

# Cyanide $^{13}\text{C}$ NMR hyperfine shifts in paramagnetic cyanide-bridged mixed-valence complexes

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Paramagnetic (hyperfine) NMR shifts in the  $^{13}\text{C}$  cyanide bridge and  $^{31}\text{P}$  resonances in a set of mixed valence complexes  $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{PPh}_3)\text{L}(\text{C}^{13}\text{N})\text{Ru}(\text{NH}_3)_5]^{n+}$  ( $\text{R} = \text{H}$ ;  $\text{L} = \text{PPh}_3, \text{CO}, \text{NO}^+$ ;  $\text{R} = \text{Me}$ ;  $\text{L} = \text{PPh}_3$ ) are sensitive to the extent of intermetallic charge-transfer, and are strongly solvent dependent.

In bimetallic cyanide-bridged mixed valence complexes the cyanide ion mediates intermetallic electronic communication. In unsymmetrical systems the extent of donor–acceptor charge transfer between the metals has, for the most part, been studied by optical and electrochemical methods.<sup>1</sup> With the exception of infra-red studies<sup>2</sup> concerning the CN stretching frequency, little attention has been given to the influence of the charge transfer on the bridging group, whose role is usually described by an empirical transfer integral. In this report we show that the distribution of unpaired electron spin across the cyanide bridge can be tracked using NMR paramagnetic shifts.

Cyanide-bridged species in which the metals have low-spin  $d^6$ – $d^5$  configurations, belong in the weakly coupled Robin–Day<sup>3</sup> Class II. If the  $d^5$  acceptor is a group VIII metal pentaammine moiety, the unpaired electron is primarily localized on this centre, and its reduction potential varies with the Gutmann<sup>4</sup> donor number (DN) of the solvent. Ligand-mediated coupling redistributes spin density from the paramagnetic ( $d^5$ ) centre towards the nominally diamagnetic ( $d^6$ ) metal and its local coordination environment. As a result pseudo-contact (dipolar) and contact contributions<sup>5</sup> to selected NMR chemical shifts can be a sensitive indicator of the consequences of the donor–acceptor interactions.

Here we identify paramagnetic (hyperfine) shifts in the  $^{13}\text{C}$  NMR signal of the linking cyanide as well as in the  $^{31}\text{P}$  resonances of phosphines coordinated to the  $d^6$  metal in a set of related compounds based on the cyclopentadienyl triphenylphosphineruthenium(II) and pentaammine ruthenium(III) moieties (Fig. 1). These shifts respond to variations in the ligand,  $L$ , and to changes in the solvent donicity.

The isotopically labelled cyanide ( $^{13}\text{C}$ ; 100%) diruthenium compounds **1–4** (Fig. 1) were synthesized† by reacting a slight excess of the diamagnetic organometallic species,  $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{PPh}_3)\text{L}(\text{C}^{13}\text{N})]$  ( $\text{R} = \text{H}$ ;  $\text{L} = \text{PPh}_3, \text{CO}, \text{NO}^+$  and  $\text{R} =$

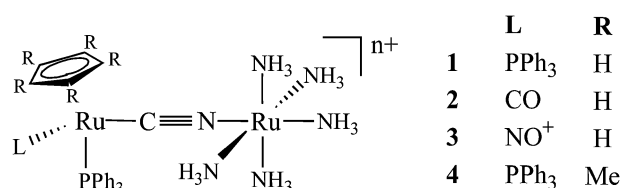


Fig. 1 Structures of ruthenium mixed valence complexes:  $n = 3$  (**1**, **2**, **4**);  $n = 4$  (**3**).  $\text{CF}_3\text{SO}_3^-$  anion.

$\text{Me}$ ;  $\text{L} = \text{PPh}_3$ ) with the labile complex  $[\text{Ru}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$  in acetone under nitrogen at ambient temperature in the dark for a few days. Analytically pure materials were isolated through recrystallization.

Apart from quite sharp peaks in the aromatic carbon region (90–150 ppm), the  $^{13}\text{C}$  NMR‡ solution spectra (298 K) of **1–4** exhibit a very broad unstructured peak (halfwidth  $\sim 300$ –4500 Hz) far downfield ( $+400$ –1300 ppm), corresponding to a paramagnetic shift between  $\sim +320$  and  $+1120$  ppm, attributed to the bridging cyanide. Representative spectra for **1–3** in acetonitrile are shown in Fig. 2.

