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New Synthetic Strategy for a Straight Linear Metal–Metal Bonded Tetranuclear Complex, the Pd–Mo–Mo–Pd System Supported by Four Tridentate 6-(Diphenylphosphino)-2-pyridonate Ligands

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Recently low-dimensional materials have attracted much interest for their unique physical (magnetic, electronic, optical) properties.[1-10] The ideal preparative method of the one-dimensional infinite metal cluster is polymerization of a multiple metal–metal bond,[11] which is schematically shown in eq 1, where n and $n-1$ denote the multiplicity of the metal–metal bond. Although many complexes bearing multiple metal–metal bonds have been prepared and their structure and bonding have been elucidated,[12] the observed reactivity of the multiple bonds of these complexes is quite different from that of analogous organic compounds such as alkenes and alkynes. The addition of metal to the axial positions of a multiple metal–metal bond forming a linear tetranuclear complex (eq 2) has not been reported. There are many examples, however for the coordination of donor ligands to the axial positions of such metal–metal complexes.[12-15] In this contribution, we report on the preparation and crystal structure of a straight linear tetranuclear complex, $Mo_2Pd_2Cl_2(pyphos)_4$ (**2**),[16] according to the method described in eq 2 by using the tridentate ligand.

$$\mathrm{M}\overset{(n)}{\text{——}}\mathrm{M} \longrightarrow 1/m\left[\!-\mathrm{M}\overset{(n-1)}{\text{——}}\mathrm{M}-\!\right]_m \qquad (1)$$

$$\mathrm{M}\overset{(n)}{\text{——}}\mathrm{M} \xrightarrow{2\ \cdot\mathrm{M'}} \mathrm{M'}\text{——}\mathrm{M}\overset{(n-1)}{\text{——}}\mathrm{M}\text{——}\mathrm{M'} \qquad (2)$$

Treatment of $Mo_2(pyphos)_4$ (**1**)[17,18] with 2 equiv of $PdCl_2(PhCN)_2$ in dichloromethane at room temperature resulted in the formation of **2**[19,20] in 20% yield upon crystallization from a solution of dichloromethane and diethyl ether. The molecular structure was investigated by single-crystal X-ray analysis as well as $^{31}P\{^1H\}$ NMR, mass spectra, and elemental analyses. Figure 1 shows the structure of **2**,[21] which is composed of a straight linear Cl–Pd–Mo–Mo–Pd–Cl fragment supported by four pyphos ligands and aligned on a 2-fold axis. The bond distances of Pd–Mo (2.689(4) and 2.679(4) Å) are regarded as single bonds.[22] The interaction of Pd(I) with the Mo_2 moiety resulted in elongation of the Mo–Mo bond (2.1208(9) Å), which is longer than that found in **1** (2.098(2) Å),[18] **3** (vide infra), and $Mo_2(mhp)_4$ (2.065(1) Å).[23] The distance of Mo–Mo in **2** is shorter than that of triple bonds, which span the range 2.167–2.276 Å.[12] The unpaired d-orbitals of two Pd(I) atoms hybridize with the σ-orbital of the Mo_2 core (bond order of 4) to give two σ-bonds between Pd and Mo.[24] The Mo_2 core in complex **2** has formally a triple bond comprising two π components and one δ component, which

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(16) Abbreviations: pyphos = 6-(diphenylphosphino)-2-pyridonate, pyphosH = 6-(diphenylphosphino)-2-pyridone.

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(18) The structure of **1** having four trans-arranged pyphos ligands was confirmed by X-ray analysis and will be reported elsewhere.

(19) **2**: red crystal, mp 237–243 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30 °C): δ 15.7 (s). ^1H NMR ($CDCl_3$, 30 °C): δ 6.03 (d, 4H), 6.25 (d, 4H), 7.16 (t, 4H), 7.33–7.46 (m, 24H), 7.50–7.57 (m, 16H). FAB-MS for $^{98}Mo^{106}Pd$: m/z 1521 ($MH^+ - Cl_2$). UV–vis (CH_2Cl_2): λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) 458 (1.1×10^4), 642 (3.0×10^4). Anal. Calcd for $C_{68}H_{52}Cl_2Mo_2N_4O_4P_4Pd_2(CH_2Cl_2)$: C, 49.52; H, 3.25; N, 3.35. Found: C, 49.97; H, 3.38; N, 3.50.

