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Intermolecular Association of Cyanide Substituted Triruthenium Carbonyl Cluster Anions: Synthesis and Crystal Structure of $[ppn]_2[Ru_6(CN)_2(CO)_{20}]$ [ppn = bis(triphenylphosphine)iminium cation]

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[ppn][CN][ppn = bis(triphenylphosphine)iminium cation] reacts with $Ru_3(CO)_{12}$ to give a cyano triruthenium carbonyl cluster anion which subsequently loses CO and dimerizes as the hexanuclear dianion $[Ru_6(\mu\text{-}CN)_2(CO)_{20}]^{2-}$· an *X*-ray structural analysis shows that the structure involves two parallel ruthenium triangles linked by two axial CN bridges.

Recent discoveries of a promoter effect of anionic nucleophiles (Nu = CN^-, $MeCO_2^-$, F^-, Cl^-, Br^-, I^-, *etc.*) on various stoicheiometric and catalytic reactions of ruthenium and osmium clusters have extended the scope of means to activate these metal clusters.[1—5] Under highly dissociating conditions, nucleophilic attack of such anions on a transition metal carbonyl cluster results in labilization of co-ordinated carbonyl groups, leading to the successive loss of some of these ligands.[6] In the case of $Ru_3(CO)_{12}$, several labile cluster anions formulated as $[Ru_3\{C(O)Nu\}(CO)_n]^-$ ($n = 11, 10$; Nu = NMe_2^-,[7] MeO^-[8,9]) or $[Ru_3\{Nu\}(CO)_n]^-$ [$n = 11, 10$; Nu = $MeCO_2^-$ or HCO_2^-,[10] NCO^- (derived from N_3^-),[11] NO^- (derived from NO_2^-),[12] Cl^-, Br^-, I^-[1]] have been traced spectroscopically but often remain incompletely characterized. Except in the case of acetate, for which an *X*-ray structure has been reported, the decacarbonyl species $[Ru_3\{\mu\text{-}Nu\}(CO)_{10}]^-$ are rather unstable, and show a marked tendency to compensate their CO ligand deficiency by increasing their nuclearity to give butterfly complexes $[ppn][Ru_4\{\mu\text{-}Nu\}(CO)_{13}]$ [Nu = NCO^-,[11] Cl^-;[13] ppn = bis(triphenylphosphine)iminium cation].

