

# Coordination chemistry of mono- and di-nitriles in $[\text{Ru}_3(\text{CO})_{12-n}(\text{RCN})_n]$ ( $n = 1-3$ ): influence of the CO/nitrile ratio on fluxionality

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## Abstract

The clusters  $[\text{Ru}_3(\text{CO})_{12-n}(\text{RCN})_n]$  ( $n = 1-3$ ; RCN = acetonitrile, adiponitrile, phenylenediacetonitrile) have been prepared in dichloromethane solution by reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with  $\text{Me}_3\text{NO}$  in the presence of the desired nitrile. The number of coordinated nitriles depends on the nitrile concentration and to a lesser extent on the  $\text{Me}_3\text{NO}/\text{Ru}_3$  ratio. The new cluster  $[\text{Ru}_3(\text{CO})_9(\text{MeCN})_3]$  is prepared and isolated in high yield. Spectroscopic IR and  $^{13}\text{C}$  NMR investigations in solution indicate that the dinitriles remain monocoordinated but only in a concentrated medium ( $1\text{M} < [\text{RCN}] < 4\text{M}$ ). Spectroscopic data suggest axial coordination of the nitriles, one on each ruthenium atom, and equatorial bridging carbonyl groups. For  $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-CO})_3(\text{MeCN})_2]$ , the two nitriles are located on each side of the triruthenium plane, whereas for  $[\text{Ru}_3(\text{CO})_6(\mu_2\text{-CO})_3(\text{MeCN})_3]$ , two MeCN are located on one side of the triruthenium plane with the third lying on the other side. Variable-temperature  $^{13}\text{C}$  NMR study reveals a fluxionality of the carbonyls around the trimetal core. The first fluxional motion involves in-plane carbonyl exchange with activation energies depending on the degree of substitution  $n$ . The influence of ligand substitution in the axial position on the mobility of the carbonyls is attributed to an increase of the  $\pi$  back-donation from the cluster to each of the remaining carbonyls with increasing substitution.

**Keywords:** Ru; Trinuclear clusters; Nitrile coordination; Fluxionality; Mechanisms

## 1. Introduction

Dinitriles and their hydrogenated products, the diamines, are key substrates in the manufacture of polyamides [1]. This is particularly true for 6,6-Nylon produced by condensation of adipic acid with hexamethylenediamine (HMD), the quality of which relies heavily on the purity of the diamine. Nowadays, HMD is produced by selective catalytic hydrogenation of adiponitrile (ADN) over metal catalysts based on Ni, Co, Fe and Ru. However, the main obstacle in this chemistry is specific impurities from some intramolecular coupling side reactions [2]. The potential industrial impact of this chemistry, as well as the lack of basic knowledge, has prompted us to embark upon a program aimed at understanding the specific interactions of dinitriles with transition metal catalysts. Many studies have been made of the coordination of mononitriles [3], especially acetonitrile, but very few on dinitriles [4].

Furthermore, these reports deal with coordination to mononuclear complexes. However, these can lead neither to multicentre coordination, as shown by Kaesz and coworkers for mononitriles, nor to adjacent coordination of the two cyano functions [5,6]. The clusters  $[\text{Ru}_3(\text{CO})_{11}(\text{MeCN})]$  and  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  first described by Foulds et al. [7] were chosen as multicentre complexes and this paper reports the preparation and structures in solution of a series of triruthenium carbonyl clusters polysubstituted by mono- and di-nitriles, and on the effect of the level of polysubstitution on the mobility of the carbonyls around the triruthenium framework.

## 2. Results

Following the method of Johnson and Lewis [7],  $[\text{Ru}_3(\text{CO})_{12}]$  is reacted with  $\text{Me}_3\text{NO}$  in dichloromethane solution at low temperature and in the presence of acetonitrile to afford the known clusters  $[\text{Ru}_3(\text{CO})_{11}(\text{MeCN})]$  (**1**) and  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  (**2**). The selectivity for **1** or **2** depends on the nitrile concentration, the

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Table 1  
IR spectral data <sup>a</sup>

