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Formation of a Dative Bond Between Pt^0 and Mo^{II} in Linear Pt^0–Mo^{II}–Mo^{II}–Pt^0 Complexes, $Mo^{II}_2Pt^0_2(pyphos)_4(PR_3)_2$, and Unique 1,4-Oxidative Addition Reaction of Diaryl Disulfides Giving $Mo^{II}_2Pt^I_2(pyphos)_4(SAr)_2$ (pyphos = 6-Diphenylphosphanyl-2-pyridonato)

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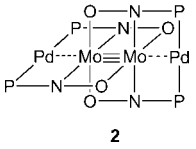
Keywords: Linear clusters / Dative bonds / Oxidative addition / Thiolates / Platinum / Molybdenum

The $Pt^0\cdots Mo^{II}$ dative bond of linear tetrametal Pt^0–Mo^{II}–Mo^{II}–Pt^0 complexes, $Mo_2Pt_2(pyphos)_4(L)_2$ [**4a**: L = PPh_3; **4b**: L = PMe_3; **4c**: L = PMe_2Ph; **4d**: L = $PMePh_2$; **4e**: L = $P(OMe)_3$], was characterized by means of spectroscopic analysis and X-ray crystallographic studies. Complex **4a** reacted with diaryl disulfides to give dithiolate Pt^I complexes, $Mo_2Pt_2(SAr)_2(pyphos)_4$ [**5a**: Ar = C_6H_4Me-4; **5b**: C_6H_4OMe-4; **5c**: $C_6H_3Me_2$-2,6; **5d**: C_6H_5], which are unique 1,4-oxidative addition products.

Introduction

Low-dimensional multimetallic molecules have attracted much interest in view of their fundamental bonding nature as well as their potential as magnetic, electronic, and optical materials.[1] They are mainly constructed by assembling dinuclear metal units[1,2] by using appropriate multidentate ligands,[3–9] or by electrochemical methods.[10–15] We previously reported the preparation of *linear heterometallic clusters* with the use of a quadruply bonded dimolybdenum(II) complex, $Mo_2(pyphos)_4$ (**1**) (pyphos = 6-diphenylphosphanyl-2-pyridonato), as a core part of metal strings, and their unique reactivity arising from the electronic anisotropy involving dative metal–metal bonds:[16] the oxidative reaction of 2 equiv. of dichloromethane to a Pd^0 cluster, $Mo_2Pd_2(pyphos)_4$ (**2**), which has two $Pd^0\cdots Mo^{II}$ dative bonds, proceeded under mild conditions to give a Pd^{II} cluster, $Mo_2Pd_2Cl_2(CH_2Cl)_2(pyphos)_4$ (**3**).[16d] Thus, the presence of the $Pd^0\cdots Mo$ dative bond of **2** enhances its reactivity toward oxidants,[16d] which is relevant to the fact that some dinuclear metal complexes with a bonding interaction between d^{10} metal centers exhibit higher reactivity compared with the corresponding mononuclear complexes.[17] In this contribution, we report the structural and spectral characterization of the $Pt^0\cdots Mo^{II}$ dative bond of linear tetrametal complexes, $Mo_2Pt_2(pyphos)_4(PR_3)_2$ (**4**), whose reactivity was assessed by an unprecedented 1,4-oxidative addition reaction of diaryl disulfides, which gives dithiolate Pt^I complexes, $Mo_2Pt_2(SAr)_2(pyphos)_4$ (**5**).



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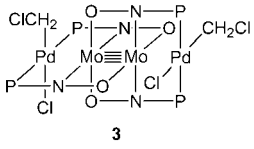

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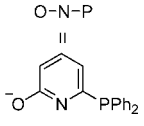

Treatment of $Mo_2(pyphos)_4$ (**1**) with 2 equiv. of $Pt(PPh_3)_4$ in THF afforded a tetrametal cluster, $Mo_2Pt_2(pyphos)_4(PPh_3)_2$ (**4a**), with a Pt^0–Mo^{II}–Mo^{II}–Pt^0 array in 85% yield. The triphenylphosphane bound to each platinum(0) atom was labile[18] and readily replaced by adding excess PMe_3, PMe_2Ph, $PMePh_2$, and $P(OMe)_3$ in THF to give the corresponding complexes $Mo_2Pt_2(pyphos)_4(L)_2$ [**4b**: L = PMe_3; **4c**: L = PMe_2Ph; **4d**: L = $PMePh_2$; **4e**: L = $P(OMe)_3$] (Scheme 1). All complexes **4a**–**e** were unequivocally characterized by spectroscopic data and combustion analysis. The $^{31}P\{^1H\}$ NMR spectra of **4a**–**e** provided two peaks with a coupling constant $J_{P\text{-}P}$ = 140–192 Hz, the value of which was comparable to the coupling constant ($J_{P\text{-}P}$ = 110 Hz) reported for a dinuclear trigonal planar complex, $Pt_2(\mu\text{-dppm})_3$.[19] This clearly indicates that complexes **4a**–**e** adopt a trigonal planar geometry at each Pt center, and this was further confirmed by X-ray analysis of **4e** (Figure 1).[20] Each platinum atom in **4e** is coordinated by two phosphorus atoms of the pyphos ligands and $P(OMe)_3$, which forms a trigonal planar geometry with P–Pt–P angles of 123.95(4), 116.98(4), and 118.96(4)° for Pt1, with a sum = 359.89°, and 124.95(4), 117.87(4), and

