Demetallation of a Dimolybdenum Cyclotetraphosphoxane Cage Complex and the Syntheses of Heterobimetallic Cages

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Selective excision of the Mo^{II} vertex in the mixed-valent, adamantanoid cage complex $Mo(CO)_4[Pr^i_2NPO]_4Mo(CO)_2I_2$ with sodium dithiocarbamate gave the metalla-ligand $Mo(CO)_4[Pr^i_2NPO]_4$ which is a precursor to novel heterobimetallic cage complexes $Mo(CO)_4[Pr^i_2NPO]_4ML_n$ where ML_n can be $Cr(CO)_4$, $W(CO)_4$, $Fe(CO)_3$, $NiBr_2$, $PtCl_2$ or $Cu(MeCN)_2BF_4$.

The dimolybdenum complex $Mo(CO)_4[Pr^i_2NPO]_4Mo(CO)_4$ **1** contains an $Mo_2P_4O_4$ adamantanoid core with distinctive chemistry including mixed-valency and intramolecular oxidative additions.[1–3] Heterobimetallic cage complexes of this type should have especially interesting chemistry though they have not yet become available owing to a lack of rational synthetic routes. While demetallation of **1** has not been achieved, the mixed-valent $Mo(CO)_4[Pr^i_2NPO]_4Mo(CO)_2I_2$ **2** contains one divalent molybdenum vertex which presents a potential site for decomplexation using dithiocarbamates.[2,4,5] We have found that treatment of **2** with two equivalents of sodium dimethyldithiocarbamate indeed selectively removed this cage atom to give complex **3** in moderate yield *via* an orange intermediate (Scheme 1).

$$Mo(CO)_4[Pr^i_2NPO]_4Mo(CO)_2I_2 + 2\ NaS_2CNMe_2$$
2
$$CH_2Cl_2 \downarrow -2NaI$$
$$Mo(CO)_4[Pr^i_2NPO]_4Mo(CO)_2(S_2CNMe_2)_2$$
orange intermediate
$$\downarrow$$
$$Mo(CO)_2(S_2CNMe_2)_2 \downarrow + Mo(CO)_4[Pr^i_2NPO]_4$$
3

Scheme 1

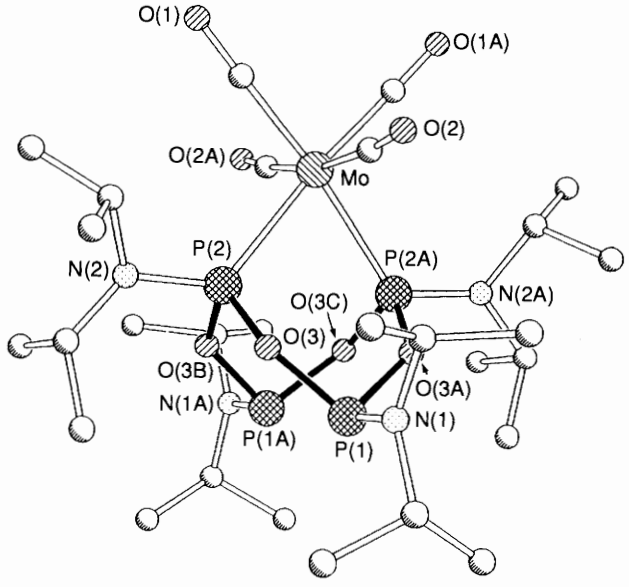
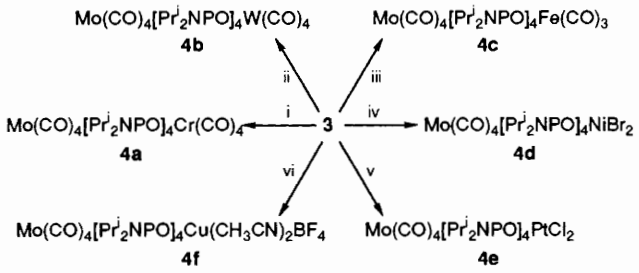


