Synthesis of a double-activated switchable molecule *via* ruthenium–acetylide barbituric derivatives

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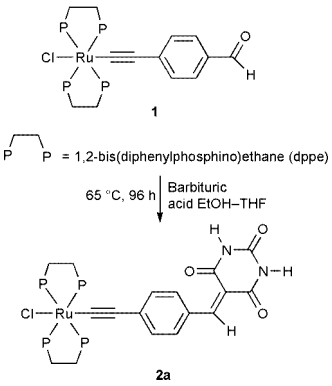
Ruthenium–σ-acetylide derivatives connected to barbituric acceptors through a π-conjugated bridge define a series of molecular systems presenting highly tunable properties.

Several molecular systems capable of performing elementary tasks on the molecular level have been synthesized in recent years.[1] In most cases, the molecular device obeys a binary rule; *i.e.* an input provides a positive or negative output response.[2] This ability to switch on/off a function through an external parameter (light, electron transfer, chemical reaction) defines the concept of a molecular switch. Another objective is the building of molecules which exhibit useful electronic/photonic functions that can be externally controlled.[3] With this in mind, organometallic and coordination compounds are currently the subject of considerable investigations.[4] Transition metal complexes with η^1-alkynyl ligands ($L_nMC{\equiv}CR$) attract particular interest, mostly as precursors of molecules containing a linear array of delocalized π-systems between two different functionalities.[5]

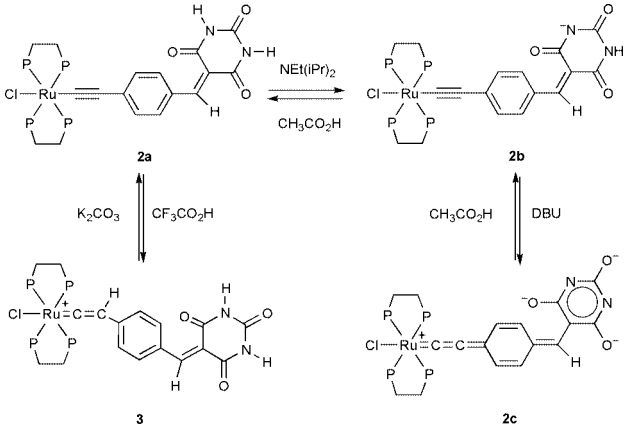
In this context, we set out to investigate metal–alkynyl donor–acceptor systems, as prototypes for molecular materials possessing switchable properties, through chemical or redox modifications. We now describe the design and synthesis of ruthenium(II)–alkynyl, connected to a barbituric acceptor, selected for its ability in stabilizing charge delocalized canonical structures through an heteroaromatic limit form, as a first example of this concept.

Knoevenagel condensation of **1**[6] (Scheme 1) with barbituric acid yields the target compound **2a** as an air-stable blue powder. Its structure was confirmed by spectrometric methods.† The UV–VIS spectra of complexes **1** and **2a**, characterized by intense ($\varepsilon \approx 1.2$–2×10^4 M^{-1} cm^{-1}) MLCTs at λ_{max} = 410 and 547 nm, respectively, in THF [Fig. 1(*a*)] proved the donor–acceptor nature of these systems.

Complex **2a** possesses three independant sites for successive protonation–deprotonation sequences (Scheme 2), which permit us to modulate the donor–acceptor coupling in **2a**, alternatively at the donor or at the acceptor head, as depicted through dramatic colour changes. The protonation on the β-carbon of transition metal acetylide complexes leading to their



Scheme 1 Synthesis of the barbituric derivative **2a**.



Scheme 2

corresponding vinylidene is a well-known process.[7,8] Addition of an excess of a strong acid (HCl, CF_3CO_2H) to **2a** was therefore monitored by ^{31}P NMR: a significant shift of the signal for the 4 equivalent phosphorus nuclei from 48.6 to 39.6 ppm was observed. This latter value is consistent with the formation of a *trans*-chlororuthenium–vinylidene cationic complex **3** (Scheme 2).[9] The presence of a quintuplet ($^4J_{[P,H]}$ = 3 Hz) at 3.96 ppm in the ^1H NMR spectrum of **3** is also in agreement with such a Ru=C=C*H* cationic fragment.

Simultaneously a rapid colour change from purple to red (λ_{max} = 495 nm, $\varepsilon = 1.7 \times 10^4$ M^{-1} cm^{-1}) [Fig. 1(*b*)] was observed. This reveals the weakening of the donor–acceptor electronic coupling arising from an alteration of the metal–acetylide moiety. This hypothesis was confirmed by electrochemical studies on the Ru^{2+}/Ru^{3+} redox couple. Complex **2a** presents a reversible oxidation wave in its cyclic voltammogram [Fig. 2(*a*)] at $E_{1/2}$ = 560 mV *vs.* SCE, in CH_2Cl_2,‡ assigned to the Ru(II)/(III) oxidation. The addition of a slight excess of trifluoroacetic acid to **2a** resulted in the total disappearance of the initial anodic wave, as expected for a vinylidene derivative [see Fig. 2(*a*,*b*)]. As the CV for **2a** reappears upon addition of K_2CO_3 to **3**, complete reversibility and high speed switching were observed for both the protonation (acetylide to vinylidene) and deprotonation (vinylidene to acetylide) reactions.

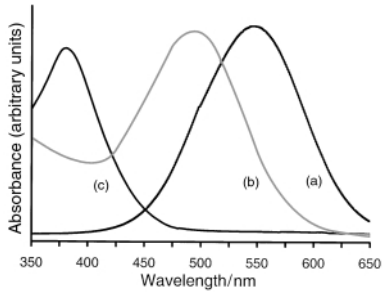


Fig. 1 Absorption spectra of **2** in THF: (*a*) pure **2a**; (*b*) after addition of 1 equiv. of CF_3CO_2H to **2a**; (*c*) after addition of 2 equiv. of DBU to **2a**.

