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Preliminary communication

Labile coordination of bis(diphenylphosphinomethyl)phenylphosphine in di- and trinuclear palladium and platinum complexes containing *ortho*-substituted aromatic isocyanide

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Abstract

Reaction of $[Pd_2(RNC)_6]^{2+}$ with $(Ph_2PCH_2)_2PPh$ (dpmp) gave $[Pd_2(dpmp)_2(RNC)_2]^{2+}$ **1**, in which dpmp ligands acted as chelating ligands. Thermal reaction of **1** underwent an elimination of isocyanide and change of a coordination mode of the dpmp ligands to give $[Pd_2(dpmp)_2(RNC)]^{2+}$ **2**. Two kinds of new dimeric complexes $[Pt_2(dpmp)_2(RNC)_2]^{2+}$ (**4**, **5**) were obtained from $[Pt_2(RNC)_6]^{2+}$ and dpmp, in which dpmp ligands acted as bi- and tridentate ligand to bridge a metal–metal bond. Compounds **4** and **5** are interconvertible. Reaction of **5** with $M_3(RNC)_6$ (M = Pt, Pd) gave a linear homo- or hetero trinuclear complex, $[Pt_2M(dpmp)_2(RNC)_2]^{2+}$ (**6**, **7**).

Keywords: Palladium; Platinum; Group 10; Triphosphine; Cluster

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The chemistry of compounds containing metal–metal bonds is of current interest [1]. Polyfunctional phosphines are one of the important candidates which can support metal–metal bonds. There is a variety of coordination modes known of the polyfunctional bis(diphenylphosphinomethyl)phenylphosphine (dpmp) ligand to transition metals: four- or six-membered chelating ring found in palladium and platinum complexes, linear trinuclear complexes found in rhodium, gold, etc. [2,3]. However, there are few examples of the dpmp complexes of palladium(I) and platinum(I) [3]. Previously we have reported that the reactions of di-nuclear complexes, $[M_2(RNC)_6]^{2+}$ (M = Pd, Pt) with diphosphine (diphos) such as $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2, 3, 4$) gave $[M_2(diphos)_2(RNC)_2]^{2+}$ [4,5].

We undertook the reactions of dimeric complexes of palladium(I) and platinum(I) containing isocyanide with dpmp in connection with diphosphine. We report here the novel chemistry of the preparation of new di- and trinuclear dpmp complexes of palladium and platinum having various coordination modes and the great change of metal frameworks.

When $[Pd_2(XylNC)_6](PF_6)_2$ (Xyl = $2,6-Me_2C_6H_3$) was treated with dpmp in CH_2Cl_2, yellow crystals of **1**, formulated as $[Pd_2(dpmp)_2(XylNC)_2](PF_6)_2$, were obtained in 84% yield [6]. The $^{31}P\{^1H\}$ NMR spectrum showed three signals at δ −38.91, −5.42, and 12.57 in a 1 : 1 : 1 intensity ratio. The first signal is assignable to an uncoordinated P atom, and the other signals to the coordinated P atoms. This assignment is in close agreement with that of $PdCl_2(dpmp)$ with the chelating dpmp ligands [2b]. The ^1H NMR spectrum in the methyl region showed only one resonance at δ 2.21 due to *o*-methyl protons. Based on these spectroscopic results, the complex is assumed to adopt a structure with two six-membered rings.

When **1** was recrystallized in the absence of xylyl isocyanide or was photochemically irradiated, an elimination of one isocyanide ligand and the change of coordination mode of the dpmp ligands occurred to give the dark-red compound **2**, $[Pd_2(dpmp)_2(XylNC)](PF_6)_2$ (Scheme 1) [7]. Compound **1** was regenerated from **2** by an addition of xylyl isocyanide; these reactions are reversible. The cation of **2** consists of a five-coordinate palladium atom bonded to a three-coordinate palladium atom. The two dpmp ligands are nonequivalent. One uses an outer and an internal phosphorus atom to bridge

