

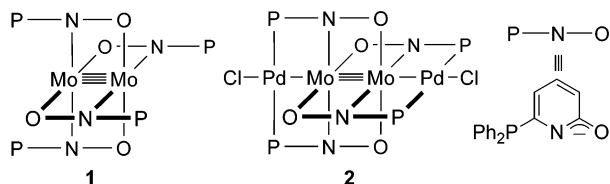
## Unique Oxidative Metal–Metal Bond Formation of Linearly Aligned Tetranuclear Rh–Mo–Mo–Rh Clusters

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The construction of one-dimensional, covalently bonded metal strings has attracted much interest in view of fundamental bonding nature as well as promising applications as extensive electronic and optoelectronic materials.<sup>1</sup> Two major synthetic approaches to these compounds have been conducted by (a) using polydentate ligands such as oligo- $\alpha$ -pyridylamid<sup>2–4</sup> and polyene<sup>5</sup> ones or by (b) partial oxidation of  $d^8$  square-planar complexes or partial reduction of the Rh(II)<sub>2</sub> complex to form metal–metal bonds (e.g., platinum blue).<sup>6</sup> Our effort has been focused on aligning transition metals by using a tridentate ligand 6-diphenylphosphino-2-pyridonate (pyphos), in which three different elements, P, N, and O, were linearly laid out by the rigid pyridone framework and could act as coordination sites for arrangement of more than two kinds of transition metals in a linear manner.<sup>7</sup> We thus have demonstrated linear heterometallic clusters containing both group 6 and group 10 metals by use of the quadruply bonded dimolybdenum(II) complex, Mo<sub>2</sub>(pyphos)<sub>4</sub> (**1**),<sup>8</sup> as a core part of metal strings such as Mo<sub>2</sub>Pd<sub>2</sub>Cl<sub>2</sub>(pyphos)<sub>4</sub> (**2**).<sup>8b</sup>

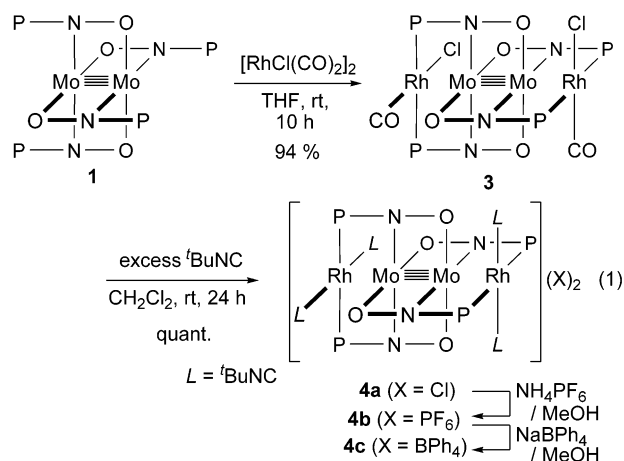


As the next stage of our continuous study, we confronted the synthesis of a new series of heterometallic tetranuclear clusters containing group 9 metals with appropriate geometries of square planar as well as octahedral to be supported by the two PPh<sub>2</sub> groups. Herein we report the synthesis of linearly aligned tetranuclear complexes bearing the Rh–Mo–Mo–Rh array. We found that oxidative reaction of Rh(I) metals at both axial positions of the Mo<sub>2</sub> cluster **1** into Rh(II) induced the formation of Rh–Mo bonds.

