

# Clusters containing metal–metal bonds linking high- and low-valent metal centres: synthesis and structure of $\text{Ru}_3(\text{CO})_{12}\{\text{Mo}(\text{NAr})_2\}$

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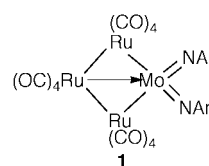
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Room temperature reaction of  $\text{K}_2[\text{Ru}_3(\text{CO})_{11}]$  with the molybdenum(vi) bis(imido) complexes  $\text{Mo}(\text{NAr})_2\text{Cl}_2(\text{dme})$  ( $\text{Ar} = \text{C}_6\text{H}_3\text{X}_2-2,6$ ;  $\text{X} = \text{Me}, \text{Pr}^i, \text{Cl}$ ;  $\text{dme} = 1,2$ -dimethoxyethane) affords new high-low valent clusters  $\text{Ru}_3(\text{CO})_{12}\{\text{Mo}(\text{NAr})_2\}$  which adopt a butterfly arrangement of metal centres with  $[\text{Ru}_3(\text{CO})_{12}]^{2-}$  acting as a ligand at a molybdenum(vi) centre.

Molecular transition metal complexes can broadly be divided into those containing the metal centre in either a high and or low oxidation state. While in most respects the chemistry displayed in these two areas is quite different, metal–metal bonding is prevalent in both. Moreover, there is an increasing number of examples in which metal–metal bonds are formed between high- and low-valent metal centres. These include the classic  $\text{W}(\text{v})$ – $\text{W}(\text{i})$  complex  $\text{Cp}^*\text{W}(\text{CO})_3$ – $\text{WO}_2\text{Cp}^*$  prepared by Alt *et al.*,<sup>1</sup> while Sundermeyer has recently reported a range of related bi- and tri-nuclear imido-containing complexes.<sup>2</sup> In these, metal–metal bonds are found between the high- and low-valent centres but, even when more than one of the former is present, there are no metal–metal bonds between the low-valent centres. That is, clusters of this type are of the linear variety. Chi and coworkers<sup>3,4</sup> have synthesised a number of group 6/8 mixed-metal clusters containing imido ligands, however, here it is noted that the  $\pi$ -donor ligands are rarely bound in a monodentate fashion,<sup>4</sup> but rather bridge two or more metal centres.<sup>3</sup> As such, all metal centres in such clusters can be considered to be of similar valency. In contrast, Puddephatt and coworkers<sup>5</sup> have prepared the tetrahedral cluster cation  $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3]^+$  where the formal metal oxidation states may be considered as  $\text{Re}(\text{vii})$  and  $\text{Pt}(0)$ , yet it is characterised by three strong Pt–Re interactions.

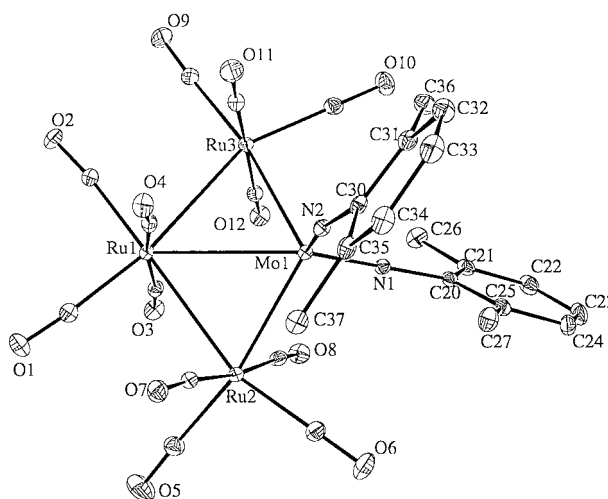
Over the past thirty years, low-valent carbonyl clusters have been the focus of intensive research and a wide range of cluster geometries have been found.<sup>6</sup> Cluster frameworks are generally soft and deformable, with the geometries adopted dependent upon the number of electrons. Further, many are easily oxidised and/or reduced and as such have the ability to act as efficient electron sinks. Both of these properties, if controllable, would make the cluster useful as a ligand. Herein we describe the use of the low-valent cluster  $[\text{Ru}_3(\text{CO})_{12}]^{2-}$  as a ligand to a high-valent, bis(imido) stabilised molybdenum centre.