(20) During the reaction course, an insoluble Pd(II) complex, $Mo_2Pd_2Cl_4(pyphos)_4$, was obtained and characterized by elementary analysis. This complex was reduced to **2** by $NaBH_4$ in dichloromethane suspension.

(21) Crystal data for **2**: FW = 1928.40 (four molecules of dichloromethane as crystalline solvent), tetragonal space group $I4_1$, $a = 17.388(4)$ Å, $c = 25.748(5)$ Å, $V = 7784(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.645$ g cm^{-3}, $\mu = 12.32$ cm^{-1}, number of parameters = 445, 3112 reflection data with $I > 3\sigma(I)$, goodness of fit = 1.19, $R = 0.032$, $R_w = 0.035$.

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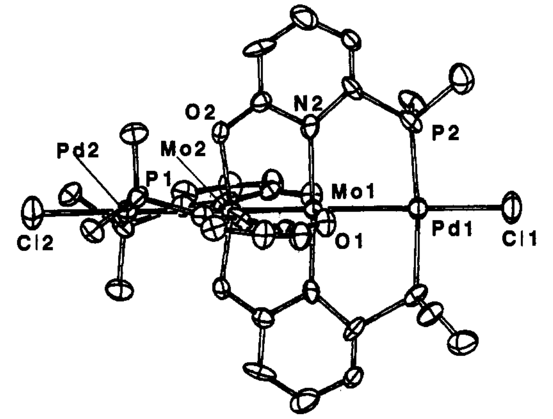
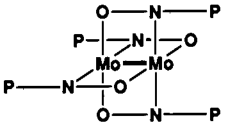
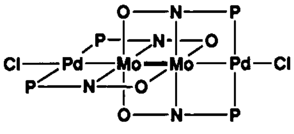


Figure 1. Drawing of **2** with a labeling scheme. Phenyl groups bound to the phosphorus atoms are omitted for clarity. Selected bond distances (Å): Mo(1)–Mo(2) 2.1208(9), Mo(1)–Pd(1) 2.689(4), Mo(2)–Pd(2), 2.679(4), Pd(1)–Cl(1) 2.42(1), Pd(2)–Cl(2), 2.42(1).

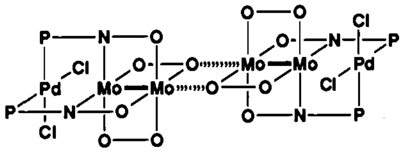
is in contrast to the reported $\sigma^2\pi^4$ configuration of the triple bond between Mo and W atoms.[12,25] Thus, we found that the multiple metal–metal bond was partially opened by the interaction of two Pd atoms with the Mo_2 core. It is interesting that each palladium atom is surrounded by two phosphorus atoms in a trans fashion, one chloro ligand, and one molybdenum atom to form a square plane, which is connected by the Mo_2 core.



1



2



3

On the other hand, *one* palladium(II) atom was now found not to interact with a Mo_2 core. The complex $[Mo_2PdCl_2(pyphos)_2(OAc)_2]_2$ (**3**)[26] was obtained in 5% yield by the treatment of $PdCl_2(pyphosH)_2$ (**4**)[27] with sodium hydroxide and a 1:1 mixture of $Mo_2(OAc)_4$ and $[Mo_2(OAc)_2(CH_3CN)_6]^{2+}$[28] in dichloromethane. Figure 2 shows the structure of complex **3**.[29] The interatomic distances between Pd and Mo (3.025(6) and 2.976(6) Å indicate the absence of metal–metal interaction. The bond distances (2.083(6) and 2.099(6) Å) of Mo–Mo in **3** are the same as those of Mo_2L_4 (bond order of 4) complexes[5,12] and are shorter than that of **2**. The Mo_2 moiety interacted with the oxygen atom of the neighboring μ-acetate ligand to form a dimeric structure, in which the distances of Mo–O are 2.55(3) and 2.56(3) Å. Such an interaction of Mo and the oxygen atom of a bridging ligand forming a dimer of the Mo_2 core has been noted for the $(Mo_2)_2$ complex supported by the dianion of 2,7-dihydroxynaphthyridine.[5d,e] In contrast to the geometry around palladium in **2**, the geometry of **Pd**(II) in **3** is square planar with two phosphorus and chloro ligands both in a cis arrangement.