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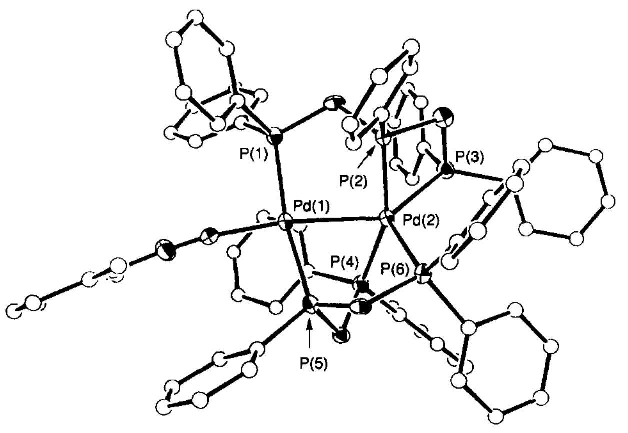


Fig. 1. Structure of $[Pd_2(dpmp)_2(XylNC)]^{2+}$ **2**. Selected bond lengths (Å) and angles [°]: Pd1–Pd2 2.702(1), Pd1–P1 2.356(3), Pd1–P5 2.310(3), Pd2–P2 2.272((3), Pd2–P3 2.380(3), Pd2–P4 2.329(3), Pd2–P6 2.510(3), Pd2–Pd1–P1 92.63(9), Pd2–Pd1–C5 171.0(3), P1–Pd1–C5 94.3(4), Pd1–Pd2–P2 85.33(9), Pd1–Pd2–P3 141.49(9), Pd1–Pd2–P4 78.52(8), Pd1–Pd2–P6 98.35(8).

the Pd–Pd bond (2.702 Å) and another outer phosphorus atom forms a four-membered ring together with an internal one. The other dpmp ligand uses each of two outer phosphorus atoms and an internal phosphorus atom to bridge the Pd–Pd bond (Fig. 1). The Pd2–P6 bond distance (2.510(3) Å) is longer by ca. 0.18 Å than other Pd–P bond distances (av. 2.329 Å), which suggests weaker bond strength.

An analogous reaction of $[Pt_2(RNC)_6](PF_6)_2$ **3** (**a**: R = Xyl; **b**: R = Mes) with dpmp afforded two compounds **4** (orange; 32% for **4a** and 33% for **4b**) and **5** (yellow; 56% for **5a** and 18% for **5b**) with the same composition, $[Pt_2(dpmp)_2(RNC)_2]$ $(PF_6)_2$ [8]. An X-ray analysis of **4a** showed that the molecule consists of four- and five-coordinated platinums, being a platinum analogue and having the structure such that as if one of the chelating phosphorus atoms in the palladium complex **2** is substituted by isocyanide and the outer phosphorus atom is coordinatively free. The isocyanide ligands are occupied with the axial positions (Fig. 2). The Pt–Pt bond length is 2.682(2) Å, shorter than that of **2**.

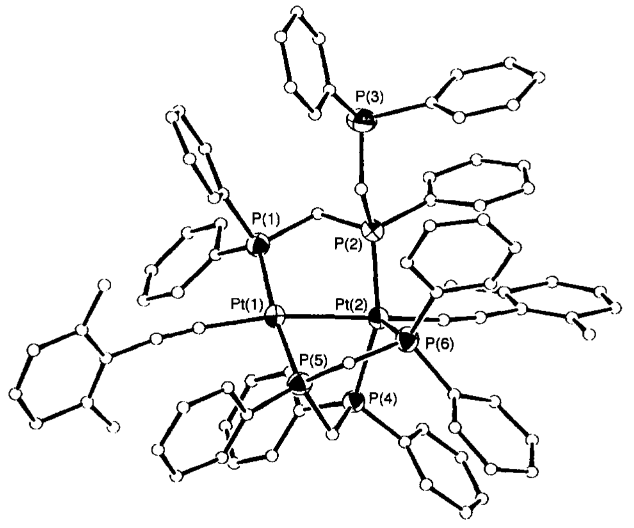
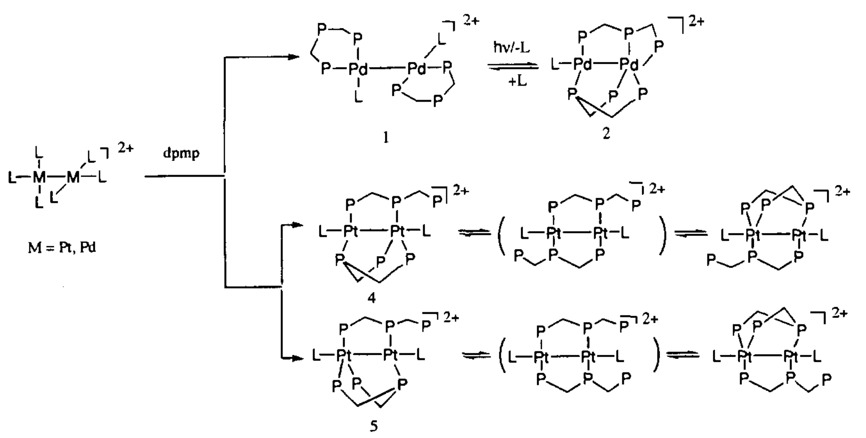


