Dative Pd(0)−Mo(II) Bonds in a Linearly Aligned Tetrametal System: Preparation, Characterization, and Reaction of a Tetranuclear Pd(0)−Mo(II)−Mo(II)−Pd(0) Supported by Four 6-Diphenylphosphino-2-pyridonate Ligands

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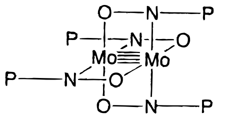
The reactivity of multiply bonded dinuclear complexes has been extensively studied.[1] We have been interested in the chemistry of metal−metal-bonded linear chain compounds,[2−4] and we have already reported some of the new reactions of the quadruply bonded dinuclear dimolybdenum(II) complex, $Mo_2(pyphos)_4$ (**1**)



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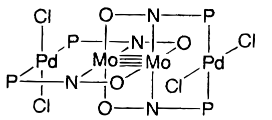

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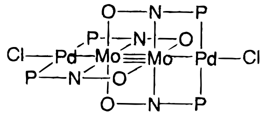

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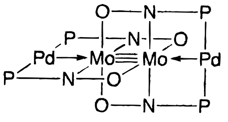

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(pyphos = 6-diphenylphosphino-2-pyridonate), with two palladium(I) species at both of the axial positions of the Mo_2 core to form the metal−metal-bonded tetranuclear complex $Mo_2Pd_2Cl_2(pyphos)_4$ (**3**), which has two single Pd(I)−Mo(II) bonds and one triple Mo−Mo bond.[5,6] This reaction involves the coordination of two Pd(II) at the axial positions of the Mo_2 core of complex **1** to form $Mo_2Pd_2Cl_4(pyphos)_4$ (**2**) and then the reduction of Pd(II) to Pd(I) as a result of the formation of Mo−Pd σ bonds. We also reported an axial interaction of the quadruple Cr−Cr bond with two platinum(II) surrounded by pyphos ligands, i.e., d−d dative bond.[7] Here we report the synthesis, characterization, and reactions of a tetrametal complex $Mo_2Pd_2(pyphos)_4$ (**4**), which has a Pd(0)−Mo(II)−Mo(II)−Pd(0) skeleton.

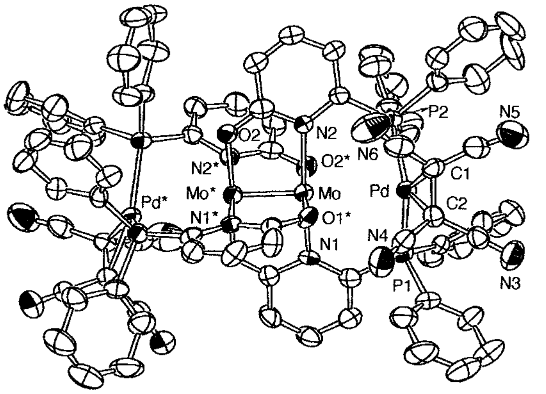
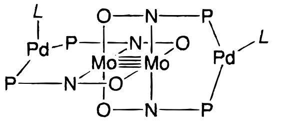


Figure 1. ORTEP drawing of **5c**. Selected bond distances (Å) and angles (deg): Mo−Mo = 2.097(2), Mo···Pd = 3.127(1), Pd−P1 = 2.373(3), Pd−P2 = 2.402(3), Pd−C1 = 2.12(1), Pd−C2 = 2.11(1), C1−C2 = 1.45(1); P1−Pd−P2 = 117.8(1), P1−Pd−C1 = 102.8(3), P1−Pd−C2 = 141.9(3), P2−Pd−C1 = 138.6(3), P2−Pd−C2 = 98.6(3), C1−Pd−C2 = 40.1(4), Pd···Mo−Mo = 164.62(5)°; a torsion angle of Pd−Mo−Mo−Pd = 138.1(2)°.

