

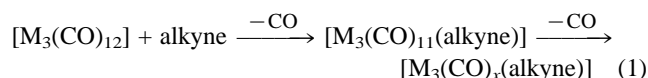
# A versatile route to $[\text{Ru}_3(\text{CO})_{11}(\text{alkyne})]$ complexes

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**Alkynes react at low temperature with  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  to afford the novel  $[\text{Ru}_3(\text{CO})_{11}(\text{alkyne})]$  complexes, which correspond to the first stage of the coordination of alkynes to metal clusters and are the precursors of the previously reported  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-alkyne})]$  derivatives.**

Although the reactions between alkynes and trimetallic carbonyl clusters  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) have been under intense scrutiny in the last two to three decades and a large number of derivatives have been characterized,<sup>1</sup> no report has yet appeared on derivatives corresponding to the first step of alkyne coordination, *i.e.* to  $[\text{M}_3(\text{CO})_{11}(\text{alkyne})]$  species containing an alkyne ligand coordinated in a  $\eta^2$ -mode to a single metallic centre. It is reasonable to think that the lack of observation of these compounds is an indication of their instability and their prompt transformation to  $[\text{M}_3(\text{CO})_x(\text{alkyne})]$  derivatives:<sup>2,3</sup> [eqn. (1);  $\text{M} = \text{Fe}, x = 9$ ;  $\text{M} = \text{Ru}, \text{Os}, x = 10$ ].



Thus the thermally activated dissociation of CO ligands from  $[\text{M}_3(\text{CO})_{12}]$  occurs at temperatures which appear to be too high to allow the observation of detectable amounts of  $[\text{M}_3(\text{CO})_{11}(\text{alkyne})]$  derivatives.

A way to overcome this problem lies in the possibility of forming the coordinatively unsaturated ' $\text{Ru}_3(\text{CO})_{11}$ ' species at low temperature and then to allow its reaction *in situ* with the alkyne ligand.

Some years ago, Keister and coworkers<sup>4</sup> reported that  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$ , in the presence of carbon monoxide, decomposes cleanly to  $[\text{Ru}_3(\text{CO})_{12}]$  (97% isolated yield). They also showed that the kinetics of this conversion are first order in  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  and independent of CO concentration. The proposed mechanism consists of the reductive elimination of  $\text{H}_2$  (through a three-centre transition state) leading to the formation of the coordinatively unsaturated ' $\text{Ru}_3(\text{CO})_{11}$ ' intermediate.

On the basis of this background information, we thought that  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  may represent an interesting 'lightly stabilized' derivative<sup>5</sup> for carrying out substitution reactions at low temperature.

The reaction between  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  and acetylene was carried out directly in the NMR tube, in  $\text{CD}_2\text{Cl}_2$  at 183 K. After few minutes the  $^1\text{H}$  NMR spectrum of the reaction mixture shows two doublets at  $\delta$  8.45 and 5.97 ( $^3J_{\text{HH}}$  8.6 Hz) assigned to  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$ , and two singlets at  $\delta$  5.42 and 1.80 assigned to free  $\text{C}_2\text{H}_4$ † and  $\text{C}_2\text{H}_2$  respectively. The  $^{13}\text{C}$  NMR spectrum at 183 K of the reaction mixture obtained by using a  $^{13}\text{C}$ -enriched sample of  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  is shown in Fig. 1. In the spectrum there are eleven carbonyl resonances of equal intensity at  $\delta$  215.0, 196.1, 194.9, 193.8, 193.1, 191.1, 190.1, 189.0, 188.4, 187.8 and 185.9.

As we approach ambient temperature, we observe that the transformation of  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  to  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)]$  takes place as clearly assessed from both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.<sup>3</sup> The observation of distinct  $^1\text{H}$  and  $^{13}\text{C}$  resonances for all the ligands present in  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  is indicative of a 'frozen' asymmetric structure in which

the acetylene occupies an axial coordination site. The observation of a carbonyl resonance significantly downfield shifted ( $\delta$  215.0) is reminiscent of a semi-bridging ligand which 'disperses' excess of charge to a neighbouring metallic centre. This may be an indication of the occurrence of some interaction of the acetylene ligand with a second ruthenium centre as shown in Fig. 2. The source of molecular asymmetry would then arise from a partial alignment of the alkyne ligand along one of the metal-metal bonds and this arrangement anticipates to some extent the coordination geometry found in  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-alkyne})]$ .<sup>3</sup>

