

## Gaseous NO as the Source of Nitrosyl Ligand in Carbonyl Clusters. X-Ray Structure of $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{C}_3\text{H}_5)(\text{NO})]$ and Fluxionality of the $\mu$ -Allyl Ligand

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Nitric oxide gas reacts with an anionic carbonyl cluster of ruthenium,  $[\text{Ru}_3(\text{CO})_9\text{C}_2\text{R}]^-$  ( $\text{R} = \text{Bu}^t$  or  $\text{SiMe}_3$ ), to give the neutral nitrosyl complex  $[\text{Ru}_3(\text{CO})_9\text{C}_2\text{R}(\text{NO})]$ , while the reactions with the dianionic carbide cluster  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  and its monoanionic  $\mu$ - $\eta^3$ -allyl derivative,  $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{C}_3\text{H}_5)]^-$ , give good yields of monoanionic  $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})]^-$  and neutral  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{C}_3\text{H}_5)(\text{NO})]$  complexes, respectively; the latter complex is unique in exhibiting fluxionality of the  $\mu$ -allyl ligand.

Nitrosyl carbonyl clusters have attracted interest as a model for the reduction of the toxic pollutant NO gas with CO by a heterogeneous catalyst and indeed a number of nitrosyl carbonyl clusters have been reported.<sup>1</sup> In most of their preparations, nitrosonium cation or nitrite anion is used to introduce the NO unit:  $\text{NO}^+$  is best studied for attacking anionic clusters<sup>2</sup> while  $\text{NO}_2^-$  is reacted most readily with neutral carbonyl clusters to give anionic nitrosyl clusters and  $\text{CO}_2$ .<sup>3</sup> Direct use of NO gas, however, has only a few precedents:  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{Os}_3(\text{CO})_{12}]$  have been reported to react with gaseous NO to give  $[\text{Ru}_3(\text{CO})_{10}(\text{NO})_2]$  and  $[\text{Os}_3(\text{CO})_{10}(\text{NO})_2]$  in low yields with a large amount of insoluble and uncharacterized material.<sup>4</sup> The basic problem with direct fixation of NO gas is that the nitrogen of this molecule donates three electrons. Even if the reaction takes place by substituting one CO ligand, the third excess electron cleaves the metal-metal bond resulting in decomposition in most cases.<sup>1</sup> In this paper, we report the successful and clean reaction of NO gas with anionic carbonyl ruthenium clusters where the neutral NO unit formally replaces  $(\text{CO})^-$ , *i.e.* CO and delocalized negative charge. Since the exhaust gases of combustion engines often contain substantial amounts of unburnt hydrocarbons as well as CO and NO, we are particularly interested in the reaction of carbonyl clusters containing hydrocarbon ligands.

Unlike the parent dodecacarbonyltriruthenium, the alkynyl(hydrido) derivative  $[\text{Ru}_3(\text{CO})_9(\text{H})(\text{C}_2\text{R})]$  (**1a**  $\text{R} = \text{Bu}^t$ ,<sup>5</sup> **1b**  $\text{R} = \text{SiMe}_3$ ) does not react with NO gas. The anionic complex derived by proton abstraction from **1** with  $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ ,  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ru}_3(\text{CO})_9(\text{C}_2\text{R})]$  (**2a**  $\text{R} = \text{Bu}^t$ , **2b**  $\text{R} = \text{SiMe}_3$ ), however, reacts smoothly. Thus, upon bubbling NO gas<sup>†</sup> slowly (typically one small bubble per second) through a THF solution of **2a** or **2b** at room temp., the orange solution turned brown-green. The reaction could easily be monitored by the  $\nu(\text{CO})$  stretching region of the IR spectra.<sup>‡</sup> Work-up by silica-gel column chromatography gave green crystals of the composition  $[\text{Ru}_3(\text{CO})_9(\text{C}_2\text{R})(\text{NO})]$  (**3a**  $\text{R} = \text{Bu}^t$ , **3b**  $\text{R} = \text{SiMe}_3$ ) in 30–45% yields and **3a** was structurally characterized as shown in Fig. 1.<sup>§</sup> The NO occupies the position initially occupied by the hydride in **1a** but the two metal atoms bridged by the NO [ $\nu(\text{NO})$  1507  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ] have no bonding any more [ $\text{Ru}(2)\text{--Ru}(3)$  3.240(1)<sup>‡</sup> Å]. From this structural change as well as the change of charge, *i.e.* monoanionic reactant to give the neutral product, it may be regarded that of the three electrons NO donates, two are used to cleave the Ru–Ru bond and the third is formally used to displace the anionic charge in **2**. So far we have been unable to determine the fate of the  $(\text{Ph}_3\text{P})_2\text{N}$  cation initially present in the reactant complex **2**.

