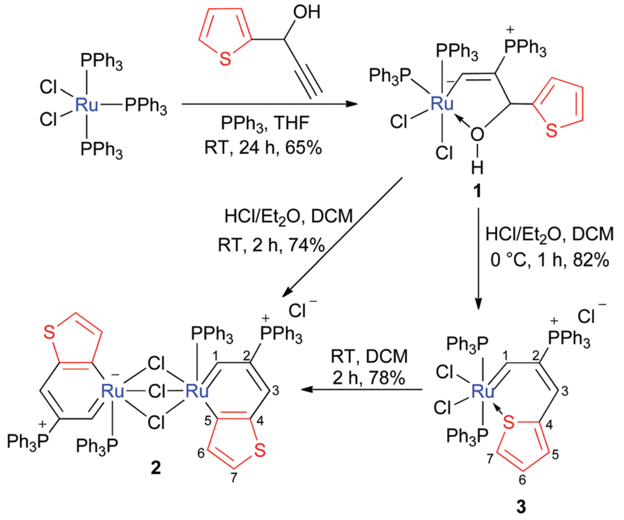


Scheme 1 Synthesis of ruthenacyclic complexes **1**, **3** and bisruthenabenzothiophene **2**.

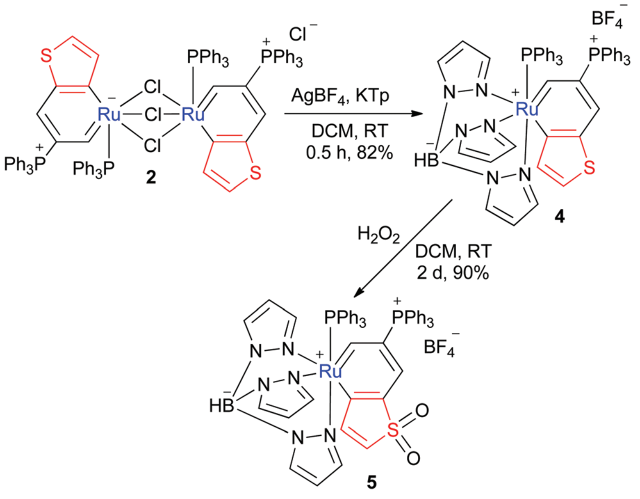
thienyl were attributed to 7.97 and 6.89 ppm, respectively. In line with this, the ^{13}C NMR spectrum exhibits seven carbon signals of the ruthenabenzothiophene rings. In particular, the seven signals were assigned at δ = 282.10 (C1), 113.53 (C2), 135.20 (C3), 132.47 (C4), 244.79 (C5), 137.96 (C6), and 143.20 (C7) ppm, with the aid of the ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC spectra. The ^{31}P NMR spectrum showed the signals of C*P*Ph$_3$ at 18.69 ppm and the signals of Ru*P*Ph$_3$ at 47.05 ppm. The molecular formula of **2** was confirmed by HRMS at *m*/*z* 1599.0867, consistent with the calculated value for the dimeric ruthenabenzothiophene cation [**2**–Cl]$^+$ (1599.0874).

When the reaction of **1** with HCl was performed in CH$_2$Cl$_2$ under 0 °C for approximately 1 hour, complex **3** was identified by *in situ* NMR (Scheme 1). Unfortunately, attempts to obtain NMR spectroscopic characterization of complex **3** failed because it was easily converted in solution. The ^{1}H NMR spectrum of **3** shows characteristic signals at 17.87 (C^1*H*), 9.19 (C^3*H*), 8.59 (C^5*H*), 7.91 (C^6*H*) and 6.71 (C^7*H*) ppm (see Fig. S6 in the ESI†). The ^{31}P NMR spectrum displays two singlet peaks at 24.18 (Ru*P*Ph$_3$) and 11.79 (C*P*Ph$_3$) ppm (Fig. S7†). As the signals are similar to those of our previously reported ruthenium carbene complex [Ru(CHC(PPh$_3$)CH(2-Py)Cl$_2$PPh$_3$]BF$_4$,[12] the analogous vinylcarbene structure of **3** was deduced. In accord with the deduced structure of **3**, the high resolution mass spectrum (HRMS) shows an ion peak at *m*/*z* 1079.1293, corresponding to [Ru(CHC(PPh$_3$)CH(2-thienyl)Cl$_2$(PPh$_3$)$_2$]$^+$. As expected, **3** can be transformed to yield the bisruthenabenzothiophene **2** by stirring a CH$_2$Cl$_2$ solution of **3** at room temperature for about 2 hours (Scheme 1). The experimental observations strongly suggest that **3** should be regarded as an intermediate in the conversion of **1** to **2**.