An estimation of the distance between the two hydrogens in the alkyne moiety was obtained by measuring the  $^1\text{H}$  NMR relaxation times at 213 K. Both hydrogens show the same  $T_1$  value of 1.6 s. On the assumption that the relaxation pathway is largely dominated by the dipolar contribution, the  $r_{\text{HH}}$  distance can be determined by eqn. (2):<sup>6</sup>

$$\frac{1}{T_1} = \frac{3}{2} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_{\text{H}}^4 \hbar^2 \tau_c}{r^6} \quad (2)$$

where  $\mu_0$  is the magnetic susceptibility in a vacuum,  $\gamma_{\text{H}}$  is the gyromagnetic value for a proton and  $\tau_c$  is the molecular reorientational time of the complex. Since  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  and  $[\text{Ru}_3(\text{CO})_{12}]$  have very similar molecular sizes, we used a value of 172 ps for  $\tau_c$  at 213 K as evaluated from a recent NMR relaxation study of  $[\text{Ru}_3(\text{CO})_{12}]$ .<sup>7</sup> The obtained  $r_{\text{HH}}$  distance is 2.48 Å. On the basis of a carbon-carbon distance of

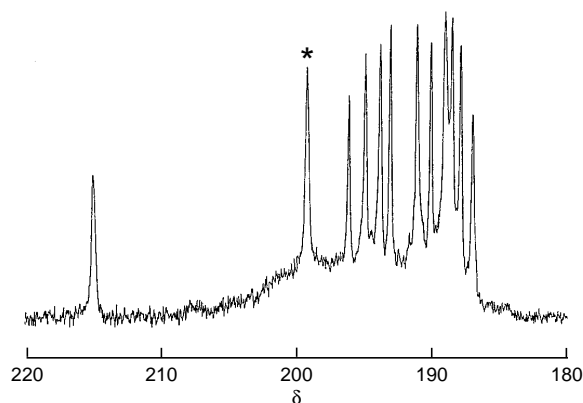


Fig. 1  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a  $^{13}\text{C}$  enriched sample of  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  [ $\text{CD}_2\text{Cl}_2$ , 183 K; \* is assigned to  $[\text{Ru}_3(\text{CO})_{12}]$ ]

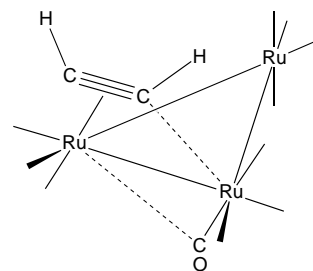


Fig. 2 Proposed structure for  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$

1.27 Å (as found for mononuclear systems containing an  $\eta^2$ -bonded acetylene molecule<sup>8</sup>) and a carbon–hydrogen distance of 1.1 Å an average value of 123.5° for the H–C–C angle was obtained.

Analogous results were obtained when  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  was reacted with substituted acetylenes. In the case of phenylacetylene only one of the two possible isomers of  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-HC}_2\text{Ph})]$  was detected as clearly established by the single resonance for the acetylenic proton observed at  $\delta$  6.18 in the NMR spectrum.

In summary the results herein reported show that  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  may represent a useful starting material for the synthesis of  $[\text{Ru}_3(\text{CO})_{11}\text{L}]$  derivatives where L may be an alkyne as well as a number of other two-electron donor ligands. This novel synthetic route to  $[\text{Ru}_3(\text{CO})_{11}\text{L}]$  species may also provide useful insights into the further development of the cluster–surface analogy,<sup>9</sup> since the first stages of the chemisorption processes are probably represented by the interaction of Lewis-base substrates at single metallic centres followed by the eventual set-up of multicentre bonding schemes.

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### Footnotes

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‡ The detection of  $\text{C}_2\text{H}_4$  seems to imply that the reactivity of  $[\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}]$  could not be limited to the loss of  $\text{H}_2$  to give ' $\text{Ru}_3(\text{CO})_{11}$ '. Another mechanism involving intermediates like  $[\text{Ru}_3\text{H}_2(\text{C}_2\text{H}_2)(\text{CO})_{11}]$  and  $[\text{Ru}_3\text{H}(\text{CHCH}_2)(\text{CO})_{11}]$  which react with  $\text{C}_2\text{H}_2$  to yield  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  and  $\text{C}_2\text{H}_4$  may occur. However, it has been observed that  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  is also formed in the reaction between  $[\text{Ru}_3(\text{CO})_{11}(\text{NCMe})]$  and  $\text{C}_2\text{H}_2$  at room temperature {even if it can be detected only in small amounts as it rapidly transforms to  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}$

$\eta^2\text{-C}_2\text{H}_2)]$ .<sup>10</sup> As MeCN is known to be a good leaving group, this observation supports the view that  $[\text{Ru}_3(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$  may be formed via the intermediate ' $\text{Ru}_3(\text{CO})_{11}$ ' species.

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