Treatment of **1** with [RhCl(CO)<sub>2</sub>]<sub>2</sub> resulted in the clean formation of [Mo<sub>2</sub>Rh<sub>2</sub>(CO)<sub>2</sub>(Cl)<sub>2</sub>(pyphos)<sub>4</sub>] (**3**), whose <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displayed two doublet signals with a coupling constant ( $J_{\text{Rh–P}} = 120.0$  Hz) at  $\delta$  25.8 and 25.9 ppm (eq 1). Inequivalence of the phosphorus nuclei in **3** was presumably due to the coordination of two different ligands, CO and Cl, to each Rh atom.<sup>9</sup>

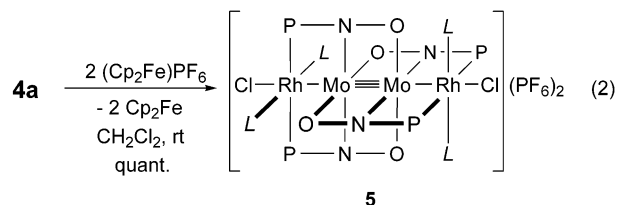
It is well-known that oxidation of rhodium atoms in several dinuclear Rh(I) complexes resulted in the Rh(II)–Rh(II) bond formation.<sup>10</sup> We thus anticipated that the oxidation of Rh(I) atoms of **3** to Rh(II) ones forms Rh–Mo bonds to give a metal–metal bonded cluster; however, the oxidation of **3** by ferrocenium cation resulted in the decomposition with the release of CO. To enhance the stability as well as the solubility, we prepared the isocyanide derivative of **3**. Reaction of **3** with excess amounts of <sup>t</sup>BuNC in dichloromethane caused the immediate change of the color of the solution from red to purple, giving a dicationic complex [Mo<sub>2</sub>Rh<sub>2</sub>(<sup>t</sup>BuNC)<sub>4</sub>(pyphos)<sub>4</sub>](X)<sub>2</sub> (**4**),

in a quantitative yield (eq 1). Four PPh<sub>2</sub> groups in **4a** were observed to be equivalent as evident from a doublet ( $J_{\text{Rh–P}} = 121.2$  Hz) at  $\delta$  31.2 ppm.

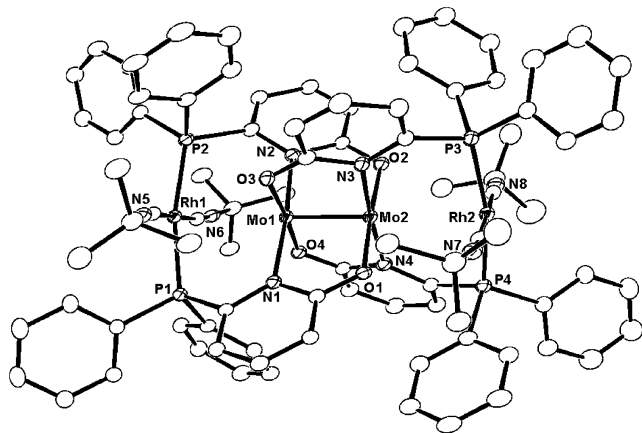


The X-ray study revealed that the cationic part of **4c**, which was obtained by treatment of **4a** with NH<sub>4</sub>PF<sub>6</sub> followed by addition of NaBPh<sub>4</sub>, consists of a linearly aligned Rh–Mo–Mo–Rh tetrametal core (Figure 1). The Mo–Mo bond distance of 2.1054(6) Å lies in a common quadruply bonded Mo(II)<sub>2</sub> distance such as the parent complex **1** (2.098(2) Å)<sup>8b</sup> and Mo<sub>2</sub>(L)<sub>4</sub> (L =  $\mu$ -acetate, 2.0934(8) Å, L = 6-methylpyridonate, 2.065(1) Å).<sup>11</sup> Although the interatomic Mo–Rh distances of 2.8462(6) and 2.8453(6) Å for **4c** falls within the range normally associated with Rh–Mo single bonds (ca. 2.77–2.95 Å),<sup>12</sup> we presumed that there is no direct  $\sigma$ -bonding interaction between each Rh atom and the Mo<sub>2</sub> core in **4c**, the same as for **3**, because the geometry around the Rh atom in **4c** adopts a square-planar geometry, as expected for the  $d^8$  Rh(I) atom.