Complex	Solid state (Nujol)		Solution
	$\nu(\text{CN})$ ( $\text{cm}^{-1}$ )	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	
[Ru <sub>3</sub> (CO) <sub>11</sub> MeCN] (1)	2304(w)		2097 (w), 2043 (vs), 2005 (m) <sup>b</sup>
[Ru <sub>3</sub> (CO) <sub>10</sub> (MeCN) <sub>2</sub> ] (2)	2295(w)	2086 (m), 2018 (vs, br), 1997 (s), 1971 (s, sh), 1952 (m,br), 1815 (s,br)	2082 (w), 2015 (vs), 1996 (s), 1954 (m), 1820 (m,br) <sup>b</sup>
[Ru <sub>3</sub> (CO) <sub>9</sub> (MeCN) <sub>3</sub> ] (3)	2290(w)	2030 (m), 2011 (m,sh), 1992 (s,br), 1954 (m,sh), 1940 (s,br), 1914 (s,sh), 1815 (m,sh), 1785 (s,br)	2032 (w), 1997 (vs), 1948 (m,br), 1854 (vw), 1802 (s,br) <sup>c</sup>
[Ru <sub>3</sub> (CO) <sub>11</sub> ADN] (4)			2097 (w), 2043 (vs), 2003 (m) <sup>b</sup>
[Ru <sub>3</sub> (CO) <sub>10</sub> (ADN) <sub>2</sub> ] (5)	2246(w)	2111 (w), 2089 (m), 2073 (w), 2021 (s,br), 2009 (s,sh), 1980 (s,br), 1932 (s,br), 1871 (w), 1818 (s,sh), 1804 (s,br)	2083 (w), 2015 (vs), 1996 (s), 1954 (m), 1820 (m) <sup>b</sup>
[Ru <sub>3</sub> (CO) <sub>9</sub> (ADN) <sub>3</sub> ] (6)			2032 (w), 1997 (vs), 1988 (sh), 1945 (m), 1932 (m,sh), 1855 (vw), 1804 (s,br) <sup>d</sup>
[Ru <sub>3</sub> (CO) <sub>11</sub> PDAN] (7)			2097 (vw), 2086 (vw), 2043 (vs), 2037 (vs), 2004 (s,br) <sup>b</sup>
[Ru <sub>3</sub> (CO) <sub>10</sub> (PDAN) <sub>2</sub> ] (8)			2085 (w), 2060 (m), 2032 (s), 2007 (s), 1966 (m,br), 1820 (m,br) <sup>b</sup>
[{Ru <sub>3</sub> (CO) <sub>10</sub> (ADN) <sub>2</sub> ] <sub>4</sub> ] (9)		2089 (m), 2021 (s,br), 2006 (s,sh), 1979 (s,br), 1933 (s,br), 1871 (w), 1818 (sh), 1805 (s,br)	2083 (w), 2015 (vs), 1996 (vs), 1954 (m,br), 1820 (m,br) <sup>d</sup>
[Ru <sub>3</sub> (CO) <sub>11</sub> (CD <sub>3</sub> CN)] (10)	2314(w)		2114 (vw), 2097 (w), 2083 (vw), 2044 (vs,br), 2014 (s), 2006 (s) <sup>c</sup>
[Ru <sub>3</sub> (CO) <sub>10</sub> (EtCN) <sub>2</sub> ] (11)	2288(vw)	2088 (m), 2012 (s,br), 1938 (s,br), 1803 (s,br)	2085 (w), 2016 (vs), 1997 (s), 1950 (m), 1819 (s) <sup>f</sup>

<sup>a</sup> Abbreviations: vs = very strong, s = strong, m = medium, sh = shoulder, w = weak, br = broad. <sup>b</sup> In dichloromethane. <sup>c</sup> In acetonitrile. <sup>d</sup> In adiponitrile. <sup>e</sup> In acetonitrile-d<sub>3</sub>. <sup>f</sup> In propionitrile.

nitrile/[Ru<sub>3</sub>(CO)<sub>12</sub>] ratio and on the Me<sub>3</sub>NO/[Ru<sub>3</sub>(CO)<sub>12</sub>] ratio (Experimental section). These clusters are difficult to separate; however, the new cluster [Ru<sub>3</sub>(CO)<sub>9</sub>(MeCN)<sub>3</sub>] (**3**) may be isolated in high yield (greater than 95%) as a light yellow microcrystalline powder by a similar reaction using a high Me<sub>3</sub>NO/[Ru<sub>3</sub>(CO)<sub>12</sub>] ratio (ca. 5) in acetonitrile solution (see Experimental section). These clusters were characterized by elemental analysis and solution studies. None of the clusters **1**, **2** and **3** are stable in solution in the absence of acetonitrile. For example, when dissolved in dichloromethane, cluster **2** slowly decomposes ( $t_{1/2}$  = 1.2 h, greater than 99%, 24 h) to afford [Ru<sub>3</sub>(CO)<sub>12</sub>]

and metallic Ru via the formation of **1** (IR evidence). Under the same conditions, **3** transforms first into **2** (greater than 95%, 1 h) which in turn decomposes as previously described. The order of stability in dichloromethane is **1** ≥ **2** > **3**. In acetonitrile solution, no decomposition to metallic Ru was observed, but the lighter clusters **1** and **2** slowly transform into **2** ( $t_{1/2}$  = 3 h) and **3** ( $t_{1/2}$  = 8 days) respectively. Within weeks in acetonitrile at room temperature, a further transformation occurs, probably to give mononuclear species of the type [Ru(CO)<sub>p</sub>(MeCN)<sub>m</sub>]. Such fragmentation is well documented for clusters containing P-donor ligands [8].

