

## ESR Spectroscopic Characterisation of a Coordinated Alkyne Radical, and Redox-induced Vinylidene–Alkyne Complex Isomerisation

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One-electron oxidation of  $[\text{Cr}(\text{CO})_2(\text{RC}_2\text{R})(\eta\text{-C}_6\text{Me}_6)]$  **1** gives paramagnetic  $[\text{Cr}(\text{CO})_2(\text{RC}_2\text{R})(\eta\text{-C}_6\text{Me}_6)]^+$  **1<sup>+</sup>** in which the unpaired electron is highly delocalised onto the alkyne; the radical cation (**1<sup>+</sup>**; R = SiMe<sub>3</sub>) is an intermediate in the oxidative isomerisation of the vinylidene complex  $[\text{Cr}(\text{CO})_2\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$  **2** to  $[\text{Cr}(\text{CO})_2(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$  (**1**; R = SiMe<sub>3</sub>).

We have noted previously that the one-electron oxidation of phosphine<sup>1</sup> (L = PR<sub>3</sub>) and alkyne<sup>2</sup> (L = RC<sub>2</sub>R) complexes  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]$  gives isolable monocations  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$ . We now present the results of a detailed ESR spectroscopic study, and an extended Hückel molecular orbital (EHMO) analysis, of these paramagnetic species, which show substantial unpaired electron density on the coordinated alkyne of  $[\text{Cr}(\text{CO})_2(\text{RC}_2\text{R})(\eta\text{-C}_6\text{Me}_6)]^+$ . We also show that the alkyne cation  $[\text{Cr}(\text{CO})_2(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$  is an intermediate in an unprecedented, oxidatively induced, vinylidene–alkyne rearrangement.

Treatment of the alkyne complexes  $[\text{Cr}(\text{CO})_2(\text{RC}_2\text{R}')(\eta\text{-C}_6\text{Me}_6)]$  (**1**; R = R' = Ph, C<sub>6</sub>H<sub>4</sub>OMe, CO<sub>2</sub>Et; R = H, R' = Ph) with  $[\text{FeCp}_2]^+$  in CH<sub>2</sub>Cl<sub>2</sub> gives solutions of the cations  $[\text{Cr}(\text{CO})_2(\text{RC}_2\text{R}')(\eta\text{-C}_6\text{Me}_6)]^+$  **1<sup>+</sup>**, which show room temperature ESR spectra consisting of a single line with four satellites attributable to coupling to the <sup>53</sup>Cr nucleus (*I* = 3/2, 9.5% abundance) and two additional satellites (R = CO<sub>2</sub>Et) with intensities consistent with coupling to two equivalent <sup>13</sup>C nuclei (1.1% abundance). For **1** (R = R' = CO<sub>2</sub>Et)  $\langle g \rangle = 1.9936$ ,  $\langle a^{\text{Cr}} \rangle = 16.8$  G,  $\langle a^{\text{C}} \rangle = 9.1$  G. Frozen CH<sub>2</sub>Cl<sub>2</sub>–thf solutions (thf = tetrahydrofuran) give rhombic spectra, but with smaller *g*-anisotropies and  $g_{\text{avg}}$  (for R = R' = CO<sub>2</sub>Et,  $g_1 = 1.979$ ,  $g_2 = 1.995$ ,  $g_3 = 2.007$ ) than normal for low-spin d<sup>5</sup> systems; e.g. the related complex,  $[\text{Cr}(\text{CO})_2(\text{PEt}_3)(\eta\text{-C}_6\text{Me}_6)]^+$  has  $g_1 = 1.994$ ,  $g_2 = 2.025$ ,  $g_3 = 2.109$ ,  $g_{\text{avg}} = 2.043$ . Moreover, the isotropic spectrum of **1<sup>+</sup>** (R = H, R' = Ph) (Fig. 1) shows a doublet coupling of 4.2 G to the alkyne proton, suggesting a  $\pi$ -spin density on the adjacent carbon of ca. 0.19, i.e. about 40% of the spin is alkyne based.<sup>3</sup> These data indicate significant differences between the electronic structures of  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$  (L = PR<sub>3</sub> and RC<sub>2</sub>R). The implication of substantial unpaired electron density on the alkyne was borne out by EHMO calculations.