Johnson and coworkers have reported the formation of  $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})]^-$  **4** by the reaction of  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$  with  $[(\text{Ph}_3\text{P})_2\text{N}][\text{NO}_2]$ , the structure of which has been elucidated from the X-ray structure of its  $[\text{AuPPh}_3]^+$  adduct.<sup>6</sup> According to our methodology, the same cluster **4** was obtained in 85% isolated yield by bubbling NO gas slowly through a  $\text{CH}_2\text{Cl}_2$  solution of the dianionic complex  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$

at room temperature. Here again NO replaced  $(\text{CO})^-$  on the anionic cluster.

Similarly, the  $\mu$ - $\eta^3$ -allyl anionic cluster  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ru}_6\text{C}(\text{CO})_{15}(\text{C}_3\text{H}_5)]$  **5**, which was prepared previously in this laboratory,<sup>7</sup> was found to react with NO gas in  $\text{CH}_2\text{Cl}_2$  solution to give a neutral complex. The air-stable complex of the composition  $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{C}_3\text{H}_5)(\text{NO})]$  **6** was isolated after work-up by silica-gel column chromatography as red-brown crystals. The reaction was best followed by the change in the  $\nu(\text{CO})$  region in the IR spectra since these absorptions in general shift to higher energy by *ca.* 30  $\text{cm}^{-1}$  on going from monoanionic to neutral.<sup>¶</sup> The  $\nu(\text{NO})$  absorption was observed at 1759  $\text{cm}^{-1}$  (*w.*, in  $\text{CH}_2\text{Cl}_2$ ) suggesting terminal coordination of the nitrosyl ligand.

Interestingly, an X-ray structural analysis on **6** (Fig. 2)<sup>||</sup> revealed that the nitrosyl group is bonded to the same ruthenium atom to which one of the allyl terminal carbons is connected  $[\text{Ru}(2)]$ , bringing about an asymmetric environment for the  $\mu$ -allyl group. There is only one bridging CO in the molecule which again is bound to the same ruthenium atom. The geometry within the  $\mu$ - $\eta^3$ -allyl moiety in **6** [ $\text{C}(\text{A}1)\text{--C}(\text{A}2)$  1.40(1),  $\text{C}(\text{A}3)\text{--C}(\text{A}2)$  1.44(1) Å] has a small tendency to asymmetry compared with that in **5** [ $\text{C}(\text{A}1)\text{--C}(\text{A}2)$  1.43(1),  $\text{C}(\text{A}3)\text{--C}(\text{A}2)$  1.45(1) Å]. Dramatically different from **5** is the coordination position of the allyl moiety in **6**, which significantly slips from the mid-point of the bridging metal-metal bond towards Ru(1), the distances  $\text{Ru}(1)\cdots\text{C}(\text{A}2)$  and  $\text{Ru}(2)\cdots\text{C}(\text{A}2)$  being 2.46(1) and 2.72(1) Å, respectively.