Table 2  
<sup>13</sup>C{<sup>1</sup>H}NMR data <sup>a</sup>

Complex	(K)	Solvent	$\delta$ (CO) (ppm)	$\delta$ (CN)(ppm)
[Ru <sub>3</sub> (CO) <sub>11</sub> MeCN](1)	183	CD <sub>2</sub> Cl <sub>2</sub>	201.8	127.6
[Ru <sub>3</sub> (CO) <sub>10</sub> (MeCN) <sub>2</sub> ](2)	173	CD <sub>3</sub> CN-CH <sub>2</sub> Cl <sub>2</sub>	197 (3; A, B); 200 (2; C or D); 200.3 (2; D or C); 256.9 (2; F); 260 (1; E)	128.8
[Ru <sub>3</sub> (CO) <sub>9</sub> (MeCN) <sub>3</sub> ](3)	243	CD <sub>3</sub> CN	201.3 (4; C, D); 227.1 (br; 6; A, B, E, F)	128.9 (1); 128.2 (2)
	243		199.4 (1; A); 199.7 (2; B); 202.8 (2; C); 204.1 (1; D); 265.6 (1; E); 266.1 (2; F)	
[Ru <sub>3</sub> (CO) <sub>10</sub> (ADN) <sub>2</sub> ](5)	293	ADN-CD <sub>2</sub> Cl <sub>2</sub>	200 (3; A, B); 203.3 (2; C); 204.8 (1; D); 265.4 (3; E, F)	129.2 (1); 128.4 (2)
[Ru <sub>3</sub> (CO) <sub>9</sub> (ADN) <sub>3</sub> ](6)	223	ADN-CD <sub>2</sub> Cl <sub>2</sub>	199.7, 199.9 (4; C, D); 226 (br; 6; A, B, E, F)	
	243	ADN-CD <sub>2</sub> Cl <sub>2</sub>	198.1 (1; A); 198.4 (2; B); 201.5 (2; C); 202.9 (1; D); 264.3 (br; 3; E, F)	
	293		198.5 (br; 3; A, B); 201.8 (2; C); 203.3 (1; D); 263 (br; 3; E, F)	129.4 (1); 128.6 (2)
[Ru <sub>3</sub> (CO) <sub>10</sub> (PDAN) <sub>2</sub> ](8)	283	CD <sub>2</sub> Cl <sub>2</sub>	200.7 (4; C, D); 225.3 (br; 6; A, B, E, F)	

<sup>a</sup> Abbreviations: br = broad. The samples were internally referenced to the solvent; for compounds **1**, **5**, **6** and **8**, CD<sub>2</sub>Cl<sub>2</sub> 53.7 ppm; compounds **2** and **3** CD<sub>3</sub>CN, 1.3 ppm.

The clusters  $[\text{Ru}_3(\text{CO})_{11}(\text{ADN})]$  (**4**),  $[\text{Ru}_3(\text{CO})_{10}(\text{ADN})_2]$  (**5**),  $[\text{Ru}_3(\text{CO})_9(\text{ADN})_3]$  (**6**),  $[\text{Ru}_3(\text{CO})_{11}(\text{PDAN})]$  (**7**) and  $[\text{Ru}_3(\text{CO})_{10}(\text{PDAN})_2]$  (**8**) (ADN = adiponitrile, PDAN = phenylenediacetonitrile) were prepared similarly in dichloromethane–dinitrile solution. Attempts to obtain these compounds in the solid state by crystallization, precipitation or other means only resulted in the formation of oily dinitrile rich residues. The order of stability of these clusters is similar to that of the acetonitrile clusters **1–3**.

The substitution of the acetonitrile in clusters **1–3** by a stoichiometric amount of the desired dinitrile was attempted to yield eventually complexes **4–8**. Thus, when  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  (**2**) reacts with 2 equivalents of ADN in acetonitrile, it affords cluster **5** in quantitative yield. When only 1 equivalent of ADN was used, the new cluster  $[\text{Ru}_3(\text{CO})_{10}(\text{ADN})_x]$  (**9**) was obtained as a yellow-brown powder. The reaction of **3** with 3 equivalents of ADN is not as straightforward since only partial replacement of the acetonitriles is observed.

Clusters **1–8** have been studied in solution by IR and  $^{13}\text{C}$  NMR spectroscopy (Tables 1 and 2).  $[\text{Ru}_3(\text{CO})_{10}(\text{ADN})_x]$  (**9**) was characterized only by its solid state IR spectrum, since it decomposes in ADN-free solutions and dissolves in the presence of ADN to afford **5** quantitatively.

The monosubstituted clusters **1**, **4** and **7** exhibit IR absorptions in the region of terminally bonded CO,

whereas the disubstituted clusters **2**, **5**, **8** and **9** revealed a further absorption at ca.  $1820\text{ cm}^{-1}$  attributed to bridging carbonyls (Table 1). The same feature has been reported previously for cluster **2**. This band shifts to  $1800\text{ cm}^{-1}$  upon further replacement of a third CO, as found in clusters **3** and **6**. This  $20\text{ cm}^{-1}$  shift is sometimes difficult to observe in a mixture of **2** and **3**, which might explain why the third member of the series  $[\text{Ru}_3(\text{CO})_{12-n}(\text{MeCN})_n]$  ( $n = 1–3$ ) has escaped detection so far. A comparable shift is observed for the terminally bonded CO ligands, the more intense absorption being shifted from  $2043\text{ cm}^{-1}$  in **1** to  $2015\text{ cm}^{-1}$  in **2**, and to  $1997\text{ cm}^{-1}$  in **3**.