We next studied the reactions of RuCl$_2$(PPh$_3$)$_3$ with other thiophenyl propynols to further investigate the aromatization step of the formation of bisruthenabenzothiophene **2**. When the substituted thiophenyl propynol, *i.e.* 1-(3-methylthiophen-2-yl)prop-2-yn-1-ol, was used as the starting material, the ruthenacycle similar to complex **1** was formed, as suggested by *in situ* NMR. The addition of HCl only led to the formation of the six-membered ruthenacycle analogous to complex **3**, which decomposed within 3 hours without the formation of the final metallaaromatic complexes. For 1-(thiophen-3-yl)prop-2-yn-1-ol, the formation of the five-membered ruthenacycle (with similar structure to **1**) can also be achieved. However, the five-membered ruthenacycle decomposed in the presence of HCl. The failure to obtain the analogous six-membered ruthenacycle may stem from the position of the sulphur atom, which would make it harder to coordinate to the metal center.

It is generally believed that the catalytic C–H bond activation/functionalization could form metal–carbon and cyclometalated species.[10] The following reductive elimination of cyclometalated species could liberate the desired product and regenerate the catalytically active metal species. We initially attempted to react the bisruthenabenzothiophene **2** with a number of ligands such as PPh$_3$, acetic acid, acetonitrile or 2,2′-bipyridine with the hope of obtaining the corresponding reductive elimination products. However, the bisruthenabenzothiophene **2** is unreactive towards those ligands, as indicated by *in situ* NMR. As shown in Scheme 2, treating a CH$_2$Cl$_2$ solution of **2** with excess potassium trispyrazolylborate (KTp) in the presence of AgBF$_4$ resulted in the formation of the ligand substitution product **4**, which was isolated as a red solid in 82% yield (Fig. 1).

Complex **4** has been characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction analysis, HRMS, and elemental analysis. X-ray diffraction analysis revealed a monomeric ruthenabenzothiophene structure with the Tp moiety directly coordinated to the metal center. Thus the Tp ligand features a tridentate coordination geometry with one of the donor sites *trans* to the phosphine ligand. Due to the tri-



Scheme 2 Reactions of bisruthenabenzothiophene **2** and ruthenabenzothiophene **4**.

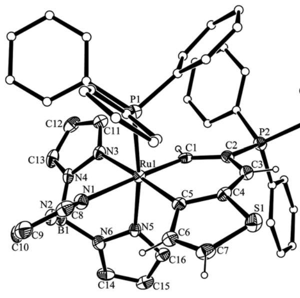


Fig. 1 X-ray structure of ruthenabenzothiophene **4** (ellipsoids at the 50% probability level), counteranions and hydrogen atoms in PPh_3 and Tp have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–C1 1.940(4), Ru1–C5 1.990(4), C1–C2 1.398(5), C2–C3 1.422(5), C3–C4 1.379(5), C4–C5 1.427(5), C5–C6 1.433(5), C6–C7 1.366(5), C7–S1 1.697(4), C4–S1 1.766(4), C5–Ru1–C1 89.12(15), Ru1–C1–C2 131.8(3), C1–C2–C3 121.5(4), C2–C3–C4 123.4(3), C3–C4–C5 126.5(4), C4–C5–Ru1 124.7(3), C4–C5–C6 107.8(3), C5–C6–C7 114.7(4), C6–C7–S1 114.1(3), C7–S1–C(4) 89.96(19).

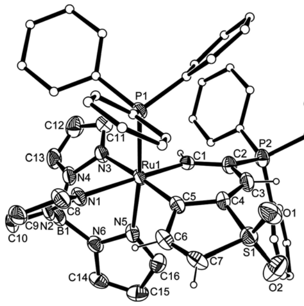


Fig. 2 X-ray structure of compound **5** (ellipsoids at the 50% probability level), counteranions and hydrogen atoms in PPh_3 and Tp have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru1–C1 1.953(5), Ru1–C5 1.935(5), C1–C2 1.402(7), C2–C3 1.395(7), C3–C4 1.379(7), C4–C5 1.427(7), C4–S1 1.768(6), C5–C6 1.495(7), C6–C7 1.329(8), C7–S1 1.762(6), S1–O1 1.435(4), S1–O2 1.438(4), Ru1–P1 2.3690(14), P2–C2 1.790(5), C5–Ru1–C1 89.0(2), Ru1–C1–C2 131.4(4), C1–C2–C3 121.8(5), C2–C3–C4 123.1(5), C3–C4–C5 126.7(5), C4–C5–Ru1 126.5(4), C4–C5–C6 107.5(5), C5–C6–C7 118.1(5), C6–C7–S1 109.8(4), C7–S1–C4 92.8(3), O1–S1–O2 117.6(3), O1–S1–C4 112.6(3), O2–S1–C4 110.5(3), C5–C4–S1 111.8(4).

dentate Tp ligand, the ruthenabenzothiophene ring deviates obviously from planarity, as reflected by the mean deviation from the least-squares plane through Ru1, C1–C7 and S1 (0.1410 Å). However, the Ru1–C1 bond (1.940(4) Å) is slightly shorter than the Ru1–C5 bond (1.990(4) Å) and the C–C distances of the metallacycle are lacking significant alternations (C1–C2 1.398(5), C2–C3 1.422(5), C3–C4 1.379(5), C4–C5 1.427(5) Å). All bond distances within the metallacycle fall within the range observed for other typical metallaaromatics,[3–8] which indicate the delocalized electronic structure of the metallacycle.