Fig. 2. Structure of $[Pt_2(dpmp)_2(XylNC)_2]^{2+}$ **4a**. Selected bond lengths (Å) and angles(°): Pt1–Pt2 2.682(2), Pt1–P1 2.305(5), Pt1–P5 2.278(4), Pt2–P2 2.292(4), Pt2–P4 2.300(4), Pt2–P6 2.468(5), P1–Pt1–P5 174.4(1), Pt2–Pt1–C1 170.6(5), Pt1–Pt2–C2 158.7(5), P2–Pt2–P4 152.2(2), P2–Pt2–P6 109.3(2), P4–Pt2–P6 95.1(2), P6–Pt2–C2 91.7(5).

The infrared spectrum of **4** showed two characteristic bands at ca. 2150 cm^{-1}, in agreement with the crystal structure. However, the ^1H NMR spectrum showed only one signal for isocyanide ligands, suggesting the presence of an equilibrium (Scheme 1) from the fact that the $^{31}P\{^1H\}$ NMR spectrum is broad. Dissociation of the Pt–P6 bond is related to the fact that the Pt–P6 bond length (2.470(3) Å) is longer than the average value (2.295(3) Å) of other Pt–P bonds.

The infrared spectrum of yellow compound **5** showed only one $\nu(N{\equiv}C)$ band at ca. 2150 cm^{-1}. The ^1H NMR spectrum indicated the presence of two kinds of isocyanide ligand, showing it to be in a different environment. Compound **5** is assumed to be an isomer of **4** (Scheme 1). Nonequivalence of isocyanide ligands is still kept, even if the equilibrium as found in **4** exists. This structure was substantiated by the fact that the reaction of **5a** with $Pd_3(XylNC)_6$ gave a linear tri-



Scheme 1. Reactions of dimeric palladium(I) and platinum(I) isocyanide complexes with dpmp.