Investigation of the  $\nu(\text{CN})$  absorption has been carried out to determine any possible shift upon polysubstitution. As the intensity of the vibration is very weak, this has been checked only in the solid state for clusters **1–3**. Cluster **1** exhibits two absorptions at  $2304$  and  $2334\text{ cm}^{-1}$ . The higher band is attributed to a combination band ( $\text{CH}_3$  and  $\text{C–C}$ ) and the lower is assigned to the  $\nu(\text{CN})$  absorption, as reported in the literature [3c]. This is further substantiated by comparing these data with those of the  $\text{CD}_3\text{CN}$ -substituted cluster  $[\text{Ru}_3(\text{CO})_{11}(\text{CD}_3\text{CN})]$  (**10**) and those of the propionitrile cluster  $[\text{Ru}_3(\text{CO})_{10}(\text{EtCN})_2]$  (**11**) which both exhibit only one band in this part of the IR spectrum (see Table 2). The same assignment was used for clusters **2** and **3**. A positive  $\Delta$  shift ( $\Delta = \nu_{\text{coordinated ligand}} - \nu_{\text{free ligand}}$ ) is indicative of end-on coordination of the nitrile. Simi-

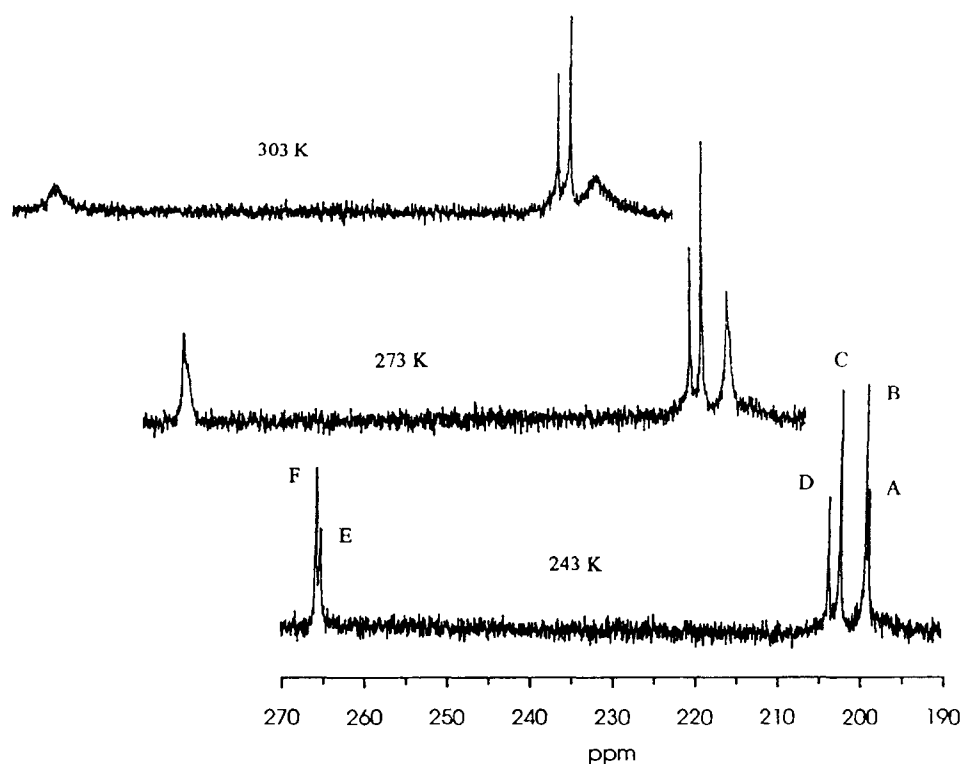
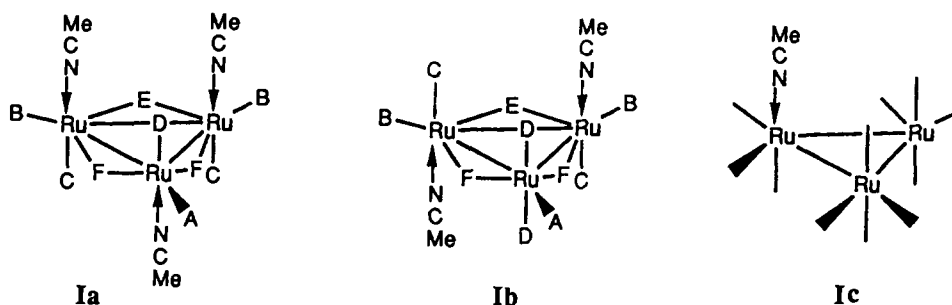


Fig. 1. Variable-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $[\text{Ru}_3(\text{CO})_9(\text{MeCN})_3]$  (**3**) in acetonitrile.



Scheme 1.

lar to the observation for the carbonyls, the coordination shift  $\Delta_n$  in the series  $[\text{Ru}_3(\text{CO})_{12-n}(\text{CD}_3\text{CN})_n]$  varies with the degree of substitution as follows:  $\Delta_1$  (+51 in **1**) >  $\Delta_2$  (+42 in **2**) >  $\Delta_3$  (+37 in **3**) ( $\Delta_n$  in  $\text{cm}^{-1}$ ).