Reaction of **1**[6] with $Pd_2(dba)_3$ in THF gives the tetrametal complex **4** in quantitative yield.[8] Alternatively, complex **4** can be prepared by reduction of the Pd(I) complex **3**[5,6] with Et_4NBH_4/CH_3OH in THF at room temperature. The ν(Mo−Mo) in the resonance Raman spectrum of **4** is observed at 389 cm^{-1}, a value that is at lower wavenumber than those found in the quadruply bonded dimolybdenum complexes **1** (394 cm^{-1}) and **2** (403 cm^{-1}) but is higher than that found for complex **3** (386 cm^{-1}), indicating the existence of a Pd(0)→Mo(II) dative bond which elongates the quadruple Mo_2 bond to some extent.[7,9]

Complex **4** has two Pd(0) centers that can react with a variety of olefinic compounds; such reactions give $Mo_2Pd_2(pyphos)_4(L)_2$ [**5**: L = acrylonitrile (**a**), fumaronitrile (**b**), tetracyanoethylene (**c**)] in moderate yields.[10] It is a notable feature that the value of ν(Mo−Mo) in the resonance Raman spectra of **5a**−**c** varied from 389 cm^{-1} (**5a**), comparable to that found for the triply bonded Mo_2 in **3**, to 399 (**5b**) and 404 cm^{-1} (**5c**), corresponding to the value found for the quadruply bonded Mo_2 of **1** and **2**. The increase in the wavenumber of ν(Mo−Mo) can be attributed to the extent of deformation from linearity of the tetrametal system and is indicative of the decrease in bonding interaction between the Pd and the Mo atoms. The crystal structure of **5c** is shown in Figure 1.[11] Unlike analogous compounds **2**, **3**, and **4**, which



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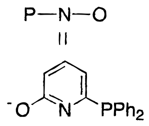

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(8) **4**: dark brown solids, mp 215−230 °C (dec); ^1H NMR (C_6D_6, 308 K, 270 MHz) δ 6.27−6.32 (m, 8H), 6.70 (t, J = 7.7 Hz, 4H), 7.07−7.08 (m, 24H), 7.51 (m, 16H);$^{31}P\{^1H\}$ NMR (C_6D_6, 308 K, 109 MHz) δ 22.8 (s); UV−vis (THF), λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 476 (20 000); Raman, ν(Mo−Mo) 389 cm^{-1}; ion spray MS m/z 1518 (M^+). Anal. Calcd for $C_{68}H_{52}Mo_2N_4O_4P_4Pd_2\cdot(C_4H_8O)$: C, 54.39; H, 3.80; N, 3.52. Found: C, 54.48; H, 4.11; N, 3.51.

(9) It might be assumed that the heterometal bond in **4** has some contribution of a Pd(I)−Mo(I) bond which results from one-electron transfer from Pd(0) to Mo(II).

(10) Preparation and spectral data of **5a**−**c** are given in Supporting Information.

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have a strictly trans arrangement of the P-donor atoms, **5c** has a cis arrangement and thus the four metals are not straight linear.

The palladium(0) complex **4** is very reactive toward oxidative addition reaction. Thus, treatment of **4** with dichloromethane at room temperature results in the formation of a palladium(II) complex, $Mo_2Pd_2Cl_2(CH_2Cl)_2(pyphos)_4$ (**6**) (eq 1),[12] which is a

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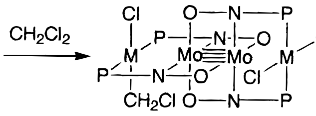

6

(1)

rare example of the oxidative addition of dichloromethane to a Pd(0) center, e.g., mononuclear Pd(0) complexes[13,14] and a dinuclear Pd(0) complex, $Pd_2(dpm)_3$ (dpm = bis(diphenylphosphino)methane),[15,16] though oxidative addition of dichloromethane to d^9 species, Rh(I) and Ir(I), readily proceeded.[17−21]

