

# New paramagnetic ruthenium complexes *via* one-electron reduction of metallacumulenes†

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**One-electron reductions of [Cl(dppe)<sub>2</sub>Ru=C=C=CR<sub>2</sub>]PF<sub>6</sub> (R = Ph, Me) and [Cl(dppe)<sub>2</sub>Ru=C=C=C=C=C=Ph<sub>2</sub>]PF<sub>6</sub> with Co(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> provide radical species with the unpaired electron localized on the trisubstituted carbon atom of the cumulene moiety as shown by hydrogen atom capture and EPR spectroscopy.**

Transition metal complexes are useful to stabilize the otherwise highly reactive  $\text{:C(=)}_n\text{CR}_2$  species which behave as strong electron withdrawing ligands. Following the development of vinylidene derivatives<sup>1</sup>  $[\text{M}]=\text{C}=\text{CR}_2$ , the Selegue methodology<sup>2</sup> has allowed the synthesis and reactivity study of a large variety of metal allenylidene  $[\text{M}]=\text{C}=\text{C}=\text{CR}_2$ .<sup>3,4</sup> This chemistry has been extensively developed towards material science<sup>5</sup> and alkene metathesis catalyst precursors.<sup>6</sup> Stimulated by the fact that radical species have been recently proposed as intermediates in metathesis<sup>7</sup> and by the design of new magnetic materials with carbon-rich chains, monoelectronic reduction of metal allenylidene and higher metallacumulenes now appears as an important field to explore. Apart from a recent specific reduction of a 3-alkylthioallenylidene complex<sup>8</sup> which leads to a heteroatom-bonded carbon-stabilized radical, no information has yet been obtained on the nature of the reduction site, *e.g.* on the metal or on the cumulene ligand. We now wish to report here the preliminary results of a general study on reduction of all carbon metallacumulenes including allenylidene<sup>9</sup>  $\text{L}_n\text{Ru}=\text{C}=\text{C}=\text{CR}_2$  and pentatetraenylidene<sup>10</sup>  $\text{L}_n\text{Ru}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{Ph}_2$  complexes. We show on the basis of electrochemical, spin trapping and EPR spectroscopic evidences that: (i) monoelectronic reduction leads to a radical stabilized on the most remote carbon of the cumulene chain as a general trend; (ii) a striking difference of reactivity of  $\text{L}_n\text{Ru}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{Ph}_2$  with respect to reduction *vs.* nucleophilic addition.

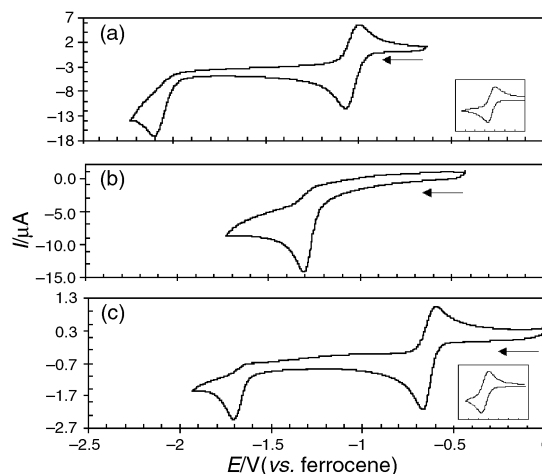
Complexes  $[\text{Cl}(\text{dppe})_2\text{Ru}=\text{C}=\text{C}=\text{CR}_2]\text{PF}_6$  [R = Ph (**1**<sup>+</sup>), Me (**2**<sup>+</sup>)<sup>9a</sup>] and  $[\text{Cl}(\text{dppe})_2\text{Ru}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{Ph}_2]\text{PF}_6$  (**3**<sup>+</sup>)<sup>10</sup> [dppe = 1,2-bis(diphenylphosphino)ethane], were studied using cyclic voltammetry (Fig. 1). Allenylidene **1**<sup>+</sup> undergoes two, well defined, one-electron reduction waves: the first one is reversible ( $E^\circ = -1.03$  V *vs.* ferrocene,  $\Delta E_p = 60$  mV,  $I_{pa}/I_{pc} \cong 1$ ), whereas the second one is irreversible ( $E_{pc} = -2.11$  V). By contrast, complex **2**<sup>+</sup> undergoes only one irreversible reduction ( $E_{pc} = -1.31$  V) which is consistent with the first reduced species undergoing following chemical reaction. The pentatetraenylidene complex **3**<sup>+</sup> shows a similar behavior to **1**<sup>+</sup>, *i.e.* a reversible reduction ( $E^\circ = -0.63$  V,  $\Delta E_p = 65$  mV,  $I_{pa}/I_{pc} \cong 1$ ) followed by an irreversible one ( $E_{pc} = -1.67$  V).