### 3. Solution structure and stereodynamic behaviour

The IR and analytical data lead to the conclusion that the nitriles are terminally bonded in all the clusters. However, coordination may still be axial or equatorial. Comparison of mono- and di-coordination of dinitriles

only makes sense if the vacant coordination sites are so disposed that they can be fitted by at least one conformation of the dinitrile. Compared with the phosphines in  $[\text{Ru}_3(\text{CO})_{12-n}(\text{PR}_3)_n]$  [8], nitriles have a preference for axial coordination [9], as reported for the clusters  $[\text{Ru}_5\text{C}(\text{CO})_{15}(\text{MeCN})]$  [10],  $[\text{Fe}_3(\text{CO})_{11}(2\text{-TolCN})]$  [11], and  $[\text{Os}_4(\mu_2\text{-H})_3(\text{CO})_{12}(\text{MeCN})_2]^+$  [12], unless geometrical constraint forces in-plane coordination as in  $[\text{Fe}_3(\mu_3\text{-PPh})_2(\text{CO})_7(\text{MeCN})_2]$  [13]. Furthermore, two nitriles will coordinate in a trans position with respect to the plane defined by the metal framework as found in  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{MeCN})_2]^+$  and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

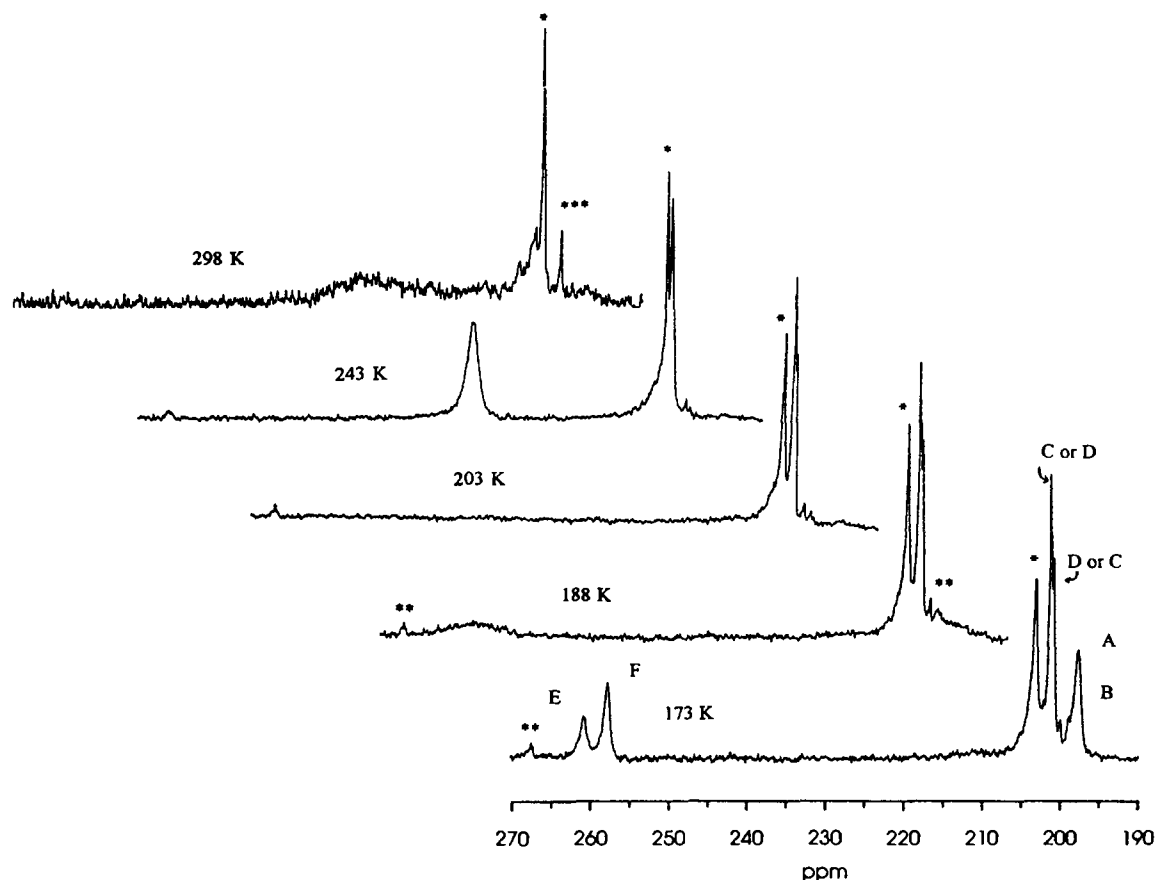
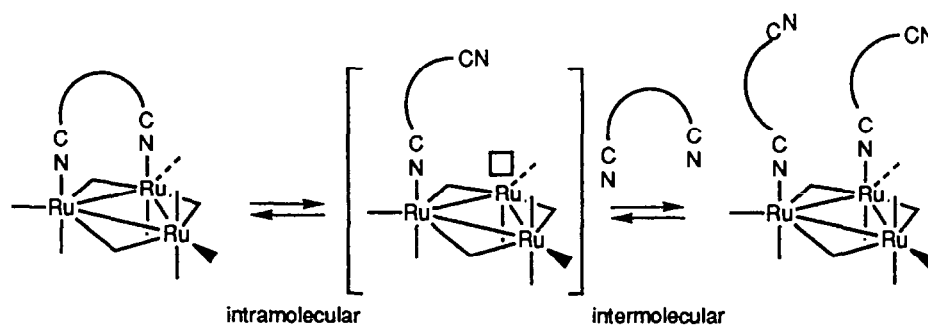


Fig. 2. Variable-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  (**2**) in an acetonitrile–dichloromethane mixture. Traces of  $[\text{Ru}_3(\text{CO})_{11}(\text{MeCN})]$  (**1**) (\*),  $[\text{Ru}_3(\text{CO})_9(\text{MeCN})_3]$  (**3**) (\*\*) and  $[\text{Ru}_3(\text{CO})_{12}]$  (\*\*\*) are indicated.



