Novel carbon-rich binuclear ruthenium complexes with bis(allenylidene) bridges

Salaheddine Guesmi,[a] Daniel Touchard[b] and Pierre H. Dixneuf[b]

[a] *Laboratoire de Chimie de Coordination et Analytique, Faculté des Sciences, Université Chouaib Doukkali, BP 20, El-Jadida, Morocco*

[b] *Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes 1, 35042, Rennes, France*

Diruthenium(II) complexes with new bis(η^1-allenylidene) bridges are produced by double activation of molecules containing two prop-2-yn-1-ol groups and offer two reversible redox processes.

Bi- and poly-metallic complexes with π-conjugated and rigid unidimensional bridges are attracting interest due to their potential in materials science,[1] the generation of liquid-crystal[2,3] and non-linear optical properties.[4,5] A search for the construction of bimetallic systems containing new types of π-conjugated carbon-rich bridges, linking two reversibly reducible metal moieties, is thus motivated. Polyynes constitute the key-stone for the building of carbon-rich ligands or molecules and their double activation is relevant to the formation of polymetallic complex bridges.[6–8] Bimetallic complexes with only carbon bridges, $L_nM(C)_xML_n$, have been made, especially from organometallic terminal alkynes,[6,9] and the activation of conjugated diynes has been used to generate bimetallic complexes with bis(vinylidene),[10] bis(alkynyl)[11] or mixed vinylidene–allenylidene[12] bridges. We now report (*i*) the synthesis of novel complexes containing two identical metal moieties linked by a bis(allenylidene) bridge *via* the double activation of molecules containing two prop-2-yn-1-ol functionalities and (*ii*) a cyclic voltammetry study of these systems, which show that the new bridges establish a communication between the two ruthenium moieties.

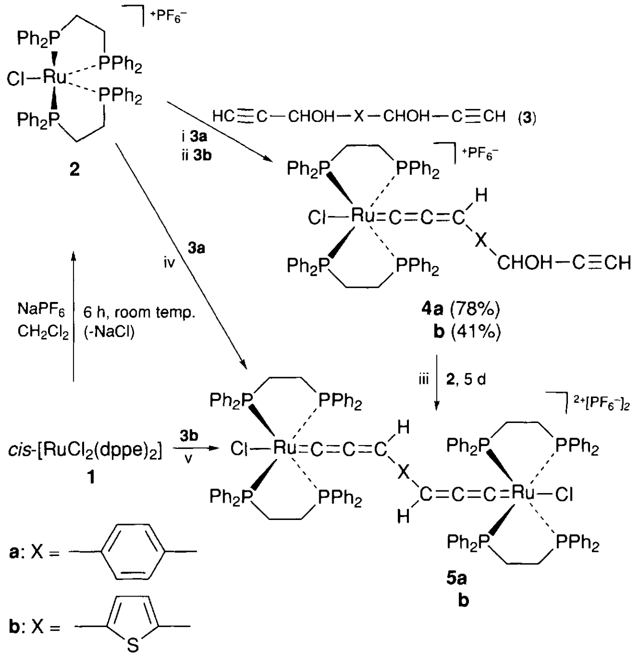
The activation of prop-2-yn-1-ols by *cis*-$[RuCl_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ complexes[13,14] has been shown to readily afford allenylidene–ruthenium(II) complexes, *trans*-$[Cl\{Ph_2P(CH_2)_nPPh_2\}_2Ru{=}C{=}C{=}CR_2]PF_6$, which were stable due to the electron-releasing character of the ruthenium moiety and the protection, by steric hindrance, of the C^1 carbon atom. This stability led us to attempt the production of bis (η^1-allenylidene) ligand bridging two ruthenium(II) sites *via* double activation of simple diynes.

The reaction of *cis*-$[RuCl_2(dppe)_2]$ **1** with $HC{\equiv}CCHOH{-}C_6H_4{-}CHOHC{\equiv}CH$ **3a** in the presence of $NaPF_6$ led only to a slow transformation of **1**, but successful experiments were obtained from the isolated 16-electron species $[RuCl(dppe)_2]PF_6$ **2** (obtained in 63% yield upon treatment of **1** with $NaPF_6$ in dichloromethane). Reaction of **3a** with 1 equiv. of **2** in CH_2Cl_2 for 48 h at room temp. led to the isolation (78% yield) of the violet mononuclear **4a** containing the mixed allenylidene–prop-2-yn-1-ol ligand [^{13}C NMR, δ 320.70 (d_{qnt}, Ru=C, $^2J_{PC}$ 14, $^3J_{CH}$ 7 Hz), 221.89 (d_{qnt}, Ru=C=*C*, $^3J_{PC}$ 2, $^2J_{CH}$ 2 Hz), 151.65 (dm, Ru=C=C=*C*, $^1J_{CH}$ 167 Hz)] (Scheme 1). The free prop-2-yn-1-ol functionality of complex **4a** can be activated by 1 equiv. of **2** in dichloromethane leading to slow formation of the bis(allenylidene) complex **5a**, isolated in 52% yield after 5 days at room temp. The same bimetallic derivative **5a** can be directly prepared from the diyne **3a** and the 16-electron species **2** and was isolated in 45% yield after stirring for 7 d (Scheme 1).