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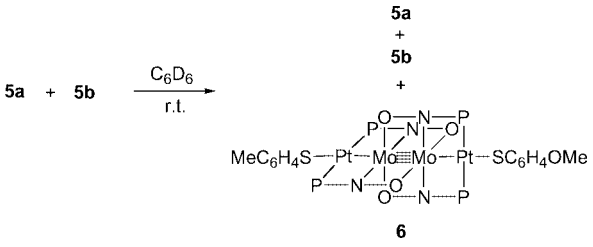
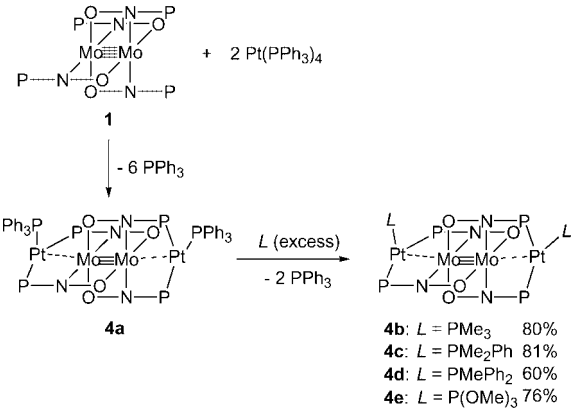
117.15(5)° for Pt2, with a sum = 359.97°, respectively. Notably, the trigonally coordinated d^{10} center, such as Pt^0 and Au^I, interacts by attracting heavier s^2 metals such as Tl^I and Pb^{II}.[21] Similar angles [114.9(2)–123.1(2)°] are reported for trigonal planar complexes such as $Pt(PPh_3)_3$[22] and $Pt_2(\mu\text{-dppm})_3$.[19,23] Each platinum atom of **4e** was slightly out of reach of the Mo_2 vector [Pt1–Mo1–Mo2 = 170.66(2)°; Pt2–Mo2–Mo1 = 167.94(2)°]. Although the distances of Pt1–Mo1 [2.9082(4) Å] and Pt2–Mo2 [2.9276(4) Å] are long, the distance of Mo1–Mo2 [2.1198(5) Å] is longer than that of quadruply-bonded Mo^{II}_2 complexes such as **1** [2.098(2) Å],[16a,16b] a Pt^{II} complex, $Mo_2Pt_2Cl_4(pyphos)_4$ [2.101(2) Å],[16b] $Mo_2(O_2CCH_3)_4$ [2.0934(8) Å],[24] and $Mo_2(mhp)_4$ [2.065(1) Å, mhp = 6-methylpyridonate],[25] and slightly shorter than that of the triple bond of the Pt^I complex $Mo_2Pt_2Cl_2(pyphos)_4$ [2.134(1) Å],[16b] which indicates that each platinum atom interacts by attracting the Mo_2 part to form a dative bond.[26] This is further supported by the Raman active ν(Mo–Mo) frequencies (382–388 cm^{-1}) observed for complexes **4a**–**e**, whose values are comparable to that of the triple bonded Mo_2 in $Mo_2Pt_2Cl_2(pyphos)_4$ (381 cm^{-1}) and its palladium derivative $Mo_2Pd_2Cl_2(pyphos)_4$ (386 cm^{-1}), but lower than that of the quadruply bonded Mo_2 in **1** (394 cm^{-1}) and $Mo_2Pt_2Cl_4(pyphos)_4$ (403 cm^{-1}).

Complex **4a** showed unique reactivity toward diaryl disulfides. The addition of excess ArSSAr (Ar = C_6H_4Me-4, C_6H_4OMe-4, $C_6H_3Me_2$-2,6, C_6H_5) to a solution of **4a** in THF yielded the corresponding 1,4-bis(thiolate) tetrametal complexes $Mo_2Pt_2(SAr)_2(pyphos)_4$ [**5a**: Ar = C_6H_4Me-4; **5b**: C_6H_4OMe-4; **5c**: $C_6H_3Me_2$-2,6; **5d**: C_6H_5] [Equation (1)], whose formulation was confirmed by NMR spectroscopic data and combustion analysis together with X-ray analysis of **5c**. A 1,4-addition of disulfides to the tetrametal skeleton of **4a** resulted in the formation of two Pt^I–Mo^{II} single bonds as a consequence of one-electron oxidation of each platinum.