Scheme 2.

[14]. Therefore, a  $^{13}\text{C}$  NMR study on the polysubstituted clusters **1**, **2** and **3** was carried out to determine the position of the nitriles.

As shown for cluster **3** (Fig. 1), the carbonyls are exchanging positions on the NMR time scale. The limiting spectrum is reached at 243 K and shows two signals in the region of bridging carbonyls (ratio 2:1) and four signals in the area of terminally bonded carbonyls (ratio 1:2:2:1) (Table 2).

Upon warming, the bridging carbonyls and the terminal equatorial carbonyls are involved in a fluxional motion, as indicated by the broadening of their signals. The coalescence temperature cannot be determined because the cluster decomposes rapidly above 323 K, at which temperature the signals have disappeared into the base line. From a coalescence temperature of more than 323 K, a minimum activation energy of  $12.7\text{ kcal mol}^{-1}$  is ascribed to this process [15].

The cyano carbon atoms of the acetonitrile ligands exhibit two signals at 129.2 and 128.4 ppm, at lower field compared with that for free acetonitrile, close to that found in  $[\text{Fe}_3(\text{CO})_{11}\text{MeCN}]$  (132 ppm) [11], and more shielded than that of a 'side-on' nitrile such as in the series  $[\text{Mn}_2(\text{CO})_6(\text{dppm})_2(\mu, \eta^2\text{-RCN})]$  (157–168 ppm) [16]. This confirms the 'end-on' bonding of the acetonitriles in **1–3**. Note that the nitriles are not to be involved in the fluxional process, since no change in their NMR signals was detected during the variable-temperature experiment. This process is likely to involve only the six equatorial carbonyls in an 'in-plane cycling process', as already described for the cluster  $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-CO})_3(\mu_2, \eta^2\text{-1,2-diazine})]$  [17]. To account for the two other carbonyl signals A and B, as well as the two cyano signals, a structure is proposed for cluster **3** (Scheme 1(a)). It depicts six equatorial (A, B, E, F) and three axial (C, D) carbonyls and three nitriles, each on one Ru, two lying above the  $\text{Ru}_3$  plane and one below.

The variable-temperature spectra of cluster **2** display similar features, although the limiting spectrum is observed at a much lower temperature (173 K) (Fig. 2). These data were analysed similarly to those of compound **3** and from the data reported for the analogous

compound  $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-CO})_3(\mu_2, \eta^2\text{-1,2-diazine})]$  [17]. A structure is proposed for **2** where the nitriles lie in axial positions, trans with respect to the triruthenium plane as in the solid state structure of the analogous cluster  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  (Scheme 1(b)) [14]. From a coalescence temperature of 213 K, an activation energy of  $8.5\text{ kcal mol}^{-1}$  is computed for the 'in-plane motion' of cluster **2**, a much lower value than that found for cluster **3**. Between 203 K and 243 K, a second fluxional process exchanging carbonyls C and D occurs. Finally, above room temperature, the signal of the in-plane carbonyls (A, B, E, F) as well as the axial carbonyls D and C become broader and tend to merge with the base line. This indicates that exchange between axial and equatorial positions is taking place at higher energies.

In the case of cluster **1**, only one signal is observed, even at the lowest temperature (173 K) before freezing of the solvent. As no bridging carbonyls are evidenced by IR spectroscopy, by analogy with the cluster  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ , a structure is proposed for cluster **1** where the nitrile lies in one of the axial position (Scheme 1(c)).

Variable-temperature  $^{13}\text{C}$  NMR experiments have been run on clusters  $[\text{Ru}_3(\text{CO})_{10}(\text{ADN})_2]$  (**5**),  $[\text{Ru}_3(\text{CO})_9(\text{ADN})_3]$  (**6**) and  $[\text{Ru}_3(\text{CO})_{10}(\text{PDAN})_2]$  (**8**). The data are similar to those found for their acetonitrile analogues **2** and **3**, reflecting the absence of electronic, coordination or steric effects on the fluxional exchange of the carbonyls. From the similarity of the data sets (NMR, IR), structures analogous to that depicted in Schemes 1(a) and 1(b) are attributed to clusters **5**, **8**, and **6**.

#### 4. Discussion

Despite the presence of two available coordination sites suited for chelate end-on coordination of the dinitriles in cluster **3**, no such bonding is observed. This is consistent with all the literature reports, although most of them have dealt with mononuclear complexes. An obvious reason is the nitrile concentration, which is

rather high (1 to 4 M) during the solution studies to avoid decomposition of the clusters. Such concentrations may just preclude chelate end-on coordination of the dinitriles because intermolecular reaction dominates the intramolecular one (Scheme 2).

Also, no isomerisation of the trans isomer  $[\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2]$  (**2**) to the cis form is observed, which would offer two coordination sites geometrically suitable for chelate end-on coordination of the dinitriles. The isolation of compound  $[\{\text{Ru}_3(\text{CO})_{10}(\text{ADN})\}_x]$  (**9**) amplifies this. An oligomeric structure involving only linear di-end-on coordination of ADN is attributed to **9** on the basis of IR and analytical data. This supports the idea that at low nitrile concentrations, linear di-end-on coordination still predominates over chelate coordination.

