

# Enhanced mobility of the cluster $\text{Ru}_3(\text{CO})_{12}$ in the solid state formed *in situ* by the reaction of CO and $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$ on silica

Silvio Aime,<sup>\*a</sup> Alejandro Arce,<sup>b</sup> Roberto Gobetto,<sup>a</sup> Daniela Giusti<sup>a</sup> and Marc Stchedroff<sup>a</sup>

<sup>a</sup> Dipartimento di Chimica Inorganica, Chimica Fisica dei Materiali, Università degli Studi di Torino, via Pietro Giuria 7, 10125 Torino, Italy. E-mail: aime@ch.unito.it

<sup>b</sup> Centro de Química Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

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The reaction of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  (physisorbed on  $\text{SiO}_2$ ) with CO in the solid state leads to  $\text{Ru}_3(\text{CO})_{12}$  and acenaphthylene in quantitative yields; the  $\text{Ru}_3(\text{CO})_{12}$  generated *in situ* is highly mobile leading to a reduced chemical shielding anisotropy.

The large magnetic anisotropy of carbonyl groups makes the solid state  $^{13}\text{C}$  MAS NMR spectra of metal carbonyls highly characteristic,<sup>1,2</sup> as they show a large number of spinning sidebands (SSBs) flanking the isotropic peaks. The onset of molecular motion in the solid state is indicated by the disappearance of these SSB manifolds. This effect is neatly illustrated by the comparison of the  $^{13}\text{C}$  MAS spectra of  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  as bulk crystals and included in the cavity of  $\beta$ -cyclodextrin.<sup>3,4</sup> The large mobility of  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  inside the  $\beta$ -CD cavity appears to be the result of a lack of strong intermolecular interactions which usually lock organometallic molecules rigidly in the crystalline state.<sup>5</sup>

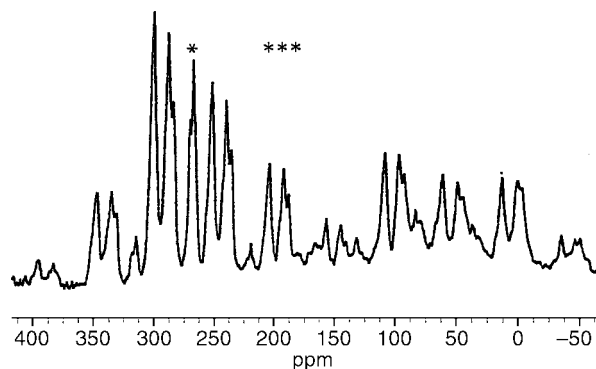
We have previously attempted many solid gas reactions with clusters. However, in almost all cases the products were disordered but static on the NMR timescale.<sup>6</sup> The subject of this communication, is the novel enhanced mobility of  $\text{Ru}_3(\text{CO})_{12}$  on a silica surface, occurring solely when the  $\text{Ru}_3(\text{CO})_{12}$  is deposited by the solid state, *in situ*, carbonylation of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  leading to substantial reduction in the chemical shift anisotropy.

$\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  is synthesised by the previously reported method.<sup>†</sup> All the samples used were synthesised using ca. 30%  $^{13}\text{C}$  enrichment.<sup>‡</sup> At low temperature the solution spectrum of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  shows seven  $^{13}\text{C}$  absorptions, one (269.3 ppm) in the bridging region and six (205.0, 202.7, 201.7, 193.9, 190.0 and 186.8 ppm) in the terminal region, consistent with the structure previously proposed.<sup>7</sup>  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  reacts readily in solution with CO quantitatively affording  $\text{Ru}_3(\text{CO})_{12}$  and free acenaphthylene. However, this reaction is considerably inhibited in the solid state at room temperature. Contrastingly, by physisorbing  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  on a surface of  $\text{SiO}_2$  (Sigma; 450–550  $\text{m}^2 \text{g}^{-1}$  surface area, 10% coverage of the silica surface) the same reaction occurs readily. After 5 min at RT under 100 Torr of CO, 7 mg of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  was transformed into  $\text{Ru}_3(\text{CO})_{12}$  and acenaphthylene (IR spectrum, KBr disk).<sup>8</sup>