The EHMO calculations<sup>4,5</sup> were carried out on model complexes  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{H}_6)]^+$  (L = PH<sub>3</sub> and  $\eta\text{-HC}_2\text{H}$ ) with idealised geometries and standard parameters. The key results are summarised in Fig. 2. For L =  $\eta\text{-HC}_2\text{H}$  the interaction of the half-filled  $d\pi$  orbital (a  $t_{2g}$ -like orbital on the d<sup>5</sup>-Cr<sup>I</sup> fragment) with the filled  $\pi_{\perp}$  orbital of the alkyne ligand has the effect of destabilising the SOMO and delocalising it onto the alkyne [in addition to delocalisation onto the carbonyl ligand, see Fig. 2(c)]. Related conclusions have been drawn from calculations on d<sup>4</sup> and d<sup>6</sup>  $[\text{ML}_2(\eta\text{-alkyne})(\eta\text{-C}_5\text{H}_5)]$  species.<sup>6–8</sup> In contrast, there is no filled phosphine orbital of suitable energy to cause such an interaction and a different pattern of orbitals emerges, essentially of the familiar  $t_{2g}^5$  type.

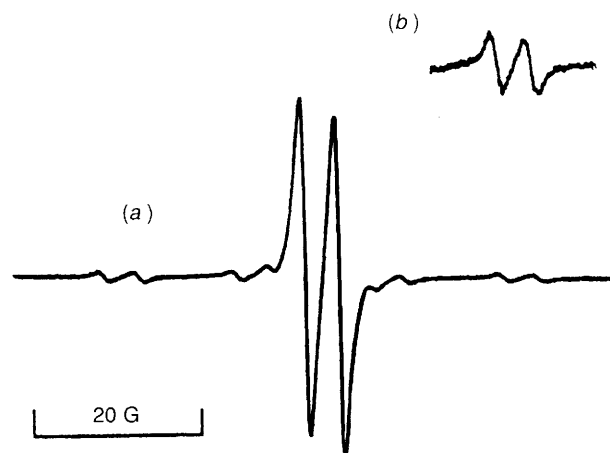
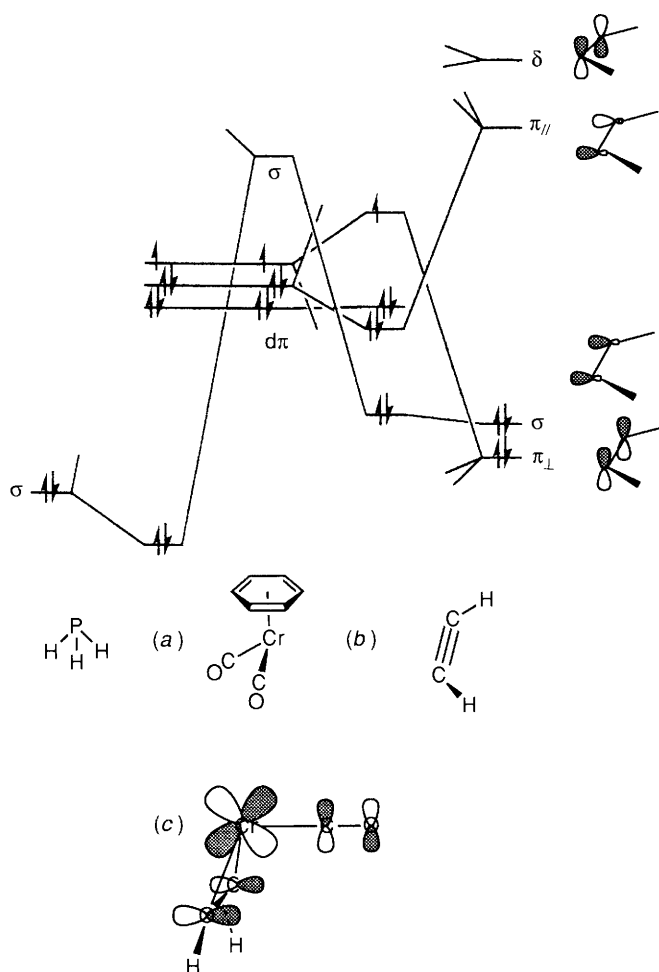
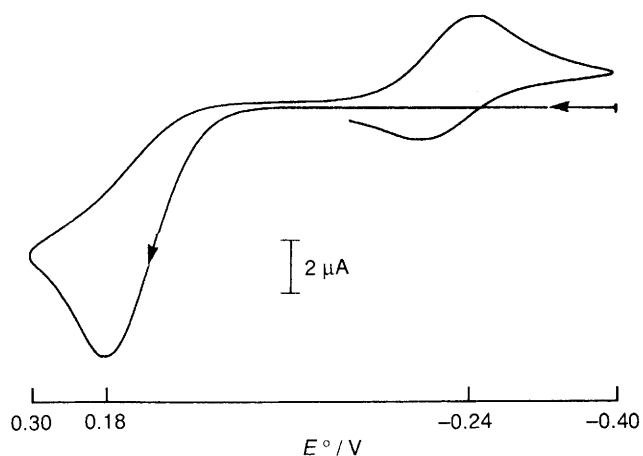