The effect of replacement of one carbonyl on the  $\nu(\text{CO})$  absorptions has been discussed and used to estimate the electronic and steric properties of ligands [18]. The influence of successive substitutions has also been examined and analysed in terms of trans- and cis-effects. However, examples are more scarce with polynuclear species, although they offer potential of multisite-coordination and intramolecular metal site exchange, which are believed to occur at the surface of heterogeneous metal catalysts [19]. Thus, it was known that introducing a hetero-ligand in the very symmetrical molecules such as  $[\text{Ru}_3(\text{CO})_{12}]$  causes a symmetry breaking which allows the study of fluxional motions such as CO scrambling. In the series  $[\text{Ru}_3(\text{CO})_{12-n}(\text{PR}_3)_n]$  ( $n = 1-3$ ), increasing the replacement of CO has a marked effect on the  $\nu(\text{CO})$  bands, reflecting increased electronic density over the triruthenium core [9]. Similar observations were reported for the  $\delta^{13}\text{C}$  NMR shifts of the carbonyls in the series  $[\text{Os}_3(\text{CO})_{12-n}(\text{PEt}_3)_n]$  ( $n = 1-3$ ) [20]. However, in the latter case, no pronounced influence of the degree of substitution on CO mobility was noted. Frozen structures were observed at  $-60^\circ\text{C}$  with coalescence temperatures ranging from 253 to 293 K (for the first fluxional process) irrespective of  $n$  [20]. It was also shown that increasing the amount of phosphorus in  $[\text{FeCo}_2(\text{CO})_{9-n}(\mu_3\text{-S})(\text{PBu}_3)_n]$  ( $n = 0-3$ ) has an effect, but only on localized carbonyl exchange involving only one metal atom, as was also observed in mononuclear compounds [21]. Reports on the series  $[\text{Ru}_3(\text{CO})_{12-n}(\text{PR}_3)_n]$  ( $n = 1-3$ ) [22], confirmed the effect of the degree of substitution on the  $\nu(\text{CO})$  frequencies but no  $^{13}\text{C}$  NMR studies were described.

Our results with the series  $[\text{Ru}_3(\text{CO})_{12-n}(\text{RCN})_n]$  ( $n = 1-3$ ) further support the idea that variations of the  $^{13}\text{C}$  chemical shift and  $\nu(\text{CO})$  frequencies with substitution reflect a change in the overall electronic density of the clusters. Such a correlation is a powerful tool for analysing molecular structure in solution. We also believe that the dependence of the activation energy of the

fluxional process on the degree of substitution reflects a change in the distribution of overall electronic density of the clusters. However, more examples are needed to confirm these correlations.

Three mechanisms have been proposed to account for the carbonyl mobility in trinuclear carbonyl metal clusters or in larger clusters [23], though they are still under investigation [24]. The results suggest that these three mechanisms operate simultaneously unless a ligand which cannot participate in a bridging motion blocks one of the processes. In the case of the clusters  $[\text{Ru}_3(\text{CO})_7(\mu_2\text{-CO})_3(\mu_2, \eta^2\text{-1,2-diazine})]$  [17] and  $[\text{Ru}_3(\text{CO})_{12-n}(\text{MeCN})_n]$  which bear such ligands in axial positions, only the 'merry-go-round' mechanism operates. However, in the series  $\text{Ru}_3(\text{CO})_{12-n}(\text{PR}_3)_n$  where the phosphines occupy equatorial sites, the in-plane motion is blocked and the carbonyls exchange at first only at axial positions. If this is true, clusters substituted at at least one axial and one equatorial position should exhibit only very high energetic carbonyl exchange process, irrespective of the metal at which substitution occurred and of any steric hindrance due to the ligands.

## 5. Experimental section

All reactions were performed in Schlenk flasks under argon. Solvents were dried and distilled under argon: dichloromethane over  $\text{CaCl}_2$ , acetonitrile over  $\text{P}_2\text{O}_5$  and tetrahydrofuran over sodium benzophenoneketyl. The chemicals  $[\text{Ru}_3(\text{CO})_{12}]$  (Interchim), adiponitrile (Rhône-Poulenc) and phenylenediacetonitrile (Aldrich) were purged under argon prior to use but not further purified.  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (Aldrich) was dehydrated by azeotropic distillation in toluene and recrystallization. IR spectra were recorded on a Bruker IFS-25 FT interferometer as dichloromethane–acetonitrile solutions or Nujol mulls. The  $^{13}\text{C}$  NMR spectra were recorded at 67.80 or 100.4 MHz on GX 270 and GSX400 FT-JEOL instruments respectively. The NMR spectra were externally referenced to  $\text{Me}_4\text{Si}$ , with downfield chemical shifts reported as positive. The NMR solvents were stored under argon over molecular sieves. Elemental analysis were performed at the Service Central d'Analyse du CNRS.