It is worth noting that by replacing the phenyl groups in **1**<sup>+</sup> with methyl groups in **2**<sup>+</sup> induces a significant cathodic shift of first the reduction wave by more than 250 mV. Lengthening the carbon chain from Ru-(C)<sub>3</sub> **1**<sup>+</sup> to Ru-(C)<sub>5</sub> **3**<sup>+</sup> surprisingly lowers the reduction potential by 400 mV and shows that the Ru-(C)<sub>5</sub> **3**<sup>+</sup> species is dramatically easier to reduce. The strong impact of these modifications of the metallacumulene on the

reduction processes is a clear indication of the key role played by the cumulene chain. It is then obvious that increasing the length of the delocalized path on the cumulene ligand has a crucial stabilizing influence on the LUMO.<sup>11</sup>

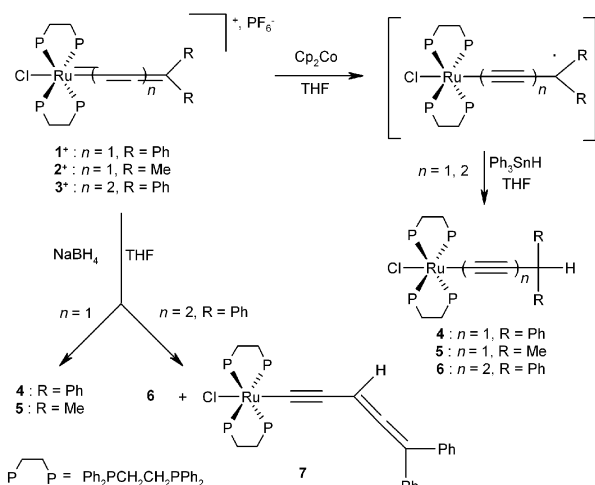
We attempted to generate *in-situ* the first reduced species allowing further spin trapping experiments or EPR spectroscopy investigations. The most appropriate reducing agent is the cobaltocene, Cp<sub>2</sub>Co, since (i) the reduction potential<sup>12</sup> ( $E^\circ = -1.33$  V *vs.* ferrocene) will selectively induce the first reduction process in **1**<sup>+</sup> and **3**<sup>+</sup>, and (ii) it is EPR-silent down to temperatures considerably below that of liquid nitrogen.<sup>12b</sup> Indeed, reduction of the deep colored cationic compounds **1**<sup>+</sup> (red), **2**<sup>+</sup> (green) and **3**<sup>+</sup> (blue), carried out with one equivalent of cobaltocene in THF, quickly lead to colorless solutions. Simultaneous addition of Ph<sub>3</sub>SnH, which is known as a specific radical quencher by H<sup>•</sup> transfer,<sup>13</sup> leads to the complete disappearance of **1**<sup>+</sup>, **2**<sup>+</sup> or **3**<sup>+</sup>, on the basis of NMR data, and to the formation of the pale yellow, neutral acetylide compounds  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CHPh}_2]$  **4**,  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CHMe}_2]$  **5** and  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CHPh}_2]$  **6** (Scheme 1). These complexes have been characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR and high resolution mass spectrometry.† In addition, characteristic IR vibration stretches are obtained:  $\nu_{\text{C}\equiv\text{C}} = 2085$  (**4**), 2086 (**5**), 2179 and 2023 (**6**) cm<sup>-1</sup>. All of these observations show that radical trapping only occurs at the end of the carbon skeleton.

Furthermore, achieving the reduction *in situ* of complexes **1**<sup>+</sup>, **2**<sup>+</sup> and **3**<sup>+</sup> by dropping a crystal of cobaltocene in a THF solution into a capped EPR tube allows the direct observation of the radical species **1**, **2** and **3**. Reduced complexes **1** and **3** generated an intense and persistent signal. By contrast, the EPR spectrum generated from **2** disappears within few seconds, indicating fast evolution of the reduced species as observed on the electrochemistry scale.<sup>14a,b</sup> All the reduced forms **1**, **2** and **3** exhibit signals at 293 K in a characteristic region for organic radicals with  $g = 2.0042$ , 2.0097 and 2.0089 respectively. The signals



**Fig. 1** Cyclic voltammetry responses (CH<sub>2</sub>Cl<sub>2</sub>, Bu<sub>4</sub>NPF<sub>6</sub> 0.1 M, scan rate 100 mV s<sup>-1</sup>) *vs.* internal ferrocene for (a) **1**<sup>+</sup>, (b) **2**<sup>+</sup> and (c) **3**<sup>+</sup>. Insets show first reduction waves.