It is noteworthy that the high symmetry of complex **5a** is reflected in the ^{31}P NMR spectrum as only one sharp singlet (δ 39.18) is observed for its eight ^{31}P nuclei. The two allenylidene groups are equivalent by ^{13}C NMR [δ 326.28 (d_{qnt}, Ru=C, $^2J_{PC}$ 15, $^3J_{CH}$ 7 Hz), 241.33 (d_{qnt}, Ru=C=*C*, $^3J_{PC}$ 3, $^2J_{CH}$ 4 Hz), 152.01 (br d, Ru=C=C=*C*, $^1J_{CH}$ 168 Hz)].

Activation of the diyne **3b**, containing two prop-2-yn-1-ol functions separated by a 2,5-thiophenylidene bridge, was also performed using **1** and **2**. With 0.5 equiv. of **2** the mononuclear complex **4b** was obtained (41% after 48 h), whereas with 2 equiv. of **1** the bimetallic complex **5b** was isolated in 49% after 11 d at room temp.

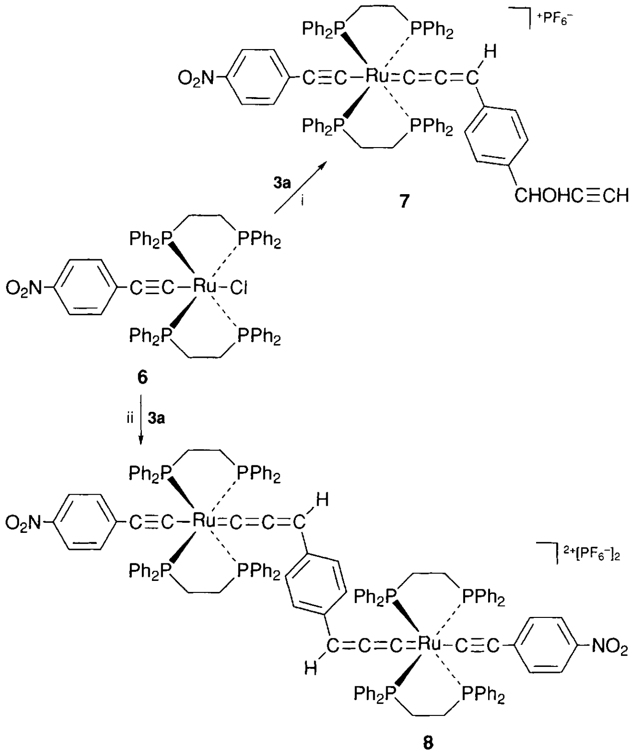
In order to evaluate the influence of a functional group on the ruthenium moieties and through the carbon-rich bridge, the introduction of a functional alkynyl ligand in the *trans* position of the bis (allenylidene) bridge was attempted. Activation of the bis(prop-2-yn-1-ol) species **3a** was carried out using the monoalkynyl ruthenium(II) precursor *trans*-$[p\text{-}O_2NC_6H_4C{\equiv}C{-}RuCl(dppe)_2]$ **6**. Thus complex **6** was reacted with 2 equiv. of the diyne **3a** in the presence of $NaPF_6$ and after 48 h the mononuclear complex **7** was obtained in 79% yield (Scheme 2). Activation of complex **7** by a second equiv. of **6**, which appeared to be much less reactive than **2** or even **1**, failed. The binuclear complex **8** was eventually obtained on treatment of **3a** with the alkynyl derivative **6** and $NaPF_6$. After 7 d the reaction



Scheme 1 *Reagents and conditions*: all reactions were performed in freshly distilled dichloromethane and at room temp: i, 1 equiv. of **2** and an excess of **3a** and $NaPF_6$, 48 h; ii, 0.5 equiv. of **2** for 1 equiv. of **3b**, excess of $NaPF_6$, 48 h; iii, 1 equiv. of **4a** and **2** for 5 d (52% of **5a**); iv, 1 equiv. of **2**, 0.5 equiv. of **3a**, for 7 d (45% of **5a**); v, 1 equiv. of **1**, 0.5 equiv. of **3b** and 2 equiv. of $NaPF_6$, for 11 d (49% of **5b**)

afforded the blue–black complex **8** with good purity in 61% yield.