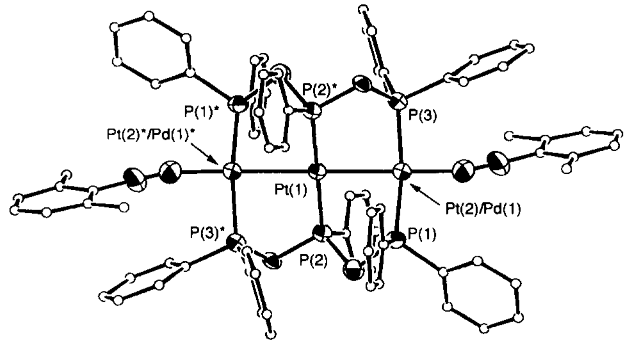


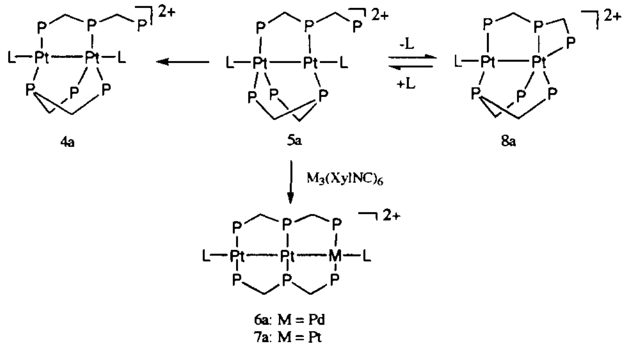
Fig. 3. Structure of $[Pt_2Pd(dpmp)_2(XylNC)_2]^{2+}$ **6a**. Selected bond lengths (Å) and angles (°): Pt/Pd–Pt(1) 2.690(1), Pt/Pd–P1 2.294(2), Pt/Pd–P3 2.293(3), Pt1–P2 2.262(2), Pt1–Pt/Pd–C1 166.9(3), Pt/Pd–C1–N1 168.2(7), P1–Pt2–P3 160.55(8).

nuclear complex, $[Pt_2Pd(dpmp)_2(XylNC)_2](PF_6)_2$ **6a**. From an X-ray analysis, compound **6a** is centrosymmetric and was analyzed as a structure that two outer metals have a Pd/Pt occupancy of 0.5 (Fig. 3 and Scheme 2) [9].

The $^{31}P\{^1H\}$ NMR spectrum showed three signals at δ 2.43, 1.05, and −16.07; the signals at δ 1.05 and −16.07 were accompanied by the satellite-peaks of the ^{195}Pt atom and were assigned to the outer and internal phosphrous atoms bound by the Pt atoms. The signal at δ 2.43 was assigned to the phosphorus atoms connected to the palladium metal, because of the absence of the satellite peaks. The ^1H NMR spectrum showed two singlets at δ 1.37 and 1.49 due to *o*-methyl protons.

Compound **5a** also reacted with $Pt_3(XylNC)_6$ to give $[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2$ **7a** [10]. The $^{31}P\{^1H\}$ NMR spectrum showed two signals at δ 0.93 and −16.76 in an intensity ratio of 2 : 1. The ^1H NMR spectrum showed a singlet δ 1.40 due to *o*-methyl protons. These spectroscopic data suggested a linear structure.

Thermal reaction of **5a** at reflux in MeCN underwent an elimination of one isocyanide ligand and an core-change to give **8a** (56%), formulated as $[Pt_2(dpmp)_2(XylNC)](PF_6)_2$ and **4a** (3%) together with a 30% recovery of the starting materials. An X-ray analysis showed that compound **8a** is the platinum analogue of **2** (Fig. 4) [11]. The configuration around Pt1 is a distorted tetrahedral except a bond connected by the Pt2 atom and that around Pt2 has a square-planar structure (containing a Pt–Pt bond). When **8a** was refluxed in MeCN in the presence of excess xylyl isocyanide, a core change occurred again and compound **5a** was regenerated in 35% yield.



Scheme 2. Reactions of **5a**.

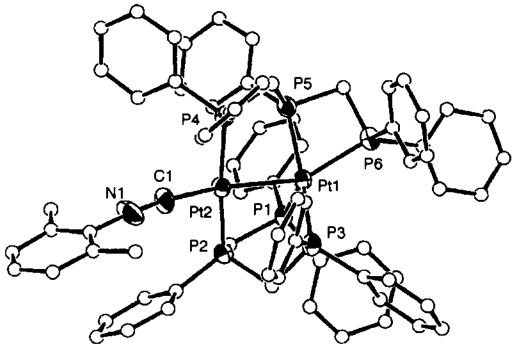


Fig. 4. Structure of $[Pt_2(dpmp)_2(XylNC)]^{2+}$ **8a**. Selected bond lengths (Å) and angles (°): Pt1–Pt2 2.7150(7), Pt1–P1 2.314(3), Pt1–P3 2.433(3), Pt1–P5 2.267(3), Pt1–P6 2.359(3), Pt2–P2 2.291(3), Pt2–P4 2.336(3), Pt2–C1 1.92(1), P1–Pt1–P6 109.2(1), P3–Pt1–P5 108.4(1), P3–Pt1–P6 118.0(1), P2–Pt2–P4 171.5(1), Pt1–Pt2–C1 172.8(4), P2–Pt2–C1 93.9(4), P4–Pt2–C1 93.6(4), Pt1–Pt2–P4 92.64(8), Pt1–Pt2–P2 80.19(8).