Fig. 1 (a) The room temperature ESR spectrum of  $[\text{Cr}(\text{CO})_2(\text{HC}_2\text{-Ph})(\eta\text{-C}_6\text{Me}_6)]^+$  in CH<sub>2</sub>Cl<sub>2</sub>:thf (2:1); (b) the high field doublet,  $\times 5$

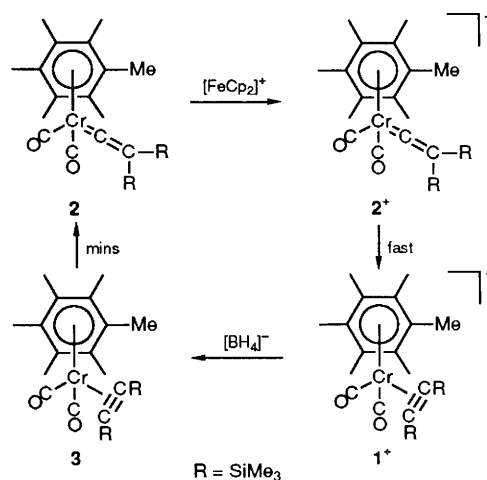


**Fig. 2** The interactions of the frontier orbitals involved in the formation of  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$  from the fragments  $[\text{Cr}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]^+$  and L for cases (a)  $\text{L} = \text{PH}_3$  and (b)  $\text{L} = \eta\text{-HC}_2\text{H}$ ; (c) the SOMO for  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$  ( $\text{L} = \eta\text{-HC}_2\text{H}$ )



**Fig. 3** The cyclic voltammogram (CV) of the vinylidene complex  $[\text{Cr}(\text{CO})_2\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$ , at a platinum disc electrode in  $\text{CH}_2\text{Cl}_2$ . Potentials are vs. the saturated calomel electrode; under the experimental conditions used  $E^\circ$  for ferrocene oxidation is 0.47 V.

Corollaries of the orbital analysis for these alkyne complexes include the following: oxidation of  $[\text{Cr}(\text{CO})_2(\eta\text{-RC}_2\text{R})(\eta\text{-C}_6\text{Me}_6)]$  should result in reduced Cr–C<sub>alkyne</sub> and increased Cr–C(O) and alkyne C–C bond distances since the depopulated orbital [the SOMO of Fig. 2(c)] is Cr–alkyne antibonding; oxidation of the neutral alkyne complexes