(1)



Scheme 1. Synthesis of complexes **4a**–**e**. O–N–P = 6-diphenylphosphanyl-2-pyridonato.

X-ray analysis of **5c** (Figure 2)[27] revealed that the two Pt^I centers adopt a square-planar geometry where two phosphorus atoms of the pyphos ligands occupy *trans* positions and the sulfur atom and the molybdenum atom are placed at the opposing corners of the square planar, which results in the formation of a linear tetrametal Pt^I–Mo^{II}–Mo^{II}–Pt^I skeleton with the angles of Pt1–Mo1–Mo2 [174.92(3)°] and Pt2–Mo2–Mo1 [173.37(3)°]. The bond lengths of Pt–Mo [2.6916(5) and 2.7306(5) Å] are short enough to have a single bond, which is comparable with that of $(CO)_3Mo(\mu\text{-}PPh_2)_2Pt(PEt_3)$ [2.766(1) Å].[28] The significantly longer Mo–Mo bond length [2.1413(8) Å] than that of **1** [2.098(2) Å][16a,16b] and **4e** [2.1196(5) Å] led us to conclude that the Mo–Mo bond had a bond order of three. The lower-shift of the ν(Mo–Mo) frequency (379 cm^{-1}) for **5c** also supported the elongated Mo–Mo bond.

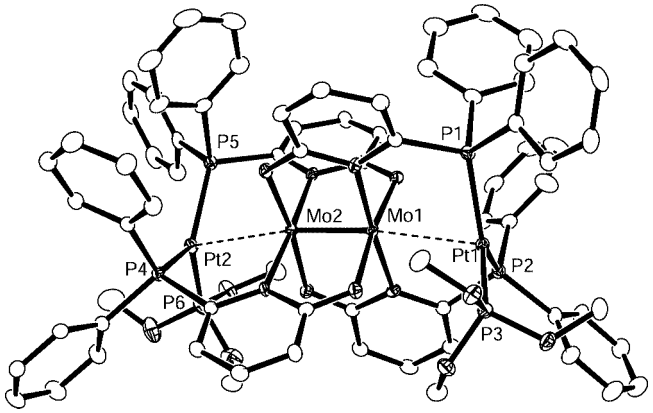


Figure 1. Molecular structure of complex **4e** with the numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity.

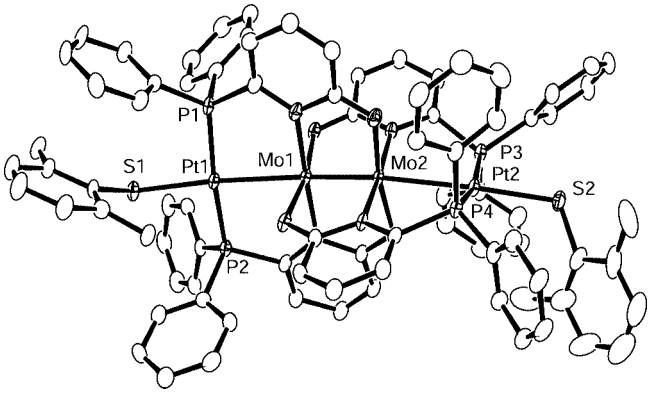
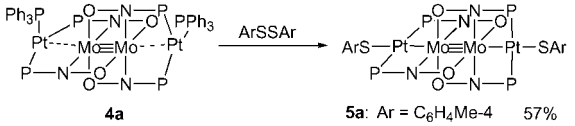


Figure 2. Molecular structure of complex **5c** with the numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity.

By mixing isolated thiolate complexes **5a** and **5b** in C_6D_6, a new mixed thiolate complex, $Mo_2Pt_2(SC_6H_4Me\text{-}4)(SC_6H_4OMe\text{-}4)(pyphos)_4$ (**6**), was generated whose $^{31}P\{^1H\}$ NMR spectrum showed new singlet signals at δ = 30.8 and 30.9 ppm [Equation (2)]. Additionally, the reaction of **5a** with 1 equiv. of bis(4-methoxyphenyl) disulfide produced complex **6** together with **5b**. In contrast, dark conditions suppressed these reactions as judged by $^{31}P\{^1H\}$ NMR spectroscopy. In a reverse reaction, the addition of 10 equiv. of PPh_3 to **5c** in C_6D_6 resulted in the slow formation of the corresponding disulfide $(XylS)_2$ (18%) together with the precipitation of **4a** after 12 h at room temperature, as monitored by ^1H NMR spectroscopy. Thus, these experimental observations suggested that the formation and cleavage of the Pt–SAr bond proceeded through a radical process.