The  $^{13}\text{C}$  cyanide chemical shift primarily depends upon the identity of ligand  $L$  and to a lesser extent upon the solvent. We find generally that  $\delta(^{13}\text{CN})$  for  $\text{L} = \text{PPh}_3 > \text{CO} > \text{NO}^+$  and, for a given ligand  $L$ ,  $\delta(^{13}\text{CN})$  in nitromethane (DN = 2.7) >

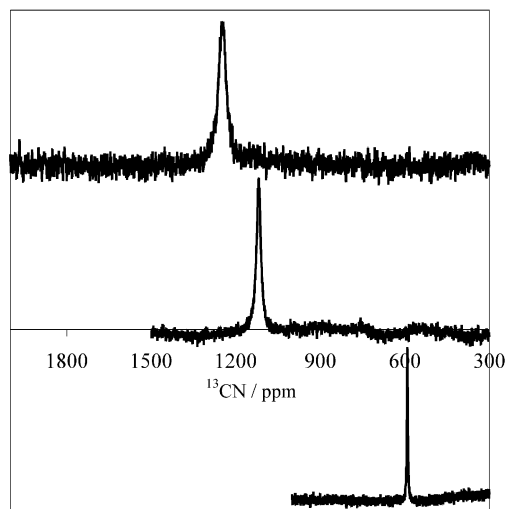


Fig. 2  $^{13}\text{C}$  NMR spectra of the cyanide-bridge in **1** (top), **2** and **3** (bottom) in  $d_3$ -acetonitrile at 298 K. Solvent reference, 1.39 ppm.

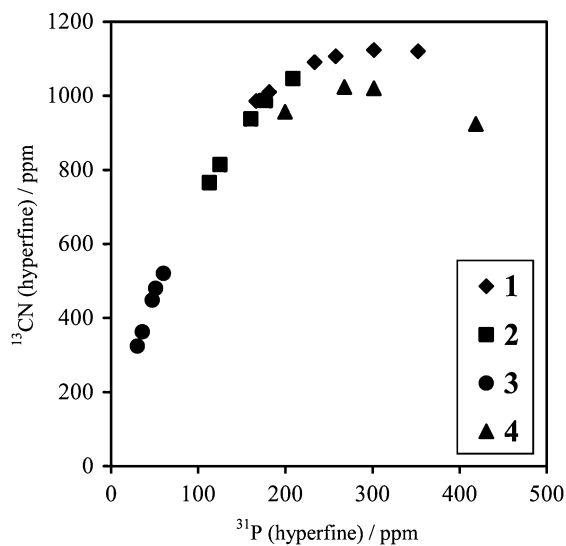
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acetonitrile (DN = 14.1) > acetone (DN = 17) > dimethylformamide (DN = 26.6) > dimethylsulfoxide (DN = 29.8). The  $^{31}\text{P}$  resonances $\ddagger$  of **1–4** follow similar trends to those of  $^{13}\text{CN}$ , showing positive paramagnetic shifts and large linewidths ( $\sim 70\text{--}400$  Hz). These trends can be rationalized in terms of the degree of redox asymmetry between the two metal centres. Optical (and electrochemical) measurements show that as the  $\pi$ -accepting ability of L increases, in the order  $\text{PPh}_3 < \text{CO} < \text{NO}^+$ , the energy of the donor metal orbitals decrease, and MMCT excited states are raised in energy. For example, in  $d_3$ -acetonitrile,  $E_{\text{MMCT}} \approx 15\,130$  (**1**),  $\approx 18\,315$  (**2**) and  $> 25\,700$  (**3**)  $\text{cm}^{-1}$ . Similarly, as the donor number of the solvent increases the pentaammineruthenium(III) centre is stabilized (through hydrogen bonding interactions) with respect to reduction, and the MMCT energy rises linearly.<sup>6–8</sup> According to Hush theory,<sup>6,9</sup> as the degree of redox asymmetry (and MMCT energy) decreases, as in the sequence **3** > **2** > **1** and in the solvent order dimethylsulfoxide > dimethylformamide > acetone > acetonitrile > nitromethane, delocalization of the  $d\pi$  electron spin increases, resulting in enhanced hyperfine interactions for nuclei directly bonded or close to the formally diamagnetic centre.