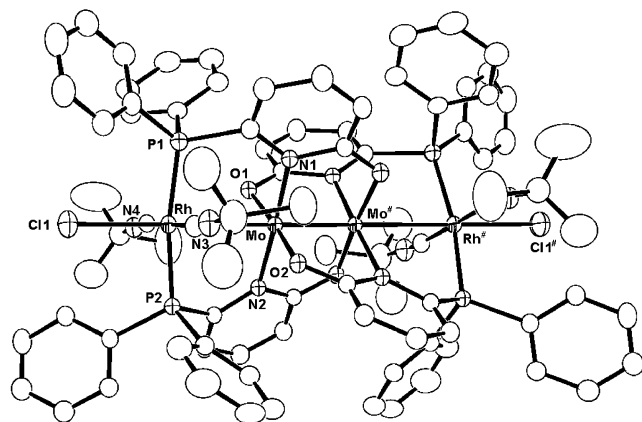
The formation of a metal nanowire, of which four transition metals are linearly bonded through three metal–metal bonds, was accomplished by oxidation of each Rh(I) atom of **4a** by 2 equiv of [Cp<sub>2</sub>Fe]PF<sub>6</sub> to afford [Mo<sub>2</sub>Rh<sub>2</sub>(Cl)<sub>2</sub>(<sup>t</sup>BuNC)<sub>4</sub>(pyphos)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> (**5**) along with the formation of two Mo–Rh(II) single bonds and the reduction of the bond order of the Mo–Mo moiety (eq 2).



Each Rh atom in **4a** was concurrently oxidized as evident from a cyclic voltammogram recorded in (<sup>n</sup>Bu)<sub>4</sub>NCl/MeCN, in which a



**Figure 1.** Molecular structure of **4c** with thermal ellipsoids at the 30% probability level. H atoms, counteranions, and solvents are omitted for clarity.



**Figure 2.** Molecular structure of **5** with thermal ellipsoids at the 30% probability level. H atoms, counteranions, and solvents are omitted for clarity.

reversible two-electron wave of **4a**<sup>0/+2</sup> was observed at  $-452$  mV vs Ag/AgCl. In the  $^{31}\text{P}$  NMR spectrum of **5** recorded in  $\text{CD}_2\text{Cl}_2$ , a doublet signal ( $J_{\text{Rh-P}} = 94.0$  Hz) was observed at  $\delta$  21.6 ppm, in which a significant decrease in  $J_{\text{Rh-P}}$  compared to that of **4a** reflected a decrease in electron density of the Rh atom of **5**. Taking into account that the dicationic complex **5** is diamagnetic despite containing  $d^7$  Rh(II) atoms, the existence of a direct bonding interaction between the  $\text{Mo}_2$  core and each Rh atom would be expected.

The X-ray diffraction study of **5** established the structural identity of the linearity of the Rh–Mo–Mo–Rh skeleton (Figure 2), and a drastic shortening of the Mo–Rh distance of **5** ( $2.7307(7)$  Å) is consistent with the result obtained from the measurement of  $^{31}\text{P}$  NMR spectroscopy mentioned above. The Mo–Mo distance of **2.124(1)** Å is slightly longer than those of **3** and **4c**, and this value lies within the range of those in Pt–Mo≡Mo–Pt and Pd–Mo≡Mo–Pd complexes reported in previous works.<sup>8</sup> The decrease in the wavenumber  $\nu_{\text{Mo-Mo}}$  observed in the resonance Raman spectra (**5**:  $389\text{ cm}^{-1}$ ) is indicative of the decrease in bond order from four (**3**:  $399\text{ cm}^{-1}$ , **4a**:  $398\text{ cm}^{-1}$ ) to three.

In summary, we have synthesized and structurally characterized a series of linear tetranuclear Rh–Mo–Mo–Rh clusters supported by four pyphos ligands and demonstrated that the two Rh(I) atoms in **4** were concurrently oxidized to yield the linear Rh(II)–Mo(II)–Mo(II)–Rh(II) metal nanowire **5**.

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**Supporting Information Available:** Detailed experimental procedures, spectral data, and crystallographic data (PDF, plain text). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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