### 5.1. $[\text{Ru}_3(\text{CO})_{11}(\text{MeCN})]$ (**1**)

A solution of  $\text{Me}_3\text{NO}$  (0.012 g, 0.16 mmol) in dichloromethane (5 ml) was added dropwise to a light orange solution of  $[\text{Ru}_3(\text{CO})_{12}]$  (0.100 g, 0.156 mmol) in a dichloromethane–acetonitrile (100:5 ml) mixture at  $-78^\circ\text{C}$ . Upon warming the solution slowly turned dark orange. At room temperature, the solvents were slowly removed under reduced pressure. In order to avoid decomposition at room temperature, some acetonitrile

(2 × 5 ml) was added during the removal of the solvents. Upon further drying, an orange microcrystalline powder was obtained, which was essentially (greater than 95% from the IR spectrum) compound **1**.

### 5.2. $[Ru_3(CO)_{10}(MeCN)_2]$ (**2**)

A solution of  $Me_3NO$  (0.026 g, 0.345 mmol) in acetonitrile (5 ml) was added dropwise (over 5 min) to a light orange solution of  $[Ru_3(CO)_{12}]$  (0.100 g, 0.156 mmol) in a dichloromethane–acetonitrile (100:10 ml) mixture at  $-78^\circ C$ . The temperature was allowed to reach ambient during which the solution slowly turned bright yellow. The solvents were removed to dryness under reduced pressure to yield quantitatively a light yellow microcrystalline powder of compound **2**. Anal. Calc. for  $C_{14}H_6N_2O_{10}Ru_3$  (Mw, 665.2): C, 25.26; H, 0.90; N, 4.21; Ru, 45.9. Found: C, 24.96; H, 0.97; N, 3.93; Ru, 46.03%.

### 5.3. $[Ru_3(CO)_9(MeCN)_3]$ (**3**)

A solution of  $Me_3NO$  (0.040 g, 0.533 mmol) in acetonitrile (5 ml) was added dropwise (over 5 min) to a light orange solution of  $[Ru_3(CO)_{12}]$  (0.100 g, 0.156 mmol) in a dichloromethane–acetonitrile (40:100 ml) mixture at  $-78^\circ C$ . Upon warming to room temperature the solution slowly turned light yellow. At room temperature, the solvents were removed under reduced pressure to yield quantitatively a light yellow microcrystalline powder of compound **3**. Anal. Calc. for  $C_{15}H_9N_3O_{10}Ru_3$  (Mw, 678.5): C, 26.56; H, 1.34; N, 6.19; Ru, 44.69. Found: C, 26.22; H, 1.32; N, 6.05; Ru, 43.14%.

### 5.4. $\{[Ru_3(CO)_{10}(ADN)]_x\}$ (**9**)

To a solution of cluster **2** prepared as described above and before evaporation of the solvents, two molar equivalents of adiponitrile (0.035 ml, 0.034 g, 0.312 mmol) were added dropwise. The solvents were slowly and carefully removed under reduced pressure to afford a light yellow solid residue. This was washed with tetrahydrofuran (2 × 20 ml) to afford analytically pure cluster **9**. Anal. Calc. for  $C_{16}H_8N_2O_{10}Ru_3$ : C, 27.8; H, 1.17; N, 4.05; Ru, 43.8. Found: C, 27.8; H, 1.36; N, 4.74; Ru, 43.4%.

Alternatively, a stoichiometric quantity of adiponitrile (0.018 ml, 0.017 g, 0.156 mmol) was added and the solvents removed, giving **9** without further purification (Calc.: C, 27.8; H, 1.17; N, 4.05; Ru, 43.8. Found: C, 27.2; H, 1.43; N, 4.54; Ru, 41.2%).

### 5.5. $[Ru_3(CO)_{10}(ADN)_2]$ (**5**)

This was obtained as described for **9** but the solid residue was analysed before treatment with tetrahydro-

furan. Anal. Calc. for  $C_{22}H_{16}N_4O_{10}Ru_3$  (Mw, 799.63): C, 33.04; H, 2.02; N, 7.01; Ru, 37.92. Found: C, 31.14; H, 2.22; N, 6.93; Ru, 37.4%.

### 5.6. $^{13}CO$ enrichment procedure

$^{13}CO$ -enriched  $[Ru_3(CO)_{12}]$  was prepared by addition of gaseous  $^{13}CO$  ( $2 \times 11 \text{ cm}^3$ , 0.98 mmol, 6.3 eq) to a solution of  $[Ru_3(CO)_9(MeCN)_3]$  prepared in situ from  $[Ru_3(CO)_{12}]$  (0.100 g, 0.156 mmol) as described above. The substitution reaction of the nitriles by  $^{13}CO$  is quantitative, as proved by IR spectroscopy of the solution which shows a  $\nu(^{13}CO)/\nu(CO)$  bands ratio of ca. 25%.

The enrichment (25% in  $^{13}CO$ ) of compounds **1**, **2**, **3**, **5**, **6** and **8**, was undertaken during their synthesis according to the procedures described above, but starting from enriched  $[Ru_3(CO)_{12}]$ .

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#### Note added in proof

During the examination of the manuscript it was noticed that a very similar work has been published by Professor Silvio Aime's group from Turin, see S. Aime, W. Dastrò, R. Gobetto, J. Krause and L. Violano, *Inorg. Chem. Acta*, **235** (1995) 357–366.