(2)

In conclusion, we successfully prepared tetranuclear Pt^0–Mo^{II}–Mo^{II}–Pt^0 clusters supported by four pyphos and two phosphane or phosphite ligands, and we provided clear structural and spectral evidence for the dative bond between two Pt^0 atoms and the Mo_2 core. The 1,4-oxidative addition of diaryldisulfides to the two platinum(0) centers linked by an Mo_2 core gave unique tetranuclear complexes with a linear ArS–Pt^I–Mo^{II}–Mo^{II}–Pt^I–SAr skeleton. Further investigation on the propensity of such a dative bond in the cluster system is in progress.

Supporting Information (see footnote on the first page of this article): Preparation of $Mo_2Pt_2(pyphos)_4(PPh_3)_2$ (**4a**–**e**), oxidative addition of bis(4-methoxyphenyl) disulfide to **4a**, view of $[Mo_2Pt_2Cl_2(C_{17}H_{13}NOP)_4(C_3H_9O_3P)_2]\cdot 1.5(hexane)$, and PLUTO view of $[Mo_2Pt_2(C_{17}H_{13}NOP)_4(2,6\text{-}Me_2C_6H_4S)_2]\cdot 4(C_4H_8O)$.

Acknowledgments

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[18] Complex **4a** in [D$_8$]THF exhibited temperature-dependent ^{1}H NMR spectroscopy due to a process of dissociation and recoordination of PPh_3, which gives thermodynamic parameters of $\Delta G^{\ddagger}(298)$ = 15(2) kcal/mol, $\Delta H^{\ddagger}$ = 11.8(9) kcal/mol, $\Delta S^{\ddagger}$ = –12(3) eu.

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[20] Crystal data for **4e**·1.5hexane: Fw = 2072.48 (0.27 × 0.20 × 0.10 mm), space group $P\bar{1}$ (#2), a = 14.35524(17), b = 16.24695(7), c = 19.5725(3) Å, α = 108.9657(8), β = 97.8677(6), γ = 106.1829(6)°, V = 4013.86(8) Å^3, Z = 2, calculated density = 1.715 Mg/m^3. Data were collected with Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K_α radiation at a temperature of 100(2) K to a maximum 2θ value of 63.0°. A total of 240 oscillation images were collected. Of the 99273 reflections that were collected, 26544 were unique (R_{int} = 0.0920); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-K_α radiation of 3.960 mm^{-1} was applied, which resulted in transmission factors ranging from 0.4898 to 0.6740. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXL-97) and refined on F^2 by full-matrix least-squares methods by using SHELXL-97.[29] Final R factors, $R1$ and $wR2$ are 0.0507 and 0.0825 for 20546 reflections with $I > 2.0\sigma(I)$, respectively. $R1$ and $wR2$ for all data are 0.0771 and 0.0891 for 26544 reflections. The number of parameters was 964. GOF values are 1.045 for $I > 2.0\sigma(I)$ and 1.045 for all data, respectively.

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[27] Crystal data for **5c**·4C$_4$H$_8$O: Fw = 2257.92 (0.33 × 0.17 × 0.10 mm), triclinic, space group $P\bar{1}$ (#2), a = 14.5331(4), b = 17.0949(6), c = 21.0655(6) Å, α = 70.6216(8), β = 70.4231(10), γ = 72.5510(10)°, V = 4545.7(2) Å^3, Z = 2, calculated density = 1.650 Mg/m^3. Data were collected with Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K_α radiation at a temperature of 100(2) K to a maximum 2θ value of 61.0°. A total of 270 oscillation images were collected. Of the 80453 reflections that were collected, 27259 were unique (R_{int} = 0.1024); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo-K_α radiation of 3.514 mm^{-1} was applied, which resulted in transmission factors ranging from 0.4844 to 0.7049. The data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods (DIRDIF-99, PATTY)[30] and refined on F^2 by full-matrix least-squares methods by using SHELXL-97.[29] Final R factors, $R1$ and $wR2$ are 0.0645 and 0.1456 for 20608 reflections with $I > 2.0\sigma(I)$, respectively. $R1$ and $wR2$ for all data are 0.0926 and 0.1585 for 27259 reflections. The number of parameters was 964. GOF values are 1.028 for $I > 2.0\sigma(I)$ and 1.028 for all data, respectively. CCDC-620212 and 620213 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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