

Preliminary communication

A-frame trinuclear complexes of platinum and palladium with a tridentate phosphine ligand
Insertion of d^{10} Pt(0) and Pd(0) fragments into a Pt–Pt σ -bondTomoaki Tanase ^{*,1}, Hiroyuki Takahata, Hirokazu Ukaji, Masaru Hasegawa, Yasuhiro Yamamoto ^{*}

Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274, Japan

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Abstract

Reactions of *anti*-[Pt₂(μ -dpmp)₂(RNC)₂](PF₆)₂ (**3**) (dpmp = bis(diphenylphosphinomethyl)phenylphosphine) with [M₃(RNC)₆] (M = Pt, Pd) afforded trimetallic A-frame clusters, [Pt₂M(μ -dpmp)₂(RNC)₂](PF₆)₂ (**6**: M = Pt, R = xylyl (Xyl); **7**: M = Pd, R = mesityl (Mes)). The d^{10} Pt⁰(RNC)₂ and Pd⁰(RNC)₂ fragments were shown to be inserted into the Pt–Pt σ -bond of complex **3** by spectroscopic and X-ray crystallographic analyses. The uncoordinated phosphine units in **3** enable the d^{10} metal to sit in the middle position of the trinuclear array. The similar A-frame tripalladium complexes, [Pd₃(μ -dpmp)₂(RNC)₂](PF₆)₂ (**8a**: R = Xyl; **8b**: R = Mes), were also prepared by the reaction of [Pd₃(RNC)₈](PF₆)₂ with dpmp.

Keywords: Platinum; Palladium; A-frame clusters; Trinuclear complexes; Triphosphine; Dpmp

1. Introduction

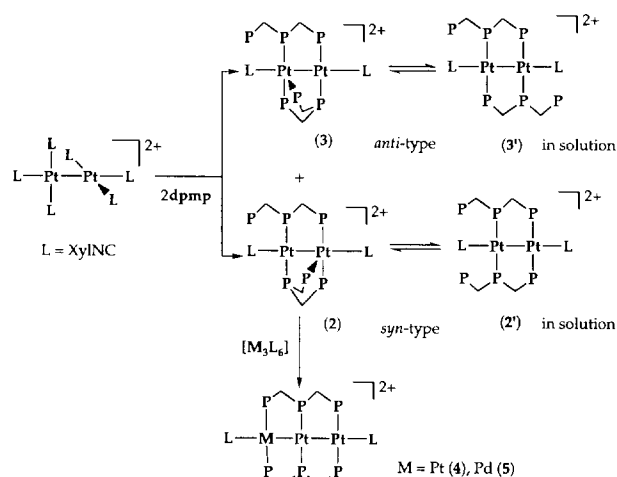
Since Hoffman and Hoffmann predicted the theoretical existence of A-frame trinuclear complexes on the basis of the isolobal analogy between CH₂, and d^{10} ML₂ and d^8 ML₄ fragments [1], several synthetic examples have been prepared through insertion of metal fragments into Pd–Pd and Pt–Pt σ -bonds bridged by diphosphines such as bis(diphenylphosphino)methane (dppm) and bis(dimethylphosphino)methane (dmpm) [2–4]. We have reported the preparation of A-frame triplatinum cluster [Pt₂(μ -PtL₂)(μ -dppm)₂L₂]²⁺ (**1**) (L = isocyanide) by the metal fragment (ML₂) insertion into the Pt–Pt bond of [Pt₂(μ -dppm)₂L₂]²⁺ [5]. The heterotrimetallic A-frame clusters [Pt₂(μ -HgCl₂)Cl₂(μ -dppm)₂] [2] and [Pt₂(μ -AuI)(C₂Bu)₂(μ -dppm)₂] [3] have been prepared by the reactions of the dppm-bridged diplatinum complexes with HgCl₂ and AuI respectively. The reaction of

[Pd₂Cl₂(dmpm)₂] with [Pt(PPh₃)₂(C₂H₄)] also led to the heterometallic cluster [Pd₂(μ -Pt(PPh₃)₂)Cl₂(μ -dmpm)₂] [4]. The metal fragment insertion into metal–metal bonds is an important process in small-size cluster architecture, but structurally characterized examples are, however, still limited.