Comparative cyclic voltammetry studies of diruthenium complexes **5a**, **5b** and **8** were undertaken in order to evaluate the behaviour of the bridge on the reduction of the ruthenium(II) moieties. Cyclic voltammograms were recorded at 20 °C in dichloromethane, with $NBu^n_4PF_6$ (0.1 M) as electrolyte between +1.2 and −0.4 V *vs.* SCE at a scan rate of 200 mV s^{-1}; results are given in Table 1.



Scheme 2 *Reagents and conditions*: all reactions were performed in freshly distilled dichloromethane and at room temp: i, complex **6** with 2 equiv. of **3a** and an excess of $NaPF_6$ for 48 h; ii, complex **6** with 0.5 equiv. of **3a** and 2 equiv. of $NaPF_6$ for 7 d

Table 1 Cyclic voltammetry data for binuclear complexes **5a**, **5b** and **8**

	$E°_1$/V	ΔE_{p1}/V	$E°_2$/V	ΔE_{p2}/V	$E°_1 - E°_2$/V
5a	−0.079	0.066	−0.281	0.081	0.202
5b	+0.095	0.071	−0.176	0.080	0.271
8	+0.082	0.071	−0.109	0.074	0.191

For each of the complexes cyclic voltammetry shows two very distinct reversible reduction waves ($E°_1 - E°_2$ = 0.19–0.27 V) leading to the electrochemically stable systems $Ru^{II}Ru^{I}$ and $Ru^{I}Ru^{I}$, respectively. This observation indicates that the bis(allenylidene) bridges are communicating electronic information from one ruthenium moiety to the other. Replacement of the transmission group 2,4-C_6H_4 (in **5a**) by 2,5-C_4H_2S (in **5b**) group favours both reductions of the ruthenium(II) moieties and also leads to the highest potential separation, $E°_1 - E°_2$, the bis(allenylidene) ligand containing the 2,5-C_4H_2S group appears to be the most efficient communicating bridge. Comparison of the reduction of **5a** and **8** shows that the replacement of the *trans* chloro groups of **5a** by the *p*-$O_2NC_6H_4C{\equiv}C$– group in **8** does not significantly modify the value $E°_1 - E°_2$ but significantly favours the reduction of each ruthenium(II) moiety.

The synthesis of linearly arranged complexes **5** and especially **8** has potential for the selective building of polymetallic oligomers containing carbon-rich bridges.

References

1 F. Diederich and Y. Gubin, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1101; J. M. Tour, *Chem. Rev.*, 1996, **96**, 537.
2 S. Takahashi, Y. Takai, H. Morimoto and K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, 1984, 3.
3 J. P. Rourke, D. W. Bruce and T. B. Marder, *J. Chem. Soc., Dalton Trans.*, 1995, 317; M. Altmann, V. Enkelmann, G. Leiser and U. H. F. Bunz, *Adv. Mater.*, 1995, **7**, 726.
4 C. Denault, I. Ledoux, D. W. Samuel, J. Zyss, M. Bourgault and H. Le Bozec, *Nature*, 1995, **374**, 339.
5 S. R. Marder, in *Inorganic Materials*, ed. D. Bruce and D. O'Hare, Wiley, 1992, p. 115.
6 U. H. F. Bunz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 969; J. E. C. Wiegelmann, U. H. F. Bunz and P. Schiel, *Organometallics*, 1994, **13**, 4649.
7 O. Lavastre, M. Even, P. H. Dixneuf, A. Pacreau and J. P. Vairon, *Organometallics*, 1996, **15**, 1530.
8 J. F. Capon, N. Le Berre-Cosquer, B. Leblanc and R. Kergoat, *J. Organomet. Chem.*, 1996, **508**, 31.
9 T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414 and references therein.
10 H. Werner, T. Rappert and J. Wolf, *Isr. J. Chem.*, 1990, **30**, 377; N. Le Narvor and C. Lapinte, *Organometallics*, 1995, **14**, 634.
11 M. S. Khan, A. K. Kakkar, S. L. Ingham, P. R. Raithby, Jack Lewis, B. Spencer, F. Wittmann and R. H. Friend, *J. Organomet. Chem.*, 1994, **472**, 247; E. Viola, C. Lo Sterzo, R. Crescenzi and G. Frachey, *J. Organomet. Chem.*, 1995, **493**, C9.
12 G. Jia, H. P. Xia, W. F. Wu and W. Sang Ng, *Organometallics*, 1996, **15**, 3634.
13 D. Touchard, N. Pirio and P. H. Dixneuf, *Organometallics*, 1995, **14**, 4920.
14 D. Touchard, S. Guesmi, M. Bouchaib, P. Haquette, A. Daridor and P. H. Dixneuf, *Organometallics*, 1996, **15**, 2579.

Received, 29th September 1996; Com. 6/06621F