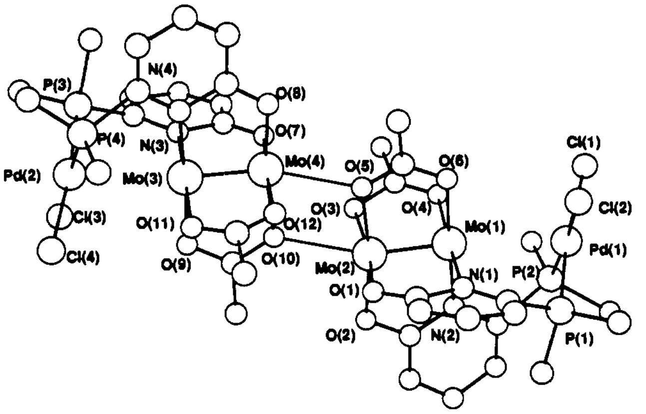


Figure 2. Drawing of **3** with a labeling scheme. Phenyl groups bound to the phosphorus atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo(1)–Mo(2)/Mo(3)–Mo(4) 2.083(6)/2.099(6), Mo(1)- - -Pd(1)/Mo(3)- - -Pd(2) 3.025(6)/2.976(6), Pd(1)–Cl(1)/Pd(2)–Cl(3) 2.30(1)/2.30(1), Pd(1)–Cl(2)/Pd(2)–Cl(4) 2.32(1)/2.37(1), Mo(2)- - -O(10)/Mo(4)- - -O(6) 2.55(3)/2.56(3); Cl(1)–Pd(1)–Cl(2)/Cl(3)–Pd(2)–Cl(4) 89.8(5)/89.5(5).

The formation of **2** provides a new methodology for the formation of straight linear tetranuclear metal–metal compounds.

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Supplementary Material Available: Experimental details for the preparation of complexes **1–4** and tables of crystallographic parameters, atomic positional and thermal parameters, full bond distances and angles, anisotropic thermal parameters, and collection procedures of **2** and **3** (40 pages); listing of observed and calculated structure factors for **2** and **3** (47 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) EHMO and molecular mechanics calculations were carried out on the simplified model complexes $Mo_2(C_5H_3NOPH_2)_4$ (**1′**) and $Mo_2Pd_2Cl_2(C_5H_3NOPH_2)_4$ (**2′**) with Mo–Mo distances based on X-ray crystal structures of **1** and **2**, respectively, on the CAChe computer system. As a result, the multiplicity (overlap population) of the Mo–Mo bond is 3.08 for complex **1′** but 2.37 for complex **2′**.

(25) (a) Chisholm, M. H. *Acc. Chem. Res.* **1990**, *23*, 419. (b) Chisholm, M. H. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 21.

(26) **3**: dark violet crystal, mp > 300 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 30 °C): δ 35.5 (s). ^1H NMR (CD_2Cl_2, 30 °C): δ 2.41 (s, 6H), 6.5–7.5 (m, 26H). FAB-MS for $^{98}Mo^{106}Pd$: *m/z*, 977 ($MH^+ - Cl_2$). UV–vis ($CHCl_3$): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 291 (2.7×10^4), 470 (2.8×10^3).

(27) **4**: yellow powder, mp 210–215 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30 °C): δ 17.1 (s). ^1H NMR ($CDCl_3$, 30 °C): δ 6.1 (t, 2H), 6.7 (d, 2H), 7.3 (d, 2H), 7.5–7.7 (m, 20H). UV–vis (CH_2Cl_2): λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 295 (1.5×10^4), 356 (1.2×10^4). Anal. Calcd for $C_{34}H_{28}N_2O_2P_2PdCl_2$: C, 55.49; H, 3.84; N, 3.81. Found: C, 54.87; H, 3.91; N, 3.65.

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(29) Crystal data for **3**: FW = 2331.66 (two dichloromethane and one ether as crystalline solvent), monoclinic space group $P2_1/n$, $a = 20.618(6)$ Å, $b = 20.264(4)$ Å, $c = 21.160(7)$ Å, $\beta = 100.27(3)°$, $V = 8699(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.780$ g cm^{-3}, $\mu = 13.32$ cm^{-1}, number of parameters = 617, 3686 reflection data with $I > 3\sigma(I)$, goodness of fit = 2.45, $R = 0.077$, $R_w = 0.098$.