Counteranion interactions also influence the redox asymmetry.<sup>8</sup> In the weak donor solvent nitromethane, the  $^{13}\text{C}$  resonance of **1** shifts by  $-3$  ppm when the trifluoromethanesulfonate anion is replaced by the more weakly interacting hexafluorophosphate anion, whereas the  $^{31}\text{P}$  peak shifts by  $+52$  ppm.

Optical measurements reveal there are strong linear correlations between  $\delta_{\text{hyp}}(^{31}\text{P})$  and  $E_{\text{MMCT}}$ . Thus,  $\delta_{\text{hyp}}(^{31}\text{P})$  (**1**)/ppm =  $-0.0467E_{\text{MMCT}}/\text{cm}^{-1} + 973.8$ ;  $R^2 = 0.994$  and  $\delta_{\text{hyp}}(^{31}\text{P})$  (**2**)/ppm =  $-0.0283E_{\text{MMCT}}/\text{cm}^{-1} + 696.7$ ;  $R^2 = 0.995$ . (Charge transfer energies for **3** are obscured in the ultraviolet.) In contrast, the relationships between  $\delta_{\text{hyp}}(^{13}\text{C})$  and  $E_{\text{MMCT}}$  are unambiguously nonlinear.

Fig. 3 shows a monotonic but nonlinear plot of the hyperfine shifts  $\delta_{\text{hyp}}(^{31}\text{P})$  against  $\delta_{\text{hyp}}(^{13}\text{C})$  for the complete set of



**Fig. 3** Correlation between  $^{13}\text{C}$  cyanide and  $^{31}\text{P}$  NMR paramagnetically induced (hyperfine) chemical shifts in **1–4** in various aprotic solvents $\ddagger$ .

observations. Within the closely related set of complexes (**1**, **2**, **3**), the range of  $^{31}\text{P}$  shifts induced by varying the solvent is  $\sim 185$ , 100 and 30 ppm, respectively. In contrast, the corresponding variations in  $^{13}\text{CN}$  shifts are  $\sim 135$ , 200 and 285 ppm. Apparently, as the degree of redox asymmetry decreases, in the sequence **3** > **2** > **1**, the phosphorus centre becomes more sensitive whereas the  $^{13}\text{CN}$  centre becomes less sensitive to the increase in spin delocalization. There appears to be a limit beyond which an increase in spin density at the  $d^6$  metal, as sensed by the  $^{31}\text{P}$  shift, does not cause a matching increase in spin density on the bridging carbon, even though they are bonded to the same metal. Moreover, for compound **4** (Fig. 3), the most strongly coupled system, the  $^{13}\text{CN}$  chemical shift reaches a maximum and begins to fall in the least basic media, whereas the  $^{31}\text{P}$  shift continues to increase. This behaviour is consistent with the cyanide bridge gating spin density to the metal–phosphorus centre from the paramagnetic ammine metal in a way that appears to restrict the population of spin within the bridge orbitals.

A preliminary analysis suggests that Fermi contact contributions dominate the  $^{13}\text{C}$  paramagnetic shifts in the cyanide bridge (and the  $^{31}\text{P}$  shifts). Based on the Hush model, less than 3% of electron spin is delocalized in these compounds,<sup>6</sup> so an estimate of the dipolar electron–nuclear interaction between the  $^{13}\text{C}$  nucleus and the  $d^5$  metal centre can be obtained from experimental EPR  $g$ -values.<sup>10</sup> On this basis pseudo-contact contributions are either far too small (for compounds **1** and **2**), or have the wrong sign (for compound **3**) to account for the observed shifts. Local ligand-centred pseudo-contact contributions arising from spin density in the  $\pi$ -system are difficult to quantify, but may be significant. Nonetheless, the  $^{13}\text{C}$  NMR cyanide resonances appear to be sensitive probes of the local spin-density in the bridge.