**Scheme 1** A 'square scheme' for vinylidene-alkyne complex oxidative isomerisation

should be easier than for corresponding complexes without the four-electron interaction (e.g.  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]$ ,  $\text{L} = \text{PR}_3$ ,  $\text{CO}$ , vinylidene etc.). Finally, the extent of delocalisation calculated for the SOMO indicates that 75% of the electron is on the  $[\text{Cr}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]$  fragment and 25% on the alkyne, in qualitative agreement with the ESR analysis. Although the quantitative results should be viewed with caution, the important conclusion to be drawn is that there is substantial delocalisation present in  $[\text{Cr}(\text{CO})_2\text{L}(\eta\text{-C}_6\text{Me}_6)]^+$  when  $\text{L} = \eta\text{-alkyne}$ .

A radical cation of the type  $[\text{Cr}(\text{CO})_2(\eta\text{-RC}_2\text{R})(\eta\text{-C}_6\text{Me}_6)]^+$  also takes part in an unprecedented redox-induced vinylidene-alkyne isomerisation process. UV irradiation of  $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)]$  with the alkyne  $\text{Me}_3\text{SiC}_2\text{SiMe}_3$  in thf gave, after crystallisation from hexane, orange crystals **2**, 61%,  $\nu(\text{CO})$  1907, 1842  $\text{cm}^{-1}$  with the elemental analysis expected for the alkyne complex  $[\text{Cr}(\text{CO})_2(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$ . However, the  $^{13}\text{C}$  NMR spectrum showed **2** to be the vinylidene complex  $[\text{Cr}(\text{CO})_2\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$  ( $\text{C}_\alpha$ ,  $\delta$  348.9;  $\text{C}_\beta$ , 106.8, in  $\text{C}_6\text{D}_6$ ).

The CV of **2** is very different from those of the reversibly oxidised alkyne complexes described above in showing an irreversible oxidation wave (peak potential = 0.18 V) accompanied by a reversible product wave centred at -0.24 V (Fig. 3). Treatment of **2** with  $[\text{FeCp}_2]^+$  in  $\text{CH}_2\text{Cl}_2$  gave an orange-yellow solution [ $\nu(\text{CO}) = 2018, 1952 \text{ cm}^{-1}$ ] which showed an ESR spectrum ( $\langle g \rangle = 1.9983$ ,  $\langle a^{\text{Cr}} \rangle = 16.8 \text{ G}$ ) almost identical to those of  $1^+$ . On addition of  $[\text{NBu}_4][\text{BH}_4]$  to this solution, two new carbonyl bands were observed (1883, 1812  $\text{cm}^{-1}$ ) due to complex **3**, which converted into **2** in ca. 20 min.

These results can be explained in terms of a 'square scheme' (Scheme 1) in which the vinylidene complex  $[\text{Cr}(\text{CO})_2\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\eta\text{-C}_6\text{Me}_6)]$  **2** undergoes oxidative isomerisation to the alkyne cation  $[\text{Cr}(\text{CO})_2(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\eta\text{-C}_6\text{Me}_6)]^+$  ( $1^+$ ;  $\text{R} = \text{SiMe}_3$ ). Its reduction to  $[\text{Cr}(\text{CO})_2(\text{Me}_3\text{SiC}_2\text{SiMe}_3)(\eta\text{-C}_6\text{Me}_6)]$  **3** is then followed by a much slower alkyne-vinylidene rearrangement to regenerate **2**. The formulation of **3** as an alkyne complex is supported by the observation that its oxidation potential (taken from the product wave in the CV of **2**) and IR carbonyl spectroscopic data are in full accord with those of other alkyne complexes [for which there is a linear correlation between  $E^\circ$  and  $\nu(\text{CO})$ ]. Alkyne-vinylidene rearrangements are well known<sup>9</sup> and EHMO calculations have provided a basis for understanding the isomerisation process when hydrogen migration is involved (i.e. with terminal alkynes).<sup>10</sup> Silyl group migration in such rearrangements is rare.<sup>11</sup> More significant, however, the redox induction of the reverse process, namely vinylidene-to-alkyne isomerisation, is unique.

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