A 400 MHz  $^1\text{H}$  NMR spectrum of **6** in  $[\text{D}_8]\text{-toluene}$  measured at  $-70^\circ\text{C}$  was consistent with the solid-state structure: besides a multiplet for the central proton at  $\delta$  0.8, two inequivalent *syn*-protons ( $\delta$  4.10 and 3.02) and two *anti* protons ( $\delta$  0.34 and  $-0.11$ ) were observed as four broad doublets. As the temperature was raised it showed typical

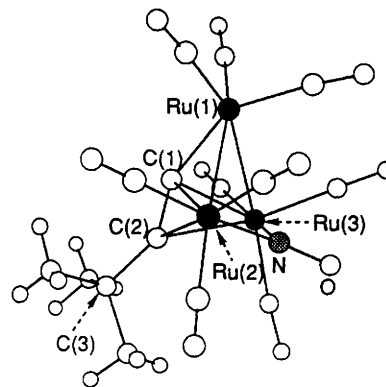
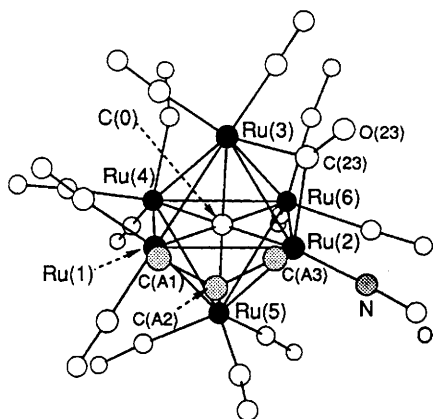
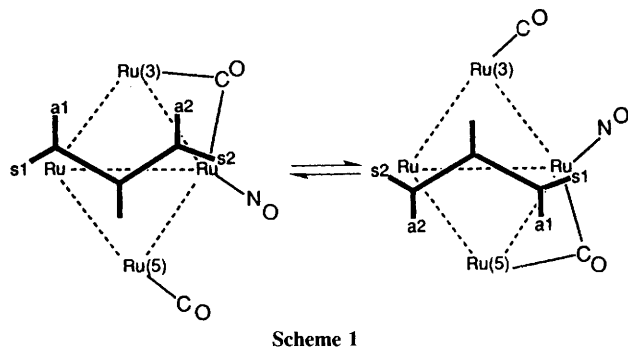


Fig. 1 Molecular structure of **3a**. Selected bond lengths (Å) and angles ( $^\circ$ ):  $\text{Ru}(1)\text{--Ru}(2)$  2.816(6),  $\text{Ru}(1)\text{--Ru}(2)$  2.813(5),  $\text{Ru}(2)\text{--Ru}(3)$  3.240(1),  $\text{Ru}(1)\text{--C}(1)$  1.958(4),  $\text{Ru}(2)\text{--C}(1)$  2.259(4),  $\text{Ru}(3)\text{--C}(1)$  2.270(4),  $\text{Ru}(2)\text{--C}(2)$  2.350(4),  $\text{Ru}(3)\text{--C}(2)$  2.377(4),  $\text{Ru}(2)\text{--N}$  2.016(4),  $\text{Ru}(3)\text{--N}$  2.010(4),  $\text{N--O}$  1.225(4),  $\text{C}(1)\text{--C}(2)$  1.276(6),  $\text{Ru}(2)\text{--Ru}(1)\text{--Ru}(3)$  70.29(1),  $\text{Ru}(2)\text{--C}(1)\text{--Ru}(3)$  77.9(3),  $\text{Ru}(2)\text{--N--Ru}(3)$  107.2(1).