We are not aware of any data on  $^{13}\text{C}$  paramagnetic shifts of cyanide ions bound through carbon to ruthenium(III). Determining the  $^{13}\text{C}$  paramagnetic shifts in the *monoruthenium(III)* compounds  $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{PPh}_3)\text{L}(\text{CN})]^+$  ( $\text{R} = \text{H}$ ;  $\text{L} = \text{PPh}_3, \text{CO}, \text{NO}^+$  and  $\text{R} = \text{Me}$ ;  $\text{L} = \text{PPh}_3$ ) would enable a limiting reference point for the  $^{13}\text{C}$  shifts observed in **1–4**. Unfortunately, electrochemical studies reveal one-electron oxidation of the organoruthenium(II) centres to be irreversible when  $\text{R} = \text{H}$ ;  $\text{L} = \text{PPh}_3, \text{CO}$ , and beyond  $+2$  V when  $\text{L} = \text{NO}^+$ . When  $\text{R} = \text{Me}$  and  $\text{L} = \text{PPh}_3$ , the  $\text{Ru(II/III)}$  couple is reversible but NMR experiments on solutions generated by the stoichiometric addition of a one-electron oxidant in an NMR tube have so far been unsuccessful. The limit of  $^{13}\text{C}$  and  $^{15}\text{N}$  shift data have been reported for low-spin  $\text{Fe(III)}$  in hexacyanoferrate(III),<sup>11</sup> porphyrins and heme proteins.<sup>5,12</sup> The  $^{13}\text{C}$  resonances are far upfield ( $\sim -2000$  to  $-4200$  ppm) whereas the  $^{15}\text{N}$  peaks are found far downfield ( $\sim +600$  to  $+1000$  ppm). The alternation in sign is indicative of a dominant contact spin-polarization mechanism. In compounds **1–4**, the downfield  $^{13}\text{C}$  shifts are consistent with a similar mechanism since the cyanide nitrogen is bonded to the paramagnetic metal centre. The peaking of the  $^{13}\text{C}$  shifts in Fig. 3 may therefore reflect the onset of competing spin delocalization and core polarization effects in mixed-valence systems, and deserves a more comprehensive theoretical treatment and experimental investigation. The sign of the  $^{13}\text{C}$  bridging cyanide

resonance might tell apart linkage isomers of Class II mixed-valence complexes<sup>13</sup> comprising cyanide-bridged diamagnetic and paramagnetic centres.

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## Notes and references

† The <sup>13</sup>C cyanide labelled organometallic precursors, [(η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)-Ru(PPh<sub>3</sub>)<sub>2</sub><sup>13</sup>CN] (R = H, Me) were synthesised from Na<sup>13</sup>CN (CSK Gas Products) and [(η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl] following published procedures.<sup>14</sup> (R = H), IR/KCl  $\nu(^{13}\text{CN}) = 2024\text{ cm}^{-1}$ ; NMR $\ddagger$ /d<sub>2</sub>-dichloromethane  $\delta(^{13}\text{CN}) = 140.4\text{ ppm}$ ,  $\delta(^{31}\text{P}) = 50.3\text{ ppm}$ ; (R = Me) IR/KBr  $\nu(^{13}\text{CN}) = 2022\text{ cm}^{-1}$ ; NMR $\ddagger$ /d<sub>6</sub>-acetone  $\delta(^{13}\text{CN}) = 148.4\text{ ppm}$ ,  $\delta(^{31}\text{P}) = 53.8\text{ ppm}$ . The nitrosyl derivative, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)(NO)(<sup>13</sup>CN)](CF<sub>3</sub>SO<sub>3</sub>), was synthesised from [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub><sup>13</sup>CN] according to the literature method,<sup>14</sup> but aqueous trifluoromethanesulfonic acid was employed instead of NH<sub>4</sub>PF<sub>6</sub> to isolate the desired salt. Analysis: found (calc.) C, 47.5 (47.6); H, 3.0 (3.2); N, 4.4 (4.4)%; IR/KBr  $\nu(^{13}\text{CN}) = 2090$ ,  $\nu(\text{NO}) = 1866\text{ cm}^{-1}$  (broad); NMR $\ddagger$ /d<sub>6</sub>-acetone  $\delta(^{13}\text{CN}) = 110.9\text{ ppm}$ ,  $\delta(^{31}\text{P}) = 39.4\text{ ppm}$ . Yield 85%.