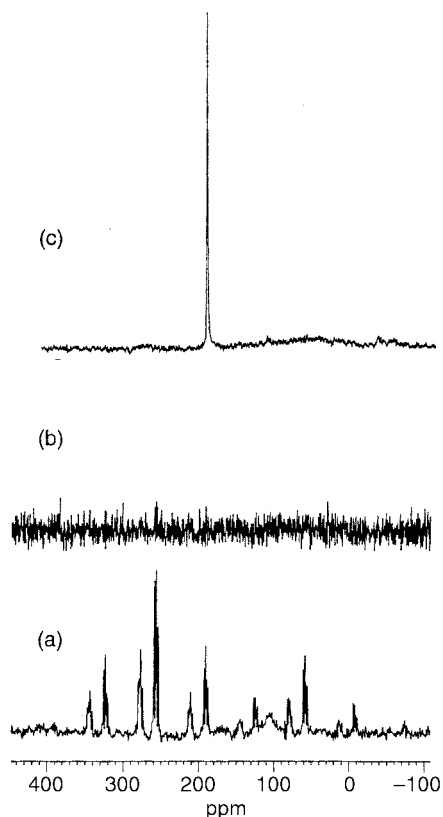
Therefore we decided to further investigate this process by  $^{13}\text{C}$  solid state NMR spectroscopy. The  $^{13}\text{C}$  CP-MAS spectrum of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  shows the bridging carbonyl at 270 ppm while the six terminal CO resonances overlap in three broad signals at 205, 190 and 185 ppm respectively. As has been previously observed for a number of examples the SSB pattern of bridging CO resonances is quite different from that of the terminal CO resonances.<sup>9</sup> This difference may be explained in terms of the reduced chemical shift anisotropy of the bridging CO ligands in respect to the terminal CO ligands, thus providing further confirmation for the assignments.

The  $^{13}\text{C}$  CP-MAS spectrum of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$ , physisorbed on  $\text{SiO}_2$  displays close similarity with the corresponding  $^{13}\text{C}$  CP-MAS spectrum of the crystalline compound [Fig. 1]. On following the reaction of CO with  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)/\text{SiO}_2$  by  $^{13}\text{C}\text{-}\{^1\text{H}\}$  HPPD-MAS (high power proton decoupled—magic angle spinning) there is a progressive decrease in the intensity of the resonances of the starting material, which are in turn replaced by an intense peak at 199.8 ppm which is unambiguously assigned to  $\text{Ru}_3(\text{CO})_{12}$ .

The most striking feature of the  $^{13}\text{C}$  MAS spectrum of the reaction products is the totally unprecedented absence of any SSB manifold flanking the carbonyl resonance of  $\text{Ru}_3(\text{CO})_{12}$  [Fig. 2(c)]. This indicates that  $\text{Ru}_3(\text{CO})_{12}$  produced *in situ* on the surface of the silica possesses a very high mobility on the NMR time scale as compared with that of the normal bulk  $\text{Ru}_3(\text{CO})_{12}$  [Fig. 2(a)].<sup>10</sup> In order to gain a fuller understanding of the causes and the generality of this uniquely enhanced mobility we carried out further experiments: (a) the physisorption of  $\text{Ru}_3(^{13}\text{C})_{12}$  and acenaphthylene on silica; (b) the reaction of  $\text{Ru}_3(\text{CO})_{11}(\text{MeCN})$  on silica with CO to form  $\text{Ru}_3(\text{CO})_{12}$  *in situ*; (c) the physisorption of an identical amount of  $\text{Ru}_3(\text{CO})_{12}$  to that used in (a) directly onto silica. In all three cases the presence of  $\text{Ru}_3(\text{CO})_{12}$  was confirmed by solid state IR spectra (KBr disk). However, in none of the three cases was the absence of sidebands, in the MAS spectra, reproduced. This indicates that the fast molecular motion was absent in the  $\text{Ru}_3(\text{CO})_{12}$  obtained in all three of these experiments. The most striking spectrum is that obtained from the direct physisorption of  $\text{Ru}_3(\text{CO})_{12}$  onto silica: the  $^{13}\text{C}$  MAS experiment [Fig. 2(b)] carried under identical conditions to highly mobile  $\text{Ru}_3(\text{CO})_{12}$  on silica produces no discernible signal. This is due to two factors; firstly all the signals of crystalline  $\text{Ru}_3(\text{CO})_{12}$  (dispersed over 350 ppm) are averaged into one signal in the highly mobile  $\text{Ru}_3(\text{CO})_{12}$ , and secondly the relaxation properties of the highly mobile  $\text{Ru}_3(\text{CO})_{12}$  are more favourable. The most plausible explanation for the motion of  $\text{Ru}_3(\text{CO})_{12}$  obtained