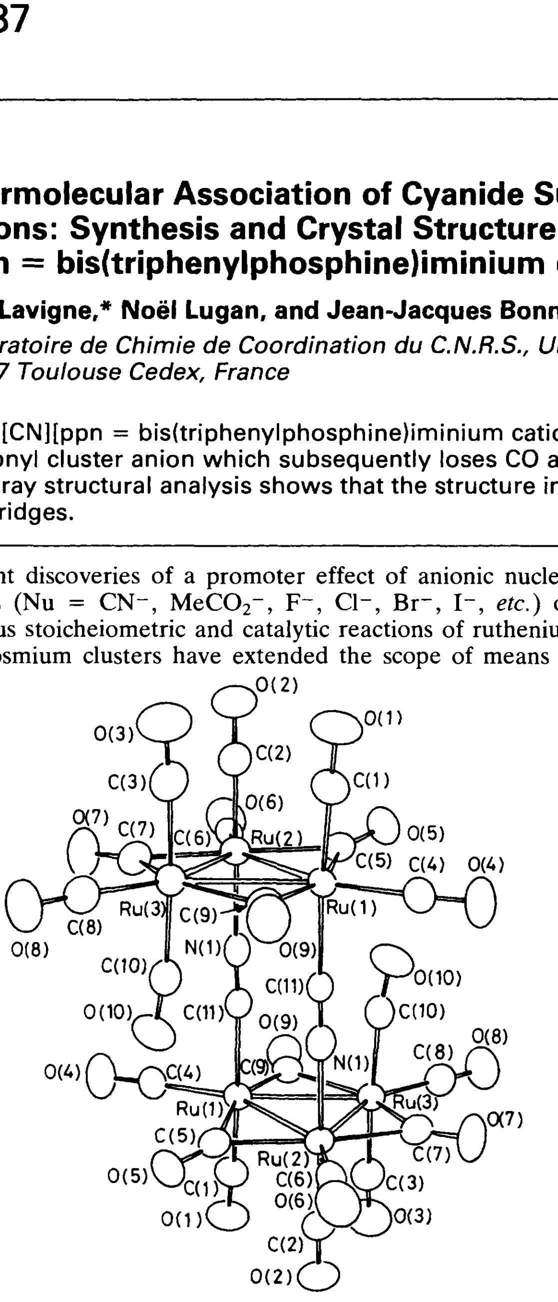

Figure 1. Perspective view of the hexanuclear dianion $[Ru_6(\mu\text{-}CN)_2(CO)_{20}]^{2-}$ of (**2**); the cyanide group is disordered over the atomic sites arbitrarily labelled as C(11) and N(1); these are both statistically occupied by 50% carbon and 50% nitrogen. Selected interatomic distances (Å): Ru(1)–Ru(2) 2.882(1), Ru(1)–Ru(3) 2.878(1), Ru(2)–Ru(3) 2.870(1), Ru(1)–C(11) 2.091(7), C(11)–N(1) 1.14(1), N(1)–Ru(2) 2.113(7), Ru(1)–C(1) 1.864(9), Ru(2)–C(2) 1.866(8), Ru(3)–C(3) 1.921(9), Ru(3)–C(10) 1.931(9), Ru(1)–C(4) 1.887(6), Ru(2)–C(6) 1.871(7), Ru(3)–C(8) 1.873(6), Ru(1)–C(5) 2.234(6), Ru(2)–C(5) 2.112(6), Ru(2)–C(7) 2.101(6), Ru(3)–C(7) 2.142(6), Ru(3)–C(9) 2.302(5), Ru(1)–C(9) 2.032(7).

Following a synthetic procedure which is general for a variety of nucleophilic anions,[1] a tetrahydrofuran (THF) solution of $Ru_3(CO)_{12}$ was treated with $[ppn][CN]\text{–}CH_2Cl_2$ at ambient temperature, leading to immediate formation of a labile anionic species (**1**) which could be stabilized under a CO

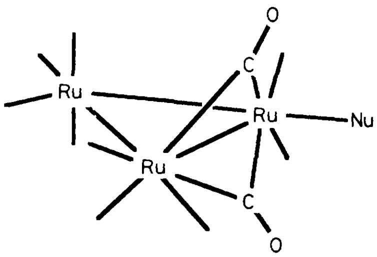

Figure 2. Possible structure of the undecacarbonyl species $[ppn][Ru_3\{Nu\}(CO)_{11}]$.[11]

atmosphere.† Upon standing in solution under an inert atmosphere, this complex was converted into a new species (**2**) over a period of several hours by loss of CO. This transformation could be achieved within three minutes *in vacuo*; the new complex was crystallized and characterized by i.r. spectroscopy and elemental analysis,‡ and subsequently formulated as $[ppn]_2[Ru_6(\mu\text{-}CN)_2(CO)_{20}]$ on the basis of an *X*-ray analysis.§ A perspective view of (**2**) (Figure 1) reveals a dimeric structure involving two parallel ruthenium triangles which are crystallographically related through an inversion centre. The link between these triangular units is achieved by two linear cyano bridges. The two symmetry related CN ligands occupy axial co-ordination sites on Ru(1) and Ru(2); they are perfectly parallel and adopt a head-to-tail arrangement. The carbon and nitrogen atoms of these ligands cannot be distinguished, owing to the occurrence of a statistical disorder. Three equatorial carbonyl ligands occupy edge bridging positions, as previously seen in $Ru_3(\mu\text{-}C_4H_4N_2)(CO)_{10}$[14] or in the acetate derivative $[ppn][Ru_3(\mu\text{-}MeCO_2)(CO)_{10}]$.[10]

An interesting property of some anionic nucleophiles co-ordinated to metal clusters is their ability to function reversibly as either terminal 1e donors or bridging 3e donors, thereby opening a vacant co-ordination site for the activation of incoming substrates.[4] A reasonable structure has been suggested for the undecacarbonyl species $[ppn][Ru_3\{Nu\}(CO)_{11}]$ (Nu = NCO)[11] where the nucleophile occupies a terminal position on the metal (Figure 2); CO labilization in this derivative is related to the ability of the nucleophile to move to an edge bridging position, giving $[ppn][Ru_3\{\mu\text{-}Nu\}(CO)_{10}]$. By analogy, the initial labile complex (**1**) seen in the case of Nu = CN may be tentatively formulated as $[ppn][Ru_3(CN)(CO)_{11}]$ on the basis of the analogy of its i.r. spectrum with that of $[ppn][Ru_3(NCO)(CO)_{11}]$.[11] In this case, however, subsequent loss of CO occurs in a different way, since linear hybridization of σ-bonding molecular orbitals within the CN group favours intermolecular association over intramolecular bridge formation.