The carbonyl, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)(CO)(<sup>13</sup>CN)], was prepared by heating [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub><sup>13</sup>CN] (0.5 g, 0.7 mmol) in deaerated decalin (~80 mL) and 1,2-dichlorobenzene (~10 mL) at ~180 °C for 2 hours whilst passing carbon monoxide through the solution. When the reaction was complete [monitored by <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta(\text{C}_5\text{H}_5) = 5.0\text{ ppm}$  (product), 4.4 ppm (reactant)] the solution was mixed with toluene and chromatographed on alumina. After washing the column with pentane the product was eluted with tetrahydrofuran, isolated by evaporation and dried under vacuum. Yield 0.3 g (89%). Analysis: found (calc.) C, 62.4 (62.2); H, 4.1 (4.2); N, 3.1 (2.9)%; IR/KCl  $\nu(^{13}\text{CN}) = 2058$ ,  $\nu(\text{CO}) = 1968\text{ cm}^{-1}$  (broad); NMR $\ddagger$ /d-chloroform  $\delta(^{13}\text{CN}) = 131.4$ ,  $\delta(^{31}\text{P}) = 53.3\text{ ppm}$ .

The known bimetallic complexes **1** and **4** were synthesised by a slight modification of the published method.<sup>6</sup> The syntheses of the new compounds **2** and **3** were achieved following a similar method, specified herewith for **2**. [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)(CO)Ru(<sup>13</sup>CN)] (0.1 g, 0.21 mmol) was pre-dissolved in dichloromethane (1–2 mL) and acetone (~20 mL) and placed under nitrogen (or argon). (Dichloromethane is unnecessary for preparing **3**). [Ru(NH<sub>3</sub>)<sub>5</sub>(OSO<sub>2</sub>CF<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (0.12 g, 0.19 mmol) was added to the stirred solution and the mixture was warmed in the dark at 30 °C for a few days. The solution was rotor-evaporated to dryness (<35 °C). The residue was dissolved in a few drops of acetone and ethanol was added dropwise to the swirled solution to produce a crystalline solid. Diethylether (~2 mL) was added dropwise to the swirled mixture which was then refrigerated (-25 °C; 2 hours). The supernatant solution was removed and the product was isolated by filtration, washed with diethylether and dried under vacuum. Typical yield 0.17 g (80%). Portions of **1** and **4** were converted to PF<sub>6</sub><sup>-</sup> salts using ammonium hexafluorophosphate in aqueous methanol.

Analytical data: **1** (blue); IR/KCl  $\nu(^{13}\text{CN}) = 1970\text{ cm}^{-1}$ ; **2** (magenta); found (calc.) C, 30.1 (30.1); H, 3.1 (3.2); N, 7.2 (7.5)%; IR/KCl  $\nu(^{13}\text{CN}) = 2064$ ,  $\nu(\text{CO}) = 1990\text{ cm}^{-1}$ ; **3** (yellow); found (calc.) C, 26.6 (26.5); H, 3.0 (2.8); N, 7.4 (7.7)%; IR/KCl  $\nu(^{13}\text{CN}) = 2122$ ,  $\nu(\text{NO}) = 1892\text{ cm}^{-1}$ ; **4** (turquoise green); IR/KBr  $\nu(^{13}\text{CN}) = 1942\text{ cm}^{-1}$ .

‡ <sup>13</sup>C NMR spectra (125.70 MHz) of the trifluoromethanesulfonate salts of the bimetallic paramagnets were recorded on concentrated samples (~15 mg in 0.5 mL) at 298 K on a Bruker AVII 500 spectrometer with a <sup>13</sup>C optimised cryoprobe in the following solvents and referenced accordingly (d<sub>3</sub>-nitromethane (except **4**) 62.54 ppm; d<sub>3</sub>-acetonitrile 1.39 ppm; d<sub>6</sub>-acetone 29.9 ppm; d<sub>7</sub>-dimethylformamide (except **4**) 163.15 ppm; d<sub>6</sub>-dimethylsulfoxide 39.5 ppm). In addition, **1** and **4** were recorded as hexafluorophosphate salts in nitromethane. Paramagnetically induced (hyperfine) shifts were calculated from the <sup>13</sup>CN resonance of the appropriate diamagnetic monometallic precursor†.

<sup>31</sup>P NMR spectra (202.38 MHz) were recorded at ~298 K on a Varian UNITY 500 spectrometer on the same samples. Chemical shifts were referenced to a capillary of D<sub>3</sub>PO<sub>4</sub> (0 ppm) inserted into each solution. Hyperfine shifts were calculated from <sup>31</sup>P resonances of the appropriate diamagnetic organometallic fragment. The <sup>13</sup>CN and <sup>31</sup>P resonances of the organometallic precursors were almost independent of solvent, varying at most by 2.5 ppm.

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