Naked eye detection of anions by alkynyl-ruthenium exo-receptors: selective recognition of fluoride anion†

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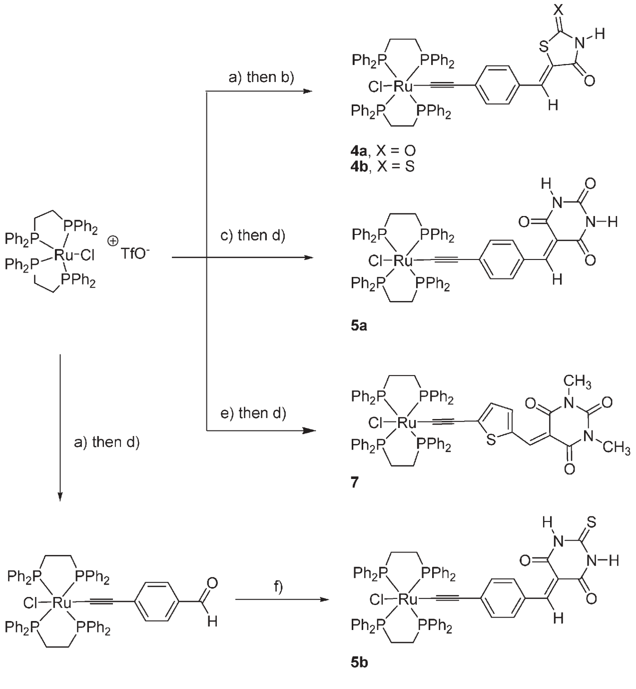
Alkynyl-ruthenium complexes bearing terminal hydrogen-bonding receptors act as efficient anion sensors exhibiting large guest-induced colour changes and show unexpectedly high selectivity to fluoride ions.

Recognition of anions by colorimetric sensors is a research area of importance due to the paramount role of these species in the environment, biology, *etc.*[1–5] Although the incorporation of transition metal subunits has led to several strategies in this field,[6] transition metal σ-acetylide complexes have rarely been considered as potential sensors for small molecules and ionic species.[7–10] As these organometallic systems, which possess an almost linear M–C≡C–R structure, allow efficient electronic coupling between the metal and the remote groups through the π-conjugated path,[11,12] even weak second-sphere interactions are expected to provoke the discernable changes required for efficient colorimetric sensing.



Scheme 1 Reagents and conditions a) $[(dppe)_2RuCl]^+TfO^-$, 4-ethynylbenzaldehyde **1**, (5*Z*)-5-(4-ethynylbenzylidene)-1,3-thiazolidine-2,4-dione **2a** or (5*Z*)-5-(4-ethynylbenzylidene)-2-thioxo-1,3-thiazolidin-4-one **2b** (1.1 equiv.), CH_2Cl_2; b) t-BuOK, THF; c) $[(dppe)_2RuCl]^+TfO^-$, 5-(4-ethynylbenzylidene)pyrimidine-2,4,6-trione **3a** (1.1 equiv.), THF; d) NEt_3, CH_2Cl_2; e) 5-[(5-ethynylthien-2-yl)methylene]-1,3-dimethyl-pyrimidine-2,4,6-trione **6** f) thiobarbituric acid, THF, EtOH, reflux, 1 week.

We report herein a series of anion sensors possessing hydrogen bonding recognition sites at the remote end of alkynyl-ruthenium derivatives. These ruthenium-acetylide based sensors were applied to the colorimetric detection of F^-, AcO^- and $H_2PO_4^-$ anions at a low analyte concentration and shed new light on electrostatic repulsive effects as a mean to discriminate these anionic species.

Compounds **4a,b** and **5a** were obtained starting from the corresponding acetylenic units bearing thiazolidinedione, rhodanine and barbituric acid moieties **2a,b** and **3a**† *via* a two step procedure (Scheme 1).[13] Compound **5b** was obtained by a Knoevenagel condensation of thiobarbituric acid with *trans*-$(dppe)_2Ru(Cl)$-($C{\equiv}C$–C_6H_4–CHO).[14] Compounds **4–5** are characterised by strong absorption bands due to a $d\pi_{(Ru)} \rightarrow \pi^*_{(C\equiv CR)}$ metal-to-ligand charge transfer transition in the visible region (**4a** λ_{max} = 490 nm in methylene chloride; $\varepsilon_{max} = 2.5 \times 10^4$ dm^3 $mol^{-1}cm^{-1}$; **5a** λ_{max} = 590 nm; $\varepsilon_{max} = 4.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

The structure of the model compound **7** indicates the planarity of the conjugated ligand and reveals the absence of steric constraints around the terminal organic receptor moiety (Fig. 1).‡

Instantaneous colour changes were observed upon addition of F^-, AcO^- or $H_2PO_4^-$ anions (Fig. 2) to **4** or **5**. Conversely no detectable colour change is observed even upon addition of large excesses of HSO_4^-, Cl^- , Br^- and NO_3^-. Not surprisingly, the colour of a methylene chloride solution of the model compound **7**,

