

Bi-edge condensation of imido–rhodium clusters leading to novel planar hexametallc structures

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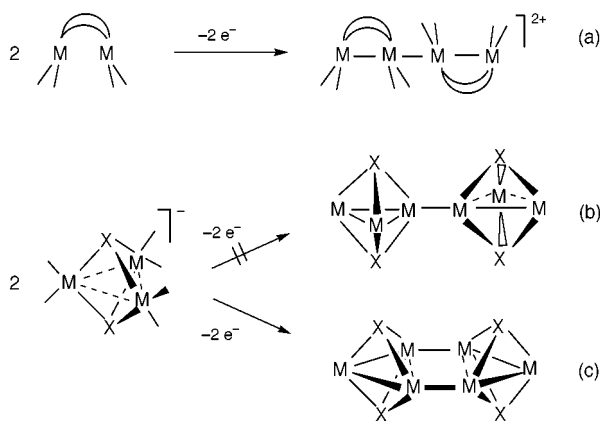
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Oxidation of $[\text{N}(\text{PPh}_3)_2][\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]$ with $[\text{FeCp}_2]\text{PF}_6$ gives the novel hexarhodium compound $[\{\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6\}_2]$, containing three nearly coplanar condensed metallic cycles forming a doubly-spiked square, by dimerisation of the trinuclear imidocomplex through the formation of unsupported metal–metal bonds.

Very recently we have reported a straightforward approach to tetrametallic rhodium and iridium chains by partial oxidation of appropriate dinuclear complexes.¹ After the electron abstraction, the hypothetical intermediate cations $[\text{M}^{\text{II}}\text{M}^{\text{II}}]^+$ promote a ‘linear condensation’ leading to an unsupported metal–metal bond between the two pairs of metal centres [Scheme 1(a)]. In a formal sense, the formation of this interdimer M–M bond could be related to simple C–C bond formation, assuming the similarity of the intermediate species $[\text{M}^{\text{II}}\text{M}^{\text{II}}]^+$ with organic radicals, for which coupling leading to dimerisation is a well known reaction. Looking for a similar condensation of triangular complexes induced by chemical oxidation one might expect doubly-spiked tetranuclear chains if a ‘vertex-condensation’ were operative [Scheme 1(b)]. However, other condensation schemes such as a ‘bi-edge-condensation’ would lead to a tetrametallic cycle [Scheme 1(c)].



Scheme 1 Possible pathways for the formation of metal chains and cycles. M = metal, X = capping ligand (NR).

We have recently reported the first tri- and tetra-nuclear organoimido rhodium clusters.² In the search to develop this chemistry, and looking for higher nuclearity imido clusters, we have turned our attention to the ‘active M–M edge’ of the trinuclear organoimido anion $[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]^-$. As the previously isolated salt³ of this anion contains the redox active cation $[\text{Rh}(\text{CO})(\text{dppm})_2]^+$, we first prepared the new yellow compound $\text{PPN}[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]$ **1** by reacting $[\text{Rh}_4(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_7(\text{cod})]_4$ with 2 mol equiv. of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ in dichloromethane and crystallization from diethyl ether.⁵

Oxidation of **1** in CDCl_3 with $[\text{FeCp}_2]\text{PF}_6$ (1 : 1 molar ratio) gives, immediately and quantitatively, an EPR silent emerald-

green solution of $[\{\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6\}_2]$ **2**. The ^1H NMR spectrum is quite surprising because it shows only two new singlets, one for the aromatic protons, which are isochronous, and the other for the methyl groups. More informative is the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, showing two carbonyl resonances (1 : 2 ratio) and four resonances corresponding to equivalent *p*-tolylimido ligands, which indicates that the trimetallic core capped by two *p*-tolylimido ligands is maintained in the new compound. Moreover, the resonances for *ipso*- and *ortho*-C appear as quartets by coupling with three rhodium atoms ($^3J_{\text{RhC}}$ 1.3 Hz). This green solution is obtained in a preparative scale in a similar way in dichloromethane. Red-green microcrystals of **2**⁶ are isolated in high yield (> 75%) after evaporation of the solution to dryness, removal of $[\text{FeCp}_2]$ by washing the residue with hexane followed by extraction with diethyl ether (to remove $[\text{N}(\text{PPh}_3)_2]\text{PF}_6$), and layering the extract with hexanes.