Mesityl isocyanide complexes led to a different result from the xylyl isocyanide complex. Thermal reactions of **4b** and **5b** were carried out spectroscopically. After **4b** was refluxed in MeCN for 6 h, the ^1H NMR spectrum showed a mixture of **4b** and **5b** in a 2 : 1 ratio. In this case a trace amount of compound **8b** was observed. Analogously, a thermal reaction of **5b** led to a mixture of **4b** and **5b** in a 2 : 1 ratio. This suggests that an equilibrium exists between **4b** and **5b** and that **4b** is more stable than **5b**.

Studies of reactivity and the mechanism of di- and tri-nuclear compounds are now in progress.

Acknowledgements

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[6] **1** (yellow, 84%): IR(nujol): 2153 (N≡C) cm^{-1}; ^{1}H NMR(250 MHz; $(CD_3)_2CO$): δ 2.21 (s, 12H, *o-Me*), 4.15 (b, 8H, C*H*$_2$), 7.1 (m, *Ph*); ^{31}P{H} NMR ($(CD_3)_2CO$): δ −38.91, −5.42, 12.57. All compounds described below gave satisfactory elememtal analyses.

[7] **2** (dark-red, 69%): IR(Nujol): 2162 (N≡C) cm^{-1}; ^{1}H NMR($(CD_3)_2CO$): δ 2.82 (s, 6H, *o-Me*), 4.72 (m, 8H, C*H*$_2$), 7.3 (m, *Ph*). Crystal data: $C_{75}H_{70}N_2P_8F_{12}Pd_2$; $M = 1688.0$; triclinic, $P\bar{1}$ (No. 2); $a = 16.420(2)$ Å, $b = 16.8498(3)$ Å, $c = 13.542(2)$ Å, $\alpha = 90.77(1)°$, $\beta = 99.97(1)°$, $\gamma = 89.08(1)°$, $V = 3689(2)$ Å^3; $D_{calcd} = 1.519$ g cm^{-3}; $Z = 2$, μ(Mo Kα) = 7.24 cm^{-1}. Data were collected with scan type ω-2θ and scan rate 8.0° min^{-1} on a Rigaku AFC5S diffractometer with graphite monochromated Mo Kα radiation. A total of 6714 ($2\theta < 45°$) reflections were measured; 4738 reflections with $I > 3.0\sigma(I)$ were used in the structure refinement. Structure solution was by direct methods for the Pd atoms; the remaining nonhydrogen atoms were located through least-squares refinement and difference Fourier synthesis. Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were occupied with an ideal position. The residual R and Rw values are 0.058 and 0.045, respectively. All calculations were performed on a TEXSAN-TEXRAY structure analysis package, molecular structure corporation. Analogous operations for structure solutions were carried out for all compounds described here.

[8] **4a** (orange, 33%): IR(nujol): 2166, 2129 (N≡C) cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$): δ 1.71 (s, 12H,*o-Me*), 4.23 (s, C*H*$_2$Cl$_2$), 5.62 (m, 8H, C*H*$_2$), 7.3 (m, *Ph*). Crystal data: $C_{83}H_{81}N_2P_8F_{12}Cl_3OPt_2$ (containing 1.5CH_2Cl_2 and H_2O); $M = 2100.9$; triclinic, $P\bar{1}$ (No.2); $a = 13.528(8)$ Å, $b = 29.89(2)$ Å; $c = 12.250(6)$ Å, $\alpha = 98.32(6)°$; $\beta = 99.41(5)°$, $\gamma = 103.06(5)°$, $V = 4675(5)$ Å^3; $D_{calcd} = 1.492$ g cm^{-3}; $Z = 2$; $\mu = 33.05$ cm^{-1}. A total of 16550 ($2\theta < 50°$); 10568 reflections with $I > 3.0\sigma(I)$ were used in the structure refinement. The residual R and Rw values are 0.051 and 0.064, respectively. **4b** (orange, 33%): IR(nujol): 2174, 2141 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.66 (s, *o-Me*), 2.19 (s, p-*Me*), 4.2–6.0 (s, *CH*$_2$), 6.4–8.5 (m, *Ph*). **5a** (yellow, 56%): IR(nujol): 2152 (N≡C) cm^{-1}; ^{1}H NMR($(CD_3)_2CO$): δ 1.45, (s, 6H, *o-Me*), 1.94 (s, 6H, *o-Me*), 4.3 (m, 8H, C*H*$_2$), 7.4 (m, Ph). **5b** (yellow, 18%): IR(nujol); 2155 cm^{-1}; ^{1}H NMR (250 MHz, CdCl$_3$): δ 1.40, 1.89 (s, *o-Me*), 2.17, 2.24 (s, p-*Me*), 3.4–5.7 (m, C*H*$_2$), 6.6–8.1 (m, *Ph*).