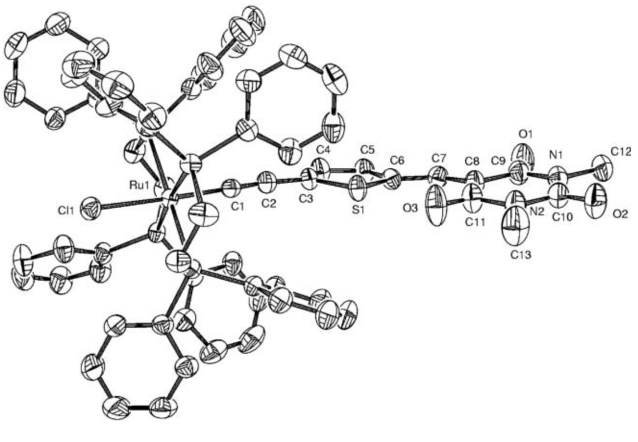


Fig. 1 ORTEP view of **7** showing 50% probability displacement ellipsoids and the atom numbering. Selected bond lengths (Å), bond angles (deg): Ru1–C1 1.977(2); C1–C2 1.204(3); C2–C3 1.406(3); C10–O2 1.214(4); Ru1–C1–C2 177.2(2); C1–C2–C3 174.0(3).

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† Electronic supplementary information (ESI) available: details of synthetic, X-ray crystallographic and spectroscopic experiments. See http://www.rsc.org/suppdata/cc/b5/b503698d/

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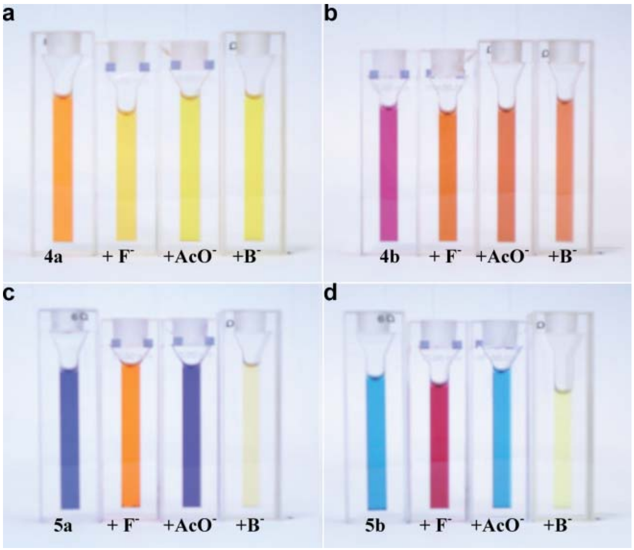

Fig. 2 Colour changes induced by the addition of anions (10 eq.) or piperidine (20 eq.) to complexes **4a** (a), **4b** (b), **5a** (c) and **5b** (d) (6.7×10^{-5} M solutions in methylene chloride). Anions were added in the form of their tetrabutylammonium salts.

which bears a dimethylbarbituric moiety, was not affected by the addition of anionic species whatever they are.[15] On the other hand, the changes observed upon addition of F^-, AcO^- and $H_2PO_4^-$ anions to complexes **4–5** are fully reversed upon addition of water which presumably competes with these anions.

Sensors **4a** and **4b** which contain only one recognition site, proved to be inefficient at distinguishing between AcO^- and F^-. Complete colour changes are observed for **4a** upon addition of 6 equiv. of F^- or 10 equiv. of AcO^- (**4a**: $\lambda_{max} = 490$ nm; $\varepsilon_{max} = 2.5 \times 10^4$ dm^3 mol^{-1}cm^{-1}; [**4a**.F$^-$] and [**4a**.AcO$^-$]: $\lambda_{max} = 415$ nm; $\varepsilon_{max} = 2.3 \times 10^4$ dm^3 mol^{-1}cm^{-1}). The presence of a thiocarbonyl unit in **4b** results in a higher sensitivity of the sensors and in the lack of discrimination between the anions. The complete colour change of the methylene chloride solution of **4b** occurs upon addition of 2 equiv. of AcO^- as well as 2 equiv. of F^-, (**4b**: $\lambda_{max} = 550$ nm; $\varepsilon_{max} = 2.6 \times 10^4$ dm^3 mol^{-1}cm^{-1}; [**4b**.F$^-$] and [**4b**.AcO$^-$]: $\lambda_{max} = 465$ nm; $\varepsilon_{max} = 2.2 \times 10^4$ dm^3 mol^{-1}cm^{-1}).