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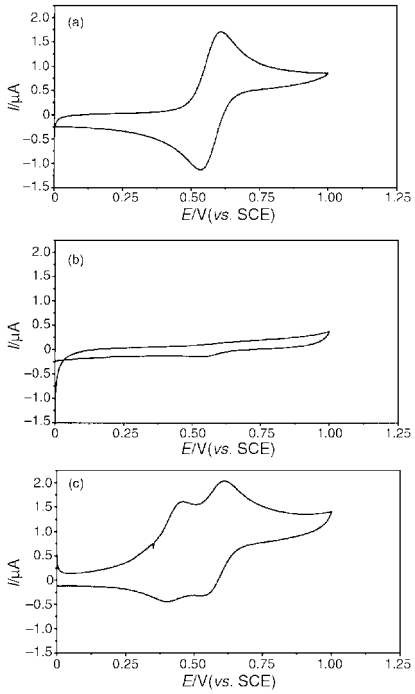

Fig. 2 Cyclic voltammograms‡ of **2a** in CH_2Cl_2, at a scan rate of 200 mV s^{-1}: (*a*) pure **2a**; (*b*) after addition of 1 equiv. of CF_3CO_2H on **2a**; (*c*) after addition of 1 equiv. of DBU on **2a** (see text).

On the other hand, the addition of a strong base (KOH, DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene)), to **2a** induces an immediate colour change from purple to pale yellow (λ_{max} = 380 nm, $\varepsilon = 1.5 \times 10^4$ M^{-1} cm^{-1}) [Fig. 1(*c*)]. A minor variation of the ^{31}P NMR shift for the phosphorus ligands, from 48.6 to 49.5 ppm, is observed. This process is perfectly reversible, upon addition of a weak acid (CH_3CO_2H). Both these observations are consistent with the weakening of the acceptor strength of the barbituric moiety as a result of its deprotonation. This hypothesis was ascertained by monitoring the modifications of the Ru(II)/(III) oxidation wave of **2a**, upon sequential addition of DBU. This resulted in the growth of a new anodic wave, at a less positive potential ($E_{1/2}$ = 460 mV *vs.* SCE, in CH_2Cl_2), in accord with the formation of a more electron rich species, whereas the initial wave ($E_{1/2}$ = 560 mV *vs.* SCE) was progressively disappearing [Fig. 2(*c*): for instance, these concomitant reversible waves were observed upon addition of 1 equiv. DBU].

Two equivalents of base were necessary to afford complete conversion from the purple compound **2a** to its yellow analogue. This process was therefore monitored by ^1H NMR spectroscopy. As expected, complete disappearance of both the NH (at 8.2 and 7.9 ppm) and a significant shift of the ethylenic CH signal (from 8.5 to 8.1 ppm) at the barbituric head resulted from the addition of 2 equiv. of DBU. Addition of 1 equiv. of base gave an unclear outcome (partial disappearance and broadening of the most significant signals of **2a**). At this stage, two ^{31}P NMR signals were observed at 48.6 and 49.5 ppm, which indicated that the deprotonation process was not complete. This process was monitored, by ^1H NMR, upon addition of a large excess of the less basic *N*-ethyldiisopropylamine. The initial signals for the NH groups disappeared, but only slight variations were observed for the ethylenic proton, at 8.5 ppm, and the aromatic system, at 8.2 and 6.4 ppm. Neither colour change (UV–VIS spectra) nor electrochemical potential shift for the oxidation of **2** were observed. Finally, complete conversion from **2a** into its yellow analogue were obtained when 1 equiv. of DBU was added to the solution containing the weaker base. We assume then that a double NH deprotonation at the barbituric head[9] is necessary to induce considerable electronic changes (Scheme 2: **2b** represents one of the ketoenolic forms of the monodeprotonated species whereas **2c** is a conceivable mesomeric form of the bi-deprotonated derivative).

This second mode of switching is different from the first one which acts more specifically on the metal–acetylide moiety. The synthesis of complex **2a** has therefore proven an effective strategy for designing highly sensitive derivatives, whose properties are adjustable alternatively at the donor or at the acceptor head. On the other hand, such a switching mode could permit us to control the hydrogen binding ability of the barbituric head, either by deprotonation on this residue or by protonation on the ruthenium moiety.

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Notes and references

† *Selected values for* **2a**: ^1H NMR ($CDCl_3$, ppm) δ 8.46 (s, 1 H, =CH), 8.20 and 6.47 (dd, 4 H, *J* 8.5 Hz, aromatic), 8.03 and 7.88 (brs, 2 × 1 H, NH), 7.4–6.9 (m, 40 H, aromatic of the dppe), 2.65 (m, 8 H, CH_2); ^{31}P NMR ($CDCl_3$, ppm) δ 48.7 (s, $RuPPh_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, ppm) δ 163.9, 161.5 and 148.9 (C=O); 159.1 (CH), 158.6 (Ru–*C*≡C), 138.8–123.2 (C aromatics), 126.9 (Ru–C≡*C*); 110.3 (Cq. barbituric), 30.5 (CH_2, dppe); IR (CH_2Cl_2, cm^{-1}) ν 2038 (C≡C); MS (FAB) *m/z* 1172.1895 $[M]^+$, calcd. 1172.1901.

‡ The electrochemistry of **2a** was carried out at 298 K in a standard three-electrode system (platinum working/auxiliary electrode and SCE reference electrode) using a 0.1 M dm^{-3} $[Bu^n_4N][PF_6]$–CH_2Cl_2 solution as electrolyte.

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