Fig. 1 Molecular structure of $Mo(CO)_4[Pr^i_2NPO]_4$ **3**. Key bond lengths (Å) and angles (°): Mo–P(2) 2.512(2), Mo–C(2) 2.027(10), Mo–C(1A) 1.978(9), P(1)–O(3) 1.671(4), P(2)–O(3) 1.623(4), P(1)–N(1) 1.655(6), P(2)–N(2) 1.642(7), P(2)–Mo–P(2A) 75.1(1), C(1)–Mo–C(1A) 87.5(5), C(2)–Mo–C(2A) 169.8(5), P(2)–Mo–C(1) 98.7(3), P(1)–O(3)–P(2) 131.6(2), Mo–P(2)–O(3) 112.1(1), O(3)–P(1)–O(3A) 102.1(3).

Complex **3** is an air-stable white solid with IR carbonyl absorptions at 2010, 1925, 1908 and 1882 cm^{-1}. Its proton-decoupled ^{31}P NMR spectrum exhibits one sharp and one broad triplet (δ 150.5 and 126.0, $^2J_{POP}$ = 2 Hz). Its solid-state molecular structure is shown in Fig. 1.† The molecule has overall C_{2v} symmetry with the expected vacant metal vertex. While the basic P_4O_4 boat–boat ring conformation in complex **1** is retained,[1] there are significant modifications in the phosphorus–oxygen bond lengths compared to the average of 1.646(4) Å found in **1**.[1] The four (Mo)–P–O bonds are shortened to 1.623(4) Å while those at the uncoordinated phosphorus atoms are lengthened to 1.671(4) Å, indicative of the enhanced P–O π-bonding at the coordinated sites at the expense of the latter.[6] Along with the previously described chair–boat and chair–chair forms,[7] this represents the third configurational isomer of the MoP_4O_4 moiety to be structurally characterized. This third geometry has not been accessible by previous direct synthesis.[7]

The convergent phosphorus lone pairs in **3** make it a likely metalla-ligand for the formation of bimetallic cage complexes. This potential has been realized in the reactions outlined in Scheme 2. These heterobimetallic products obtained in moderate to high yields have been characterized by elemental analyses and spectral data. In addition, complex **4d** has been found to have the solid-state molecular structure shown in Fig. 2.† The pseudo-tetrahedral coordination geometry around the nickel vertex is consistent with its paramagnetic behaviour.[8] Again, the eight cage phosphorus–oxygen bonds have readjusted to this new coordination mode; the four (Ni^{II})–P–O distances now average 1.633(8) Å while the four (Mo^0)–P–O distances average to a marginally longer, 1.650(9) Å.



Scheme 2 All reactions were run in refluxing hexane. *Reagents*: i, $Cr(CO)_4$(norbornadiene); ii, $W(CO)_4$(norbornadiene); iii, $Fe_2(CO)_9$; iv, $NiBr_2$·dimethoxyethane; v, $PtCl_2$(norbornadiene); vi, $Cu(MeCN)_4BF_4$.