It should be noted that the complex $[ppn]_2[Ru_6(\mu\text{-}CN)_2(CO)_{20}]$ has no direct implication in the cyanide promoted catalytic substitution of CO by phosphines in $Ru_3(CO)_{12}$,[1] which occurs at an earlier stage of the interaction of the nucleophilic anion with the cluster. However, the formation of this species highlights the ease of intermolecular association *via* bridging cyanide, which may account for a facile intermolecular transfer of this anion.

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† *Experimental conditions:* The synthesis was conducted under a dry nitrogen atmosphere at 25 °C in a Schlenk flask. $Ru_3(CO)_{12}$ (0.469 mmol) was dissolved in 100 ml of freshly distilled THF. A stoicheiometric amount of [ppn][CN] (0.469 mmol) was dissolved in the minimum amount of CH_2Cl_2 (*ca.* 2 ml) and added with a syringe. An instantaneous darkening of the orange colour is indicative of complex formation. I.r. spectrum of the solution: [complex (**1**)] ν(CO), THF, 2060m, 2027s, 2005—1987br., 1980—1960br., 1930sh, 1825br. cm^{-1}. Low temperature ^{13}C experiments under CO show fluxionality at −100 °C (current studies in collaboration with H. D. Kaesz). Spectral changes, observed at ambient temperature over a period of several hours, are indicative of the formation of a new species (**2**) [ν(CO) (THF), 2080w, 2018vs, 1984s, 1953sh, 1939m, 1814ms cm^{-1}]. The conversion (**1**) → (**2**) is prevented under CO, and accelerated *in vacuo*. After complete solvent removal, the complex was recovered with the minimum amount of acetone; ethanol was added, and the mixture kept at −30 °C overnight, leading to the quantitative formation of bright yellow crystals suitable for *X*-ray analysis (the complex crystallizes with one molecule of acetone in the asymmetric unit).

‡ *Spectral data* for (**2**): i.r.; ν(CO) (CH_2Cl_2) 2084w, 2020vs, 1990s, 1953sh, 1939m, 1855sh, 1804ms cm^{-1}; ^{13}C n.m.r., low temperature experiments show fluxionality at −100 °C.

§ *Crystal data* for $[ppn]_2[Ru_6(CN)_2(CO)_{20}]\cdot 2Me_2CO$: $C_{50}H_{36}N_2O_{11}P_2Ru_3$, $M_r = 1206.00$, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.128(4)$, $b = 16.805(4)$, $c = 11.390(3)$ Å, $\alpha = 100.87(2)$, $\beta = 111.79(2)$, $\gamma = 63.47(2)°$; $U = 2405$ Å^3 [by least-squares refinement on diffractometer angles for 25 reflections in the range $12 < \theta$ (Mo-K_α) $< 15°$ ($\lambda = 0.7107$ Å)], $Z = 2$, $D_C = 1.585$ g cm^{-3}. Crystal dimensions (distances from faces to centre): 0.087 (110, $\bar{1}\bar{1}0$) × 0.15 (100, $\bar{1}00$) × 0.19 (011, $0\bar{1}\bar{1}$) × 0.20 ($01\bar{1}$, $0\bar{1}1$) mm, crystal volume = 0.026 mm^3, μ (Mo-K_α) = 9.5 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer, ω–θ scan mode with ω scan width 1.0 + 0.35 tan θ, ω scan speed 2° min^{-1}, graphite monochromated Mo-K_α radiation (take off angle, 2.4°); 5688 reflections measured ($2 < 2\theta < 46°$), giving 5128 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Intensities corrected for absorption; no intensity decay observed. Structure analysis and refinement was by direct methods (MULTAN) for location of Ru, P atoms. The model was extended through a combination of Fourier difference maps and full-matrix least-squares refinements (SHELX). Phenyl rings were treated as rigid groups (D_{6h} symmetry, C–C = 1.395 Å, C–H = 0.97 Å). Hydrogen atoms were entered in idealized positions, and were not refined. In attempts to distinguish carbon from nitrogen within the cyanide group, comparative refinements with two alternate combinations led to abnormal thermal parameters, revealing the occurrence of a disorder in the orientation of this group. The problem was solved by considering each site equally occupied with 50% carbon and 50% nitrogen. A free acetone molecule (solvent) was located in the lattice and included in the model. In final refinements, unit weights were found to be the most appropriate to the data. Final R_w and R values were 0.036 and 0.036, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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