The molecular structure of **2**, determined by single crystal X-ray diffraction,⁷ reveals a hexanuclear metallic core. Thus, the novel organoimido rhodium cluster $[\{\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6\}_2]$ **2** consists of an almost planar tetrarhodium square with two opposite spiked edges generating a tricyclic hexametallc arrangement (Fig. 1) while four *p*-tolylimido ligands cap either side of the two metal triangles. Electron counting for **2** gives 94 valence electrons, *i.e.* two electrons less than the expected value (96 ve) for a cyclic hexametallc cluster, and two electrons over the expected counting for a doubly-spiked tetrametallic square (92 ve). The extra electron pair may be the cause of the long Rh–Rh separations for the edges connecting the fused cycles $[\text{Rh}(1)\cdots\text{Rh}(2)$ 3.1127(10) Å] when compared with the short Rh–Rh distances [2.7188(10) and 2.7048(9) Å] within the triangles, and the unsupported Rh–Rh bonds $[\text{Rh}(1)\text{---}\text{Rh}(2')] 2.9921(9)$ Å] in the central square.

The formation of **2** from $[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]^-$ can be envisaged as a one-electron oxidation reaction leading to the neutral radical complex $[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]^\cdot$, which dimerises through the formation of two new unsupported Rh–Rh bonds. Accordingly, cyclic voltammetry measurements on **1** show an irreversible one-electron oxidation process at 0.57 V *vs.* SCE in CH_2Cl_2 . However, a close inspection of this wave at fast scan rates ($> 1 \text{ V s}^{-1}$) shows the observation of a very small reduction wave, which disappears at moderate scan rates, in accordance with a EC_{irrev} mechanism. In this case the C_{irrev} reaction ought to be the dimerisation process.

Furthermore, it is noteworthy that the major tendency of complex **1** is to undergo M–M coupling rather than C–C bond formation upon oxidation. Oxidative C–C coupling through the *para* carbon of the phenyl group in dinuclear rhodium phenyl imido/amido complexes has been reported by Sharp and coworkers,⁸ and interpreted assuming that the proposed radical should be centred in the phenyl group. In our case, complex **1** shows a tunable donicity, *i.e.* it is able to coordinate metal fragments at the arene ring or at one rhodium–rhodium edge,⁹ and therefore both processes, C–C coupling involving the phenyl group, and M–M coupling involving the Rh–Rh edge could *a priori* be possible. Most probably, the unpaired electron

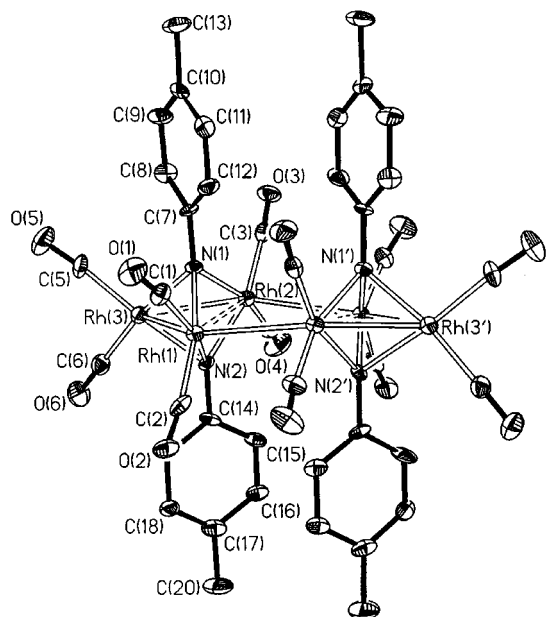


Fig. 1 Molecular diagram of $[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]_2$ **2**; the molecule has internal crystallographic twofold symmetry. Selected bond interatomic distances (Å) and angles ($^\circ$): Rh(1)–Rh(3) 2.7188(10), Rh(1)–Rh(2') 2.9921(9), Rh(2)–Rh(3) 2.7048(9), Rh(1)–Rh(2) 3.1127(10), Rh(1)–N(1) 2.028(6), Rh(1)–N(2) 2.069(6), Rh(2)–N(1) 2.081(6), Rh(2)–N(2) 2.041(6), Rh(3)–N(1) 2.051(7), Rh(3)–N(2) 2.063(6); Rh(2)–Rh(1)–Rh(3) 54.77(2), Rh(2)–Rh(1)–Rh(2') 88.43(3), Rh(2')–Rh(1)–Rh(3) 142.98(3), Rh(1)–Rh(2)–Rh(3) 55.19(2), Rh(1)–Rh(2)–Rh(1') 90.38(3), Rh(1')–Rh(2)–Rh(3) 144.83(3), Rh(1)–Rh(3)–Rh(2) 70.05(3), Rh(1)–N(1)–Rh(2) 98.5(3), Rh(1)–N(1)–Rh(3) 83.6(2), Rh(2)–N(1)–Rh(3) 81.8(2), Rh(1)–N(2)–Rh(2) 98.5(3), Rh(1)–N(2)–Rh(3) 82.3(2), Rh(2)–N(2)–Rh(3) 82.5(2) (primed atoms are related to their unprimed equivalent by the symmetry transformation: $y - 1, 1 + x, -z$).

in the proposed neutral radical $[\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]^\cdot$ is delocalized in the trimetallic core. This interpretation provides a facile explanation for the formation of the hexamer cluster by fusion of the two edges from two trimetallic triangles leading to **2**, in which the metals present formal fractional oxidation states.