Room temperature addition of the solutions of  $\text{K}_2[\text{Ru}_3(\text{CO})_{11}]$ <sup>7</sup> and  $\text{Mo}(\text{NAr})_2\text{Cl}_2(\text{dme})$ <sup>8</sup> resulted in the formation of very dark solutions which were left to stir overnight. Work-up in an aerobic atmosphere resulted after chromatography in the isolation of  $\text{Ru}_3(\text{CO})_{12}$  and the new clusters  $\text{Ru}_3(\text{CO})_{12}\{\text{Mo}(\text{NAr})_2\}$  **1a–c** in yields of 20–30%. Clusters **1a–c** show good solubility in hexane and are air-stable in this solvent. Characterisation was made on the basis of IR, NMR and mass spectra.<sup>†</sup> Crystals of **1a** suitable for X-ray analysis were easily grown upon cooling a saturated hexane solution to  $-20^\circ\text{C}$ , the results of which are summarised in Fig. 1.<sup>‡</sup>



$\text{Ar} = \text{C}_6\text{H}_3\text{R}_2-2,6$ : **a** R = Me, **b** R =  $\text{Pr}^i$ , **c** R = Cl

The molecule consists of a butterfly arrangement of one molybdenum and three ruthenium atoms, with a fold angle of  $25.4^\circ$  about the hinge vector, Mo(1)–Ru(1). The molybdenum centre retains its two imido ligands while each ruthenium centre is ligated by four CO ligands. Of the three ruthenium–molybdenum interactions, two are extremely short [Mo(1)–Ru(2) 2.7165(5), Mo(1)–Ru(3) 2.7025(4) Å] while the third, the hinge vector, is much longer [Mo(1)–Ru(1) 3.1094(8) Å]. Indeed, as far as we are aware, these bonds within **1a** span the range of all known molybdenum–ruthenium bonds in mixed-metal clusters.<sup>9</sup> The very short Mo–Ru interactions are probably a result of the smaller radii of high- vs. low-valent metal centres and high polarity of the heterometallic interaction  $\text{M}^{\delta+}$ – $\text{M}^{\delta-}$  as noted previously by Sundermeyer *et al.*<sup>2</sup> The longer hinge vector is dative in origin, the electron-rich ruthenium tetracarbonyl unit acting as a donor to the high-valent molybdenum centre. One way of looking at **1a** is as a molybdenum(vi) bis(imido) centre bound to a chelating  $[\text{Ru}_3(\text{CO})_{12}]^{2-}$  ligand. In the free state this dianion would lose CO to afford



**Fig. 1** Molecular structure of **1a** with selected bond lengths (Å) and angles ( $^\circ$ ): Mo(1)–Ru(1) 3.1094(8), Mo(1)–Ru(2) 2.7165(5), Mo(1)–Ru(3) 2.7025(4), Ru(1)–Ru(2) 2.9315(5), Ru(1)–Ru(3) 2.9556(5), Mo(1)–N(1) 1.766(2), Mo(1)–N(2) 1.761(2), Ru(2)–Mo(1)–Ru(3) 115.88(2), Mo(1)–Ru(3)–Ru(1) 66.50(2), Ru(3)–Ru(1)–Ru(2) 102.54(2), Ru(1)–Ru(2)–Mo(1) 66.68(2), N(1)–Mo(1)–N(2) 112.39(7), Mo(1)–N(1)–C(20) 163.60(13), Mo(1)–N(2)–C(30) 162.26(13).

[Ru<sub>3</sub>(CO)<sub>11</sub>]<sup>2-</sup>, however, on the basis of a localised bonding model it would be expected to contain one long and two short ruthenium–ruthenium vectors. Ruthenium–ruthenium distances [Ru(1)–Ru(2) 2.9315(5), Ru(1)–Ru(3) 2.9556(5) Å] are *ca.* 0.1 Å longer than the average of 2.854 Å found in Ru<sub>3</sub>(CO)<sub>12</sub>,<sup>10</sup> however, this is expected as the outer ruthenium atoms carry a negative charge, while the Ru(2)–Ru(3) distance of 4.593 Å is clearly non-bonding. Thus, the triruthenium unit has the attributes expected of [Ru<sub>3</sub>(CO)<sub>12</sub>]<sup>2-</sup>. Ignoring the dative Ru–Mo interaction, the molybdenum centre is approximately tetrahedral and related tetrahedral bis(imido) units are common for Mo(vi)<sup>11</sup> and known for Mo(iv).<sup>12</sup> Metal–nitrogen bond lengths in imido complexes are known to vary only slightly over a wide-range of complexes,<sup>13</sup> with no clear distinction between Mo(vi) and Mo(iv). Molybdenum–nitrogen distances in **1a** [Mo(1)–N(1) 1.766(2), Mo(1)–N(2) 1.761(2) Å] and the N(1)–Mo(1)–N(2) angle of 112.39(7)° are within the ranges found for both Mo(vi) and Mo(iv) complexes.<sup>11–13</sup>