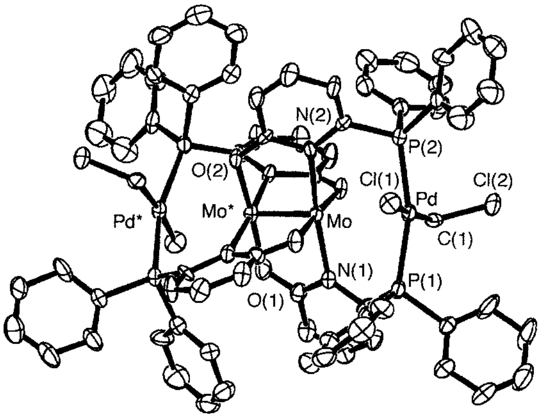

Figure 2. ORTEP drawing of **6**. Selected bond distances (Å) and angles (deg): Mo−Mo* = 2.106(2), Mo···Pd = 2.945(2), Pd−Cl(1) = 2.368(6), Pd−P(1) = 2.340(6), Pd−P(2) = 2.358(6), Pd−C(1) = 2.06(2), Cl(2)−C(1) = 1.81(2); Mo−Pd−Cl(1) = 95.1(1), Mo−Pd−C(1) = 92.6(5), Mo−Pd−P(1) = 81.8(1), Mo−Pd−P(2) = 82.8(1), Pd−C(1)−Cl(2) = 105.8(9).

The crystal structure of **6** is shown in Figure 2;[22] there is a 2-fold axis perpendicular to the Mo−Mo vector passing through the center of the Mo−Mo bond. Four of the metal atoms, Pd, Mo, Mo, and Pd, are aligned linearly. Each of the palladium atoms is coordinated to a chlorine atom and a chloromethyl group in square planar geometry.

In summary, we prepared a novel straight linear $Mo^{II}{}_2Pd^0{}_2$ tetranuclear complex **4**. We found the facile oxidative addition of dichloromethane to the Pd(0) center of the complex **4**. The chemical reactivity of **4** is now under investigation.

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Supporting Information Available: Experimental details for the preparation of **4**−**6**; final positional parameters and final thermal parameters for **5c** and **6** and figures giving additional atom labeling for **5c** and **6** (40 pages, print/PDF). 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 and Web access instructions.

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[11] Structure determination of **5c** is given in Supporting Information.

[12] **6**: 67% yield, dark red microcrystals, mp 299−300 °C (dec); ^1H NMR (CD_2Cl_2, 308 K, 270 MHz) δ 3.27 (dt, $^2J_{HH} = 14$ Hz, $^3J_{PH} = 5$ Hz, 2H), 3.58 (dt, $^2J_{HH} = 13$ Hz, $^3J_{PH} = 5$ Hz, 2H), 5.99 (d, $^3J_{HH} = 9$ Hz, 2H), 6.37 (d, $^3J_{HH} = 8$ Hz, 2H), 6.78 (m, 4H), 7.07 (m, 4H), 7.18−7.54 (m, 36H), 7.83 (m, 4H), 7.94 (m, 4H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 308 K, 202 MHz) δ 23.29 (d, $^2J_{PP} = 406$ Hz), 24.80 (d); UV−vis (CH_2Cl_2), λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 478 (3.7×10^3); FABMS spectrum m/z 1688 (M^+). Anal. Calcd for $C_{70}H_{56}N_4O_4P_4Mo_2Pd_2Cl_4\cdot(CH_2Cl_2)$: C, 48.11; H, 3.30; N, 3.16. Found: C, 48.53; H, 3.30; N, 3.50. We measured the $^{31}P\{^1H\}$ NMR spectrum of **4** in dichloromethane-d_2, which exhibited some peaks due to transient species together with a weak singlet peak due to **3**. However, we have not been able to determine their structures except for **3**. We are now making efforts to elucidate this reaction mechanism.

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[22] Structure determination of **6** is given in Supporting Information.