The bisruthenabenzothiophene **2** and the ruthenabenzothiophene **4** were found to be thermally stable both in the solid state and in solution under air. While the solid sample of **2** can be heated in air at 120 °C for at least 5 hours without noticeable decomposition, the solid sample of **4** is even stable at 200 °C for at least 5 hours. Additionally, nitrobenzene solutions of **2** and **4** are persistent at 100 °C in air for 3 hours. The remarkable thermal stability of **2** and **4** may be attributed to the aromaticity of the ruthenabenzothiophene rings. It is worthy of mention that **4** is unreactive towards $CuCl_2$, I_2 or KIO_4 while the reaction of **4** with H_2O_2 or *meta*-chloroperoxybenzoic acid (mCPBA) only led to the oxidation of the thiophene ring. As shown in Scheme 2, mixing **4** with excess H_2O_2 in CH_2Cl_2 at room temperature for 2 days affords **5** in 90% yield after work-up. The solid-state molecular structure of **5** was determined by single-crystal X-ray diffraction studies (Fig. 2). The structural parameters of **5** associated with the ruthenabenzene ring are very similar to those of **4**. As revealed by X-ray diffraction analysis, the oxidation process only took place in the thiophene moiety of **4**, which led to the dearomatization of the thiophene ring and the formation of the thiophene-*S*,*S*-dioxide backbone in **5**. The unoxidizable feature in the above observations may also arise from the aromaticity of the ruthenabenzene rings.

To further evaluate the aromaticity of **2**, **4** and **5**, density functional theory (DFT) calculations at the B3LYP level of theory have been performed (*cf.* ESI† for details). Generally, negative values of nucleus-independent chemical shift (NICS) calculations[13] indicate aromaticity while positive values suggest anti-aromaticity. As shown in Scheme S1,† the NICS $(1)_{zz}$ values of the metallacycles of **2**, **4** and **5** are all negative (−9.6 and −15.7 ppm for **2**; −6.4 and −15.9 ppm for **4**; −10.5 ppm for **5**), indicating that these complexes are aromatic (when the environments at points 1 Å above and below the ring centres are not equivalent, the averaged values were used for $\text{NICS}(1)_{zz}$ values). The strain-balanced "isomerization stabilization energy" (ISE)[14] method was also employed. The isomerization stabilization energies of these complexes were calculated based on the unsubstituted model complexes **2′**, **4′** and **5′**, in which the PPh_3 groups were further replaced by the PH_3 groups. The calculated ISE values are comparable to those reported for other metallaaromatics.[3a–c,e,f,i] The ISE value of **5′** ($-11.5\ \text{kcal mol}^{-1}$) is reduced markedly from the ISE values of the **2′** ($-19.7\ \text{kcal mol}^{-1}$) and **4′** ($-20.4\ \text{kcal mol}^{-1}$), which is in good agreement with the dearomatization of the thiophene ring in **5′** (Scheme S1†).

The redox behaviour of bisruthenabenzothiophene **2**, the ruthenabenzothiophene **4** and the ruthenabenzene **5** was probed by using cyclic voltammograms (CVs) collected in CH_2Cl_2 containing 0.10 M Bu_4NPF_6 as the supporting electrolyte. Similar to our bisruthenabenzene,[7a] weak but appreciable electronic interactions between the metal centres in bisruthenabenzothiophene **2** can be observed from the two continuous oxidation waves (A, B) in the CV of **2**. The two oxidation waves at $E_{p,a}$ = +0.80 V (A) and $E_{p,a}$ = +1.27 V (B) are partly overlapping. In contrast to bisruthenabenzothiophene **2**, ruthenabenzothiophene **4** is more difficult to oxidize, as suggested by the positive shift of oxidative potential in the anodic CV scan of **4**

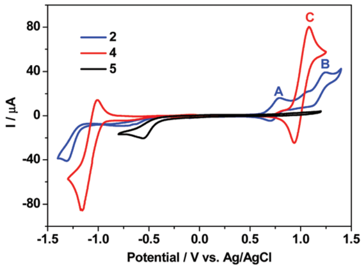


Fig. 3 Cyclic voltammograms of **2**, **4** and **5** measured in CH_2Cl_2 with 0.10 M $n\mathrm{Bu_4NPF_6}$ as the supporting electrolyte at a scan rate of 0.10 V s^{-1}.

($E_{p,a}$ = +1.08 V (C)) (Fig. 3). Experimentally, **2** is more reactive to oxidants than **4** so that the reaction of **2** with H_2O_2 at room temperature led to the decomposition of the metallacycles and the formation of several unidentified species as indicated by *in situ* NMR.

Conclusions

In summary, new metallaaromatics with a second-row transition metal, *i.e.* ruthenabenzothiophenes were achieved through the C–H activation of thiophenes. Both experimental and theoretical studies suggest that the ruthenabenzothiophenes exhibit aromatic character. The ligand substitution of Tp led to the increase of the antioxidative properties of the aromatic ruthenacycles, as demonstrated by the electrochemical studies. The present results not only open a promising avenue for the construction of new metallaaromatics containing a second-row transition metal, but also provide insight into catalytic processes of sp^2 C–H activation.

Acknowledgements

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