Butterfly clusters are usually associated with an effective atomic number (EAN) of 62 electrons. As the imido ligands are linear [Mo(1)–N(1)–C(20) 163.60(13), Mo(1)–N(2)–C(30) 162.26(13)°] then both might be expected to be able to act as four-electron donors and such a scenario would give the expected 62-electron count. However, there are only three d orbitals of  $\pi$ -symmetry on any one metal centre, and thus the total donor capacity of the two imido ligands is six.<sup>13</sup> This suggests that cluster **1** has only 60 electrons and is formally electron deficient at molybdenum.

The mode of formation of **1** is not yet fully understood. Clearly CO scavenging must occur and this would be a reasonable explanation for the moderate yields obtained. The major byproduct of all reactions is Ru<sub>3</sub>(CO)<sub>12</sub>. This probably results from electron-transfer being competitive with nucleophilic substitution. We have also, however, noted that while **1a–c** are all indefinitely stable in hexane, thf solutions decompose over a period of hours under anaerobic conditions giving Ru<sub>3</sub>(CO)<sub>12</sub> and an as yet unidentified molybdenum product. The differing stabilities of **1** in coordinating and non-coordinating solvents may reflect the strong polarisation of the Mo–Ru bonds and the electron deficiency at molybdenum.

Attempts to extend this type of cluster to aryl imido ligands without *ortho* substituents has so far been fruitless. For example, addition of K<sub>2</sub>[Ru<sub>3</sub>(CO)<sub>11</sub>] to Mo(NPh)<sub>2</sub>Cl<sub>2</sub>(dme) yielded Ru<sub>3</sub>(CO)<sub>12</sub> and H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub> as the only tractable products. The reason for this is unclear but given the instability of **1a–c** in thf (the reaction solvent), it may be that Ru<sub>3</sub>(CO)<sub>12</sub>–{Mo(NPh)<sub>2</sub>} decomposes as rapidly as it is generated. We are currently exploring different solvents for these reactions, and plan to extend the metathesis methodology to other group 8 cluster anions and high-valent metal complexes, and explore the reactivity of this new class of high-low valent cluster complexes.

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## Notes and references

† *Spectroscopic data*: for **1a**: IR (C<sub>6</sub>H<sub>14</sub>)  $\nu$ (CO) 2106m, 2070s, 2055m, 2038w, 2030s, 2026(sh), 2006m, 2003w cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.98 (s, 6H, Ar), 2.17 (s, 12H, Me); MS(FAB<sup>+</sup>) *m/z* 945 (M – CO); Anal. Calc. for MoRu<sub>3</sub>C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O<sub>12</sub>, C, 34.53, H, 1.85, N, 2.87. Found: C, 34.77, H, 1.83, N, 2.95%.

‡ *Crystal data*: X-ray intensity data were collected on a Siemens CCD diffractometer using Mo-K $\alpha$  radiation and the  $\omega$ -scan mode; *T* = 293 K, MoRu<sub>3</sub>C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O<sub>12</sub>, *M<sub>r</sub>* = 973.59, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 19.409(4), *b* = 9.887(2), *c* = 17.947(4) Å,  $\beta$  = 109.98(3)°, *F*(000) = 1880, *D<sub>c</sub>* = 1.998 g cm<sup>-3</sup>, *Z* = 4,  $\mu$  = 1.81 mm<sup>-1</sup>, 2 $\theta$ (max) = 58.4°, *R*(*R<sub>w</sub>*) = 0.0192 (0.0441) for 8668 reflections [*I* > 2 $\sigma$ (*I*)] and 487 parameters. CCDC 182/1499. See <http://www.rsc.org/suppdata/cc/a9/a908982i/> for crystallographic files in .cif format

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