More striking results were obtained upon addition of anions to **5a** and **5b**, as these compounds exhibit unexpectedly high selectivity to fluoride ions, even in the presence of other anions. Thus, **5a** undergoes a blue ($\lambda_{max} = 590$ nm; $\varepsilon_{max} = 4.0 \times 10^4$ dm^3 mol^{-1}cm^{-1}) to orange fluoride anion-induced colour change ($\lambda_{max} = 480$ nm; $\varepsilon_{max} = 2.6 \times 10^4$ dm^3 mol^{-1}cm^{-1}). Even if they result from "incipient proton-transfer reactions"[16] these colour changes differ from those observed in the deprotonation process as monitored by addition of piperidine in methylene chloride, ($\lambda_{max} = 340$ nm; $\varepsilon_{max} = 2.2 \times 10^4$ dm^3 mol^{-1}cm^{-1}).[17] Complete colour change is effected upon the addition of 4 equiv. of F^- to **5a**. Colour changes upon addition of AcO^- or $H_2PO_4^-$ anions require significantly larger amounts of these salts (**5a**: 260 equiv. of AcO^- or more than 1000 equiv. $H_2PO_4^-$).

Various stoichiometries were tested and rationalized with respect to the quality of the fitting parameters and the physical significance of the calculated spectra.[18,19] The equilibrium constants were first estimated based on 1:1 (host–guest) binding models for complexes **4–5**. The calculated K_1 (Table 1) values for F^-, AcO^- and $H_2PO_4^-$ anions are qualitatively in agreement with their basicity. These values confirm that complexes **4** with a sole binding site are definitely not selective. The plots for **5a,b** suggest that the stoichiometry of the host–guest complexes is not simply 1:1. Since there are two potential binding sites in **5a** and **5b**, it is reasonable to assume a 1:2 stoichiometry for the corresponding host–guest complexes.

Table 1 Affinity constants for compounds **4** and **5** (M^{-1}) with anionic substrates in dichloromethane at 22 °C

Anion	4a	4b	5a	5b
F^-				
log K_1	5.2 ± 0.1	6.7 ± 0.2	4.2 ± 0.1[a]	4.7 ± 0.1[a]
log $K_1 \cdot K_2$			10.6 ± 0.1	11.2 ± 0.1
AcO^-				
log K_1	5.0 ± 0.1	7.1 ± 0.4	4.0 ± 0.1	4.6 ± 0.1
log $K_1 \cdot K_2$			7.1 ± 0.2	8.8 ± 0.2
$H_2PO_4^-$				
log K_1	4.2 ± 0.1	nd[b]	3.4 ± 0.1	4.4 ± 0.1
log $K_1 \cdot K_2$			nd[c]	7.6 ± 0.3

[a] Maximal values. [b] Non-determined because of competitive deprotonation. [c] The second equilibrium was suppressed during the fitting process because of the very low concentration of [**5a**.$(H_2PO_4)_2$]$^{2-}$.

The first complexation of F^- and AcO^- anions leads to association constants of rather close values (**5a** log $K_1 \approx 4$) indicating that differences in their intrinsic basicity and electronegativity are not dominant. The selectivity of **5a** and **5b** with respect to these anions results from the considerable differences in the K_2 values (**5a** F^- log $K_2 \approx 6$; AcO^- log $K_2 \approx 3$). Thus, the discrimination between fluoride and other anions by **5a** and **5b** is mainly due to their relative capability to achieve 1:2 host–guest complexes. This suggests that the discrimination between AcO^- and F^- results from modifications of the density of charge in the exo-receptor because of the complexation of a first anionic species. As carbonyl (or thiocarbonyl) groups face approaching anions, we assume that electrostatic repulsions[20–22] exerted by these groups over antagonist groups (C=O; P=O) are enhanced by the complexation of a first anion to receptors **5** and disfavor subsequent binding of oxoanions. F^- is thus the anion which presents the most suitable characteristics (electronegativity and size) to establish a strong H-bond interaction with the remaining –NH binding site of the receptors [**5**.A$^-$].

In summary, alkynyl-ruthenium derivatives linked to non pre-organized receptors provide an unexplored class of anion receptors that are adapted to the visual detection of anions in methylene chloride. Additionally, compounds **4–5** consist of receptors where carbonyl units face the complexed anions resulting in an unprecedented model of discrimination between anionic species.

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Notes and references

‡ Crystal data. $C_{65}H_{57}ClN_2O_3RuS$, $M = 1206.59$, triclinic, $a = 10.9596(2)$, $b = 14.6367(4)$, $c = 18.5586(6)$ Å, $\alpha = 78.498(1)$, $\beta = 81.692(1)$, $\gamma = 77.416(1)^\circ$, $V = 2831.2(1)$ Å^3, $T = 293$ K, space group $P\bar{1}$, $Z = 2$, $\lambda(\mathrm{MoK}\alpha) = 0.71073$ Å, $\mu = 5.23\ \mathrm{cm}^{-1}$, 63203 reflections measured. 15716 independent reflections from which 11629 with $I > 2.0\sigma(I)$. $R = 0.040$, $Rw = 0.0101$. CCDC 243761. See http://www.rsc.org/suppdata/cc/b5/b503698d/ for crystallographic data in CIF or other electronic format.

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