[9] **6a** (red, 57%) containing two molecules of acetone; IR(nujol): 2133 (N≡C) cm^{-1}; ^{1}H NMR(CDCl$_3$): $\delta = 1.37$, (s, 6H, o-*Me*), 1.49(s, 6H, o-*Me*), 2.17 (s, 12H, *Me*$_2$CO), 4.62 (m, 8H, C*H*$_2$), 7.3 (m, Ph); ^{31}P{H} NMR(100 MHz): $\delta = -16.07$ ($^{1}J_{PPt} = 2774$ Hz, $^{2}J_{PPt} = 81$ Hz), 1.05 ($^{1}J_{PPt} = 2802$ Hz, $^{2}J_{PPt} = 87$ Hz), 2.43. Crystal data: $C_{94}H_{100}N_2P_8F_{12}PdPt_2$, Crystals for an X-ray analysis contain four molecules of acetones; $M = 2294.2$; triclinic, $P\bar{1}$ (No. 2); $a = 13.906(7)$ Å, $b = 16.084(7)$ Å, $c = 11.866(7)$ Å, $\alpha = 95.68(4)°$, $\beta = 110.09(4)°$, $\gamma = 76.68(4)°$, $V = 2425(5)$ Å; $D_{calcd} = 1.571$ g cm^{-3}; $Z = 1$; μ(Mo Kα) = 32.88 cm^{-1}. Of 4967 ($2\theta < 45°$) reflections; 4251 reflections with $I > 3.0\sigma(I)$ were used in the structure refinement. The residual R and Rw values are 0.036 and 0.033, respectively.

[10] Red crystals **7a** (64%) containing one molecule of acetone; IR(nujol): 2130 (N≡C) cm^{-1}; ^{1}H NMR (250 MHz; CDCl$_3$): δ 1.40 (s, 12H, o-*Me*), 2.15 (s, *Me*$_2$CO), 4.86 (m, 8H, *CH*$_2$), 7.7 (m, Ph): ^{31}P{H} NMR (100 MHz; $(CH_3)_2CO$): δ −16.76 (1P, $^{1}J_{PPt} = 2777$ Hz, $^{2}J_{PPt} = 84$ Hz), 0.93 (2P, $^{1}J_{PPt} = 2946$ Hz, $^{2}J_{PPt} = 84$ Hz).

[11] Crystal data for **8a**: $C_{73}H_{64}NP_8F_{12}Pt_2$, triclinic, $P\bar{1}$ (No. 2), $a = 16.490(2)$ Å, $b = 16.615(2)$ Å, $c = 13.553(1)$ Å, $\alpha = 90.530(8)°$, $\beta = 101.427(7)°$, $\gamma = 90.968(9)°$, $V = 3639(1)$ Å^3, $Z = 2$; $Dc = 1.665$ g cm^{-3}, μ(Mo Kα) = 41.24 cm^{-1}. A total of 12810 ($2\theta < 50°$) reflections were measured; 7021 reflections with $I > 3.0\sigma(I)$ were used in the structure refinement. Structure solution was by direct methods for the Pt atoms; the remaining nonhydrogen atoms were located through least-squares refinement and difference Fourier synthesis. Nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were occupied with an ideal position. The residual R and Rw values are 0.044 and 0.045, respectively.