**Fig. 1**  $^{13}\text{C}$  HPPD MAS spectrum of a  $^{13}\text{C}$  enriched sample of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3:\eta^2:\eta^3:\eta^5\text{-C}_{12}\text{H}_8)$  supported on  $\text{SiO}_2$ : 67.8 MHz, spinning speed 3200 Hz, 500 scans (\* denotes isotropic peaks).



**Fig. 2**  $^{13}\text{C}$  HPPD MAS spectrum of (a) crystalline  $\text{Ru}_3(\text{CO})_{12}$ , 240 transients, 5 kHz; (b)  $\text{Ru}_3(\text{CO})_{12}$  physisorbed on silica, 240 transients, 5 kHz; (c)  $\text{Ru}_3(\text{CO})_{12}$  on silica obtained by the reaction of  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3\text{:}\eta^2\text{:}\eta^3\text{:}\eta^5\text{-C}_{12}\text{H}_8)$  physisorbed on  $\text{SiO}_2$  with  $^{13}\text{CO}$ : 67.8 MHz, spinning speed 5300 Hz, 24 scans. The net amount of  $\text{Ru}_3(\text{CO})_{12}$  on the silica in samples (b) and (c) is identical.

from  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3\text{:}\eta^2\text{:}\eta^3\text{:}\eta^5\text{-C}_{12}\text{H}_8)$  with CO on  $\text{SiO}_2$  surface is that  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{C}_{12}\text{H}_8$  formed are unable to yield microcrystalline aggregates. This would fully account for the lack of the observed SSB manifold in the solid state experiments.

$T_1$  measurements on a  $^{13}\text{C}$  enriched sample of the highly mobile  $\text{Ru}_3(^{13}\text{CO})_{12}$ /acenaphthylene/silica samples were carried out. The experiments, although carried out in the solid state, were performed using a commercial solution spectrometer (operating frequency 100.5 MHz for  $^{13}\text{C}$ ) in normal 5 mm solution tubes and a standard solution probehead. The fact that the signal was observable in this way indicates just how fast the molecular motion is in order to average the shielding anisotropy to this extent. At ambient temperature the measured  $T_1$  is markedly shorter than that found for the same compound in

solution at the same magnetic field strength (350 ms vs. 4280 ms) indicating that the extent of motion occurring in the solid state system is significantly lower than that occurring in a highly mobile liquid phase.

An analysis of  $T_1$  versus temperature shows that there is an incipient minimum value at 250 K, from which it is possible to obtain an estimate of the molecular reorientation time. By using this calculated  $\tau_c$  value and assuming that the observed  $T_1$  is determined mainly by the chemical shift relaxation pathway,<sup>11</sup> it is possible to obtain a  $\Delta\sigma$  value of 350 ppm that is not dissimilar to the values reported in literature measured respectively from wide-line,<sup>1</sup> MAS<sup>12</sup> and variable field-solution state experiments.<sup>10</sup> On fitting the observed  $T_1$  vs. temperature data an activation energy of 16.9 kJ mol<sup>-1</sup> for the molecular reorientational motion of  $\text{Ru}_3(\text{CO})_{12}$  in this system is obtained.

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## Notes and references

†  $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})(\mu_3\text{:}\eta^2\text{:}\eta^3\text{:}\eta^5\text{-C}_{12}\text{H}_8)$  is recovered in 91% yield from the reaction of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{C}_{12}\text{H}_8$  for 24 h in refluxing heptane followed by separation by preparative TLC. IR (CO, KBr, cm<sup>-1</sup>) 2042, 2030, 2010, 1996, 1953, 1770.

‡  $^{13}\text{C}$  was obtained from Isotec Inc 99%  $^{13}\text{C}$ ; enrichment of  $\text{Ru}_3(\text{CO})_{12}$  using the standard technique of exchange in cyclohexane solution at 80 °C. Gas reactions were carried out using the neat  $^{13}\text{C}$ CO gas.

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