**Fig. 2** Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.981(1), Ru(1)–C(A1) 2.213(10), Ru(2)–C(A3) 2.191(10), Ru(1)–C(A2) 2.460(10), Ru(2)–C(A2) 2.721(9), C(A1)–C(A2) 1.401(14), C(A2)–C(A3) 1.439(14), Ru(2)–N 1.759(8), Ru(2)–C(23) 2.057(8), Ru(3)–C(23) 2.088(10), Ru(3)–Ru(2)–N 148.3(3), Ru(5)–Ru(2)–N 107.8(3), C(A1)–C(A2)–C(A3) 123.8(9). Dihedral angle C(A1)–C(A2)–C(A3)/Ru(1)–Ru(2)–C(0) 91°.



pattern for a fluxionality: at  $-30\text{ }^{\circ}\text{C}$ , the two *syn*-H peaks as well as two *anti*-H peaks coalesced completely while at  $70\text{ }^{\circ}\text{C}$  *syn*-protons were observed as a moderately sharp doublet at 3.81 ( $J$  7 Hz) and *anti*-protons as a well resolved double doublet centered at  $\delta$  0.53 ( $J$  12 and 2 Hz).\*\* As a mechanism for this equalization of two *syn* as well as two *anti* protons at high temperature, we propose fluxionality by a least motion process depicted in Scheme 1, *i.e.* rotation of the  $\eta^3$ -allyl group and concomitant movement of CO ligands *via* a bridged–unbridged mode. In contrast to intensively studied fluxionality of mononuclear allyl complexes,<sup>8</sup> that for dinuclear and polynuclear  $\mu$ -allyl complexes has few precedents to our knowledge. Fluxional behaviour of hydrocarbon ligands in metal clusters is of importance since it may be relevant to the mobility of small organic molecules on metal surfaces.

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## Footnotes

† The high purity (>99.7%) NO gas was purchased from Sumitomo-Seika Co. The impurities were  $\text{N}_2$  (0.2%) and  $\text{N}_2\text{O}$  (0.1%).

‡ IR spectra [ $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ] in  $\text{CH}_2\text{Cl}_2$ : **3a** 2096w, 2072vs, 2050vs, 2028vs, 2019s, 1990m; **3b** 2097w, 2074vs, 2051vs, 2028vs, 2017s, 1988m.

§ *Crystal data* for **3a**,  $\text{C}_{15}\text{H}_9\text{NO}_{10}\text{Ru}_3$ ,  $M$  666.53, monoclinic, space group  $P2_1/n$ ,  $a$  12.406(1),  $b$  16.492(1),  $c$  10.992(2) Å,  $\beta$  107.10(1)°,  $V$  2149 Å<sup>3</sup>,  $Z$  4,  $D_c$  2.060  $\text{g cm}^{-3}$ ,  $F(000)$  1272,  $\mu$  20.90  $\text{cm}^{-1}$ , crystal size 0.35  $\times$  0.29  $\times$  0.23 mm, radiation Mo-K $\alpha$  ( $\lambda$  = 0.7107 Å), number of data ( $I \geq 3\sigma$ ) 4337, number of parameters 299, final  $R$  0.0286,  $R_w$  0.0305.

¶ IR spectra [ $\nu(\text{CO})$ ,  $\text{cm}^{-1}$ ] in  $\text{CH}_2\text{Cl}_2$ : 2084m, 2046s, 2041sh, 2029sh, 1992w, 1836m.

|| *Crystal data* for **6**,  $\text{C}_{18}\text{H}_5\text{NO}_{15}\text{Ru}_6$ ,  $M$  1081.66, orthorhombic, space group  $Pna2_1$ ,  $a$  22.571(3),  $b$  10.693(1),  $c$  10.915(2) Å,  $Z$  4,  $D_c$  2.728  $\text{g cm}^{-3}$ ,  $F(000)$  2016,  $\mu$  33.64  $\text{cm}^{-1}$ , crystal size 0.43  $\times$  0.41  $\times$  0.07 mm, radiation Mo-K $\alpha$  ( $\lambda$  = 0.7107 Å), number of data ( $I \geq 3\sigma$ ) 3740, number of parameters 362, final  $R$  0.0291,  $R_w$  0.0302. For **3a** and **6**, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

\*\* At higher temperatures, the peak of *syn* protons should appear also as a double doublet with gem-coupling of 2 Hz. The temperature could not be raised further, however, due to decomposition of the complex.

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