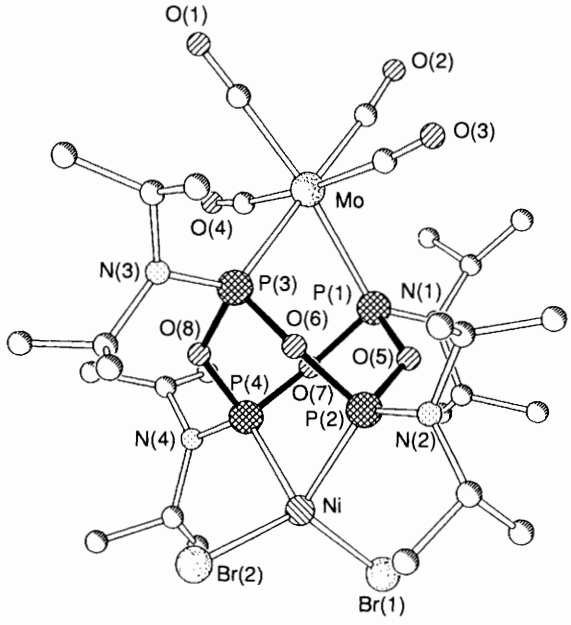


Fig. 2 Molecular structure of $Mo(CO)_4[Pr^i_2NPO]_4NiBr_2$, **4d**. Key bond lengths (Å) and angles (°): Mo–P(1) 2.494(4), Mo–P(3) 2.493(4), Mo–C(1) 2.004(15), Mo–C(2) 1.987(17), Mo–C(3) 2.047(17), Mo–C(4) 2.019(17), Ni–Br(1) 2.320(3), Ni–Br(2) 2.318(3), Ni–P(2) 2.254(4), Ni–P(4) 2.266(4), P(1)–O(5) 1.639(9), P(1)–O(7) 1.661(9), P(2)–O(6) 1.627(8), P(2)–O(5) 1.654(9), P(3)–O(6) 1.653(9), P(3)–O(8) 1.649(9), P(4)–O(7) 1.623(9), P(4)–O(8) 1.631(8), P(1)–Mo–P(3) 77.9(1), C(1)–Mo–C(2) 85.2(6), C(3)–Mo–C(4) 172.7(6), Br(1)–Ni–Br(2) 128.9(1), Br(1)–Ni–P(2) 110.6(1), Br(2)–Ni–P(2) 111.3(1), P(2)–Ni–P(4) 85.7(1), P(1)–O(5)–P(2) 131.7(5), P(1)–O(7)–P(4) 132.1(5), P(2)–O(6)–P(3) 133.6(5), P(3)–O(8)–P(4) 127.8(5).

† *Crystal data* for complex **3**: $C_{28}H_{56}MoN_4O_8P_4$, colourless, M = 796.61, tetragonal, $P4_2/mnm$, a = 18.028(5), c = 14.003(4) Å, V = 4551(2) Å^3, Z = 4, T = 297 K, D_c = 1.256 g cm^{-3}, μ(Mo-Kα) = 4.63 cm^{-1}. Of 4447 data collected (4° ≤ 2θ ≤ 50°), 2194 were independent and 1563 were observed (4σF_o). The isopropyl groups attached to N(2) were disordered and occur in several positions. A badly disordered solvent molecule is also found in the unit cell. These atoms were assigned as carbon, and the reported density, but not the elemental formula, includes their contribution. Final R = 5.59%, R_w = 8.44%.

Crystal data for complex **4d**: $C_{28}H_{56}Br_2MoN_4NiO_8P_4$, dark red, monoclinic, $C2/c$, a = 20.339(3), b = 13.204(2), c = 35.484(7) Å, β = 93.45(2)°, V = 9512(3) Å^3, Z = 8, T = 297 K, D_c = 1.418 g cm^{-3}, μ = 25.06 cm^{-1}. Of 6642 data collected (4° ≤ 2θ ≤ 45°), 6199 were independent and 3253 were observed (4σF_o). Corrections were made for a 14% linear decay in check reflection intensity and for absorption, using a semi-empirical ψ-scan method. Final R = 6.03%, R_w = 7.54%.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The well resolved a_1 carbonyl stretching frequency of the *cis*-$Mo(CO)_4$ moiety in complexes **1–4** also provides a sensitive gauge of possible intracage effects, although the shifts are small and more examples are required for confirmation.[9] Specifically, in the monometallic Mo^0 complex **3** it is at 2010 cm^{-1}, in the Mo^0/Mo^0 complex **1** it is shifted to 2015 cm^{-1}, in the Mo^0/Cu^I complex **4f** it is at 2019 cm^{-1}, while in the Mo^0/Ni^{II} complex **4d** it has increased to 2024 cm^{-1}. These data suggest transmission of the increasing electron demand of the second cage metal to the molybdenum vertex. We aim to explore the redox and the reaction chemistry of these novel heterobimetallic cage complexes.

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