† Electronic supplementary information (ESI) available: selected spectroscopic data. See <http://www.rsc.org/suppdata/cc/b0/b008893p/>



Scheme 1

are resolved only in the case of **1** and **2**. The EPR spectrum of **2** gave a poorly resolved quintet [Fig. 2(b)] showing the hyperfine coupling with the four phosphorus nuclei with  $a_{\text{P}} = 3.0$  G. For compound **1**, the EPR spectrum is complex [Fig. 2(a)]. This could be best rationalized by the coupling of the unpaired electron with the four phosphorus nuclei on one hand and further coupling with the *ortho*, *meta* and *para* hydrogens of the phenyl group of the carbon-rich bridge. These results suggest that the radical is centered on the organic bridges in **1**, **2**, **3** and is stabilized by delocalization along the two neighbouring phenyl rings in **1**. In the case of **2**, identification of such a radical neighbouring methyl groups is quite unexpected. These EPR data added to the trapping experiments indicate the organic nature of radicals **1**, **2** and **3** and show that the radical stabilization on the cumulene chain takes place at the trisubstituted carbon atom and thus is not controlled by the presence of a heteroatom bonded to the unsaturated chain.<sup>8</sup>

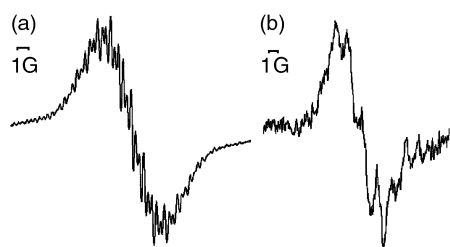


Fig. 2 EPR spectra resulting from reduction of (a) **1**<sup>+</sup>,  $g = 2.0042$ ; (b) **2**<sup>+</sup>,  $g = 2.0097$ .

The synthesis of complexes **4–6** were achieved on successive addition to the cumulene chain of one electron and one hydrogen atom. This led us to study the reactivity difference with the simultaneous addition, *i.e.* the nucleophilic addition, of  $\text{H}^-$ . Nucleophiles are susceptible to attack either the  $\text{C}_\alpha$  or the  $\text{C}_\gamma$  atom of an allenylidene ligand,<sup>3,11a</sup> but using the bulky phosphines additions only occur on  $\text{C}_\gamma$ .<sup>9b</sup> Reductions were performed using  $\text{NaBH}_4$  in THF (Scheme 1). As expected for **1**<sup>+</sup> and **2**<sup>+</sup>, additions of  $\text{H}^-$  take place at the  $\text{C}_\gamma$  carbons yielding the acetylide compounds  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CHPh}_2]$  **4** and  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CHMe}_2]$  **5**. When complex **3**<sup>+</sup> was reduced, a mixture of two compounds was obtained. The presence of  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CH}=\text{C}=\text{CPh}_2]$  **7** (42% estimated by <sup>1</sup>H NMR), which displays a <sup>13</sup>C NMR signal at  $\delta$  216.7 characteristic for the cumulenic carbon ( $\text{C}=\text{C}=\text{C}$ ),<sup>†</sup> is consistent with the electrophilicity of carbon  $\text{C}_\gamma$  in **3**<sup>+</sup>.<sup>10</sup> The main product

$[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CHPh}_2]$  **6** (58%) shows the unknown electrophilic character of the  $\text{C}_\epsilon$  atom. The fact that **7** is not observed in the free radical trapping experiment with  $\text{H}^\bullet$  is very promising, suggesting the location of the radical on the  $\text{C}_\epsilon$  atom in **3** and the higher selectivity of radical addition *vs.* nucleophilic attack.

This last observation associated with cyclic voltammetry, trapping experiments and EPR spectroscopy re-enforces the conclusion that the reduction of Ru(II) allenylidene or pentatetraenylidene generate radical species located on the termini of the cumulene chain that can be written as shown in Scheme 1. More detailed investigations are in progress, including the study of the striking difference in selectivity between reduction/radical trapping and nucleophilic attack on the pentatetraenylidene complex and the potential of cumulenylidene in radical chemistry.

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## Notes and references

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- These results are in agreement with previous theoretical studies on analogous allenylidene  $[(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Ru}=\text{C}=\text{C}=\text{CH}_2]^+$  and  $[(\text{C}_5\text{H}_7)(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}=\text{CH}_2]^+$  suggesting that the LUMO is strongly located on the cumulenic ligand. See: (a) M. A. Esteruelas, A. V. Gomez, A. Lopez, J. Modrego and E. Oñate, *Organometallics*, 1997, **16**, 5826; (b) V. Cadierno, M. P. Gamasa, J. Gimeno, M. González-Cueva, E. Lastra, J. Borge, S. García-Granda and E. Pérez-Carreño, *Organometallics*, 1996, **15**, 2137.
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- (a) The irreversibility of the reduction wave of **2**<sup>+</sup> was also observed in THF at room temperature and at low temperature ( $-30$  °C). (b) Many organometallic species are known to undergo reductive coupling reactions *via* radical intermediates. For examples see: ref. 13(b); Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1996, **118**, 7843; E. J. Roskamp and S. F. Pedersen, *J. Am. Chem. Soc.*, 1987, **109**, 3152. However, in the present reaction we have observed that evolution of **2** led to a mixture of products. The two main compounds have been identified as **5** and  $[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{C}(\text{=CH}_2)\text{CH}_3]$ , certainly result from an intermolecular hydrogen abstraction [such an intermolecular abstraction reaction has already been reported for ketyl radicals, see ref. 13(b)].