The condensation reactions induced by oxidation [Scheme 1(a) and (c)] operate selectively depending on the structure of the starting materials and products, *i.e.* tetrametallic chains ('linear condensation') result from dinuclear complexes and tetrahedral cycles ('bi-edge condensation') from a trinuclear complex. The origin of the selectivity is probably related to the presence of the third metallic centre, which plays a non-innocent role, since the metal–metal edge in the trinuclear complexes is more accessible for a close approach of a substrate to both metals than in a dinuclear species, thus allowing the formation of the tetrametallic cycle for the former whilst vertex condensation is preferred for the latter.

The result of an electron transfer reaction on a cluster is, in general, quite unpredictable. Fragmentation, isomerisation, rearrangement and distortion of clusters are common outcomes from cluster redox reactions in addition to well documented cases where the electron loss/addition processes proceeds cleanly with M–M bond formation/cleavage.^{10,11}

Clusters with fixed capping groups based on group 15 elements are versatile in undergoing oxidation and/or reduction reactions.¹² However, to the best of our knowledge, a dimerisation of clusters induced by oxidation, such as shown here, is unusual. Moreover, the chemical oxidation of polynuclear compounds of low-valent electron-rich metals with capping groups in which metal–metal bonds are not evident represents a significant challenge for the creation of higher nuclearity species by methods other than redox-condensation using mononuclear metal fragments.

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Notes and references

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- The analytical data for **1** (Anal. Calc. for $\text{C}_{56}\text{H}_{44}\text{N}_3\text{O}_6\text{P}_2\text{Rh}_3$: C, 54.88; H, 3.62; N, 3.43. Found: C, 55.12; H, 3.71; N, 3.28%) are in accord with the proposed formulation, and the spectroscopic data are essentially identical to those described for the anion in $[\text{Rh}(\text{CO})(\text{dppm})_2][\text{Rh}_3(\mu\text{-NC}_6\text{H}_4\text{Me-}p)_2(\text{CO})_6]$.
- IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})/\text{cm}^{-1}$ 2062s, 2046s, 2021m, 2002m. ^1H NMR (300 MHz, CDCl_3 , room temp.): δ 6.316 (s, 4H), 2.039 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , room temp.): δ 187.5 (d, J_{RhC} 63 Hz, 8C, CO), 187.4 (d, J_{RhC} 75 Hz, 4C, CO), 164.8 (m, *ipso*-C), 135.1(*p*-C), 127.3(*m*-C), 120.4(q, J_{RhC} 1.3 Hz, *o*-C), 20.5(Me).
- Crystal data* for **2**: $\text{C}_{40}\text{H}_{28}\text{N}_4\text{O}_{12}\text{Rh}_6$, $M = 1374.12$, tetragonal, space group $P4_32_12$, $a = 12.1187(8)$, $c = 29.753(3)$ Å, $V = 4369.7(6)$ Å³, $Z = 4$, $D_c = 2.089$ g cm^{-3} , $\mu = 2.278$ mm⁻¹. Crystal dimensions 0.09 × 0.07 × 0.02 mm. Bruker SMART CCD diffractometer, $T = 153(1)$ K, Mo-K α radiation ($\lambda = 0.71073$ Å). A complete hemisphere of data was scanned on ω (0.30° per frame) with a run time of 20 s. Absorption corrections were applied using SADABS. From 15970 reflections measured, 5400 were unique ($R_{\text{int}} = 0.1223$). The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares on F^2 (SHELXL-97). Only half of the hexanuclear complex is crystallographically independent: 285 parameters; $R = 0.0619$ (3329 reflections with $F \geq 4\sigma(F_o)$), $wR2 = 0.0722$ and $S = 0.959$. Absolute structure checked with Flack parameter, $x = -0.11(6)$. CCDC 182/1461. See <http://www.rsc.org/suppdata/cc/1999/2387/> for crystallographic files in .cif format.
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