Recently, we demonstrated that the reaction of [Pt₂(XylINC)₆]²⁺ (Xyl = 2,6-dimethylphenyl) with bis(diphenylphosphinomethyl)phenylphosphine (dpmp) afforded a mixture of isomeric diplatinum complexes, *syn*- and *anti*-[Pt₂(μ -dpmp)₂(XylINC)₂]²⁺ (**2** and **3**), where the central P atoms of dpmp ligands bind to the same metal center in **2** (*syn*-type) and to the different metal centers in **3** (*anti*-type) (Scheme 1) [6]. Complexes **2** and **3** are fluxional in solution via the symmetrical structures **2'** and **3'**. The *syn*-type dimer **2** was readily transformed, by treatment with d^{10} M(XylINC)₂ fragments, to linear homo- and heterotrinuclear clusters, *linear*-[Pt₂M(μ -dpmp)₂(XylINC)₂]²⁺ (**4**: M = Pt, **5**: M = Pd), where the additional metal is trapped in a terminal position of the trinuclear array (Scheme 1) [6,7]. Here, we wish to report the reaction of *anti*-[Pt₂(μ -dpmp)₂(XylINC)₂]²⁺ (**3**) with d^{10} ML₂ fragments (M = Pt, Pd; L = isocyanide), leading to formation of A-

^{*} Corresponding authors.

¹ Present address: Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan.



frame-type homo- and heterotrimeric clusters. The analogous Pd clusters are also reported.

2. Experimental results

2.1. Analytical and spectroscopic data for **6**

Anal. Found: C, 45.71; H, 3.50; N, 1.23. $C_{82}H_{76}F_{12}N_2P_8Pt_3$. Calc.: C, 45.80; H, 3.56; N, 1.30%. IR (nujol) cm^{-1} : 2130 (N≡C). 1H NMR (acetone- d_6): δ 1.76 (s, *o*-Me), 4.6–5.8 (m, CH_2), 6.9–8.4 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ -34.0 (m, $^1J_{PtP} = 2863$ Hz, $^2J_{PP'} = 412$ Hz, 2P), 1.9 (m, $^1J_{PtP} = 2581$ Hz, 2P), 23.0 (m, $^1J_{PtP} = 2900$ Hz, $^2J_{PP'} = 412$ Hz, 2P). UV-vis (CH_2Cl_2) nm: λ_{max} (log ϵ) 311 (3.99). Yield 70%.

2.2. Crystal data for **6**

$C_{82}H_{76}N_2P_8F_{12}Pt_3$, monoclinic, $C2/c$ (No. 15), $a = 15.353(2)$ Å, $b = 23.436(3)$ Å, $c = 22.974(8)$ Å, $\beta = 102.96(2)^\circ$, $V = 8056$ Å³, $Z = 4$, $D_{calcd} = 1.773$ g cm⁻³, $T = 23$ °C, $R = 0.035$, and $R_w = 0.041$ for 4326 unique reflections with $I > 3\sigma(I)$. The reflection data were collected on a Rigaku AFC5S diffractometer equipped with Mo K α radiation, and the structure was solved by direct methods (MITHRIL) and refined with full-matrix least squares technique by using the TEXSAN program package.

2.3. Analytical and spectroscopic data for **7**

Anal. Found: C, 48.33; H, 3.39; N, 1.29. $C_{84}H_{80}F_{12}N_2P_8PdPt_2$. Calc.: C, 48.28; H, 3.86; N, 1.34%. IR (nujol) cm^{-1} : 2128 (N≡C). 1H NMR (acetone- d_6): δ 1.83 (s, *o*-Me), 2.21 (s, *p*-Me), 4.81, 5.12, 5.68 (m, CH_2), 6.9–8.2 (m, Ar). $^{31}P\{^1H\}$ NMR

(acetone- d_6): δ -29.8 (m, $^1J_{PtP} = 2805$ Hz, $^2J_{PP'} = 426$ Hz, 2P), -10.2 (m, $^2J_{PtP} = 341$ Hz, 2P), 16.2 (m, $^1J_{PtP} = 2746$ Hz, $^2J_{PP'} = 426$ Hz, 2P). UV-vis (CH_2Cl_2) nm: λ_{max} (log ϵ) 396 (3.64). Yield 31%.

2.4. Crystal data for **7**

$C_{84}H_{80}N_2P_8F_{12}Pt_2Pd$, monoclinic, $C2/c$ (No. 15), $a = 22.209(6)$ Å, $b = 23.777(4)$ Å, $c = 20.136(3)$ Å, $\beta = 117.44(1)^\circ$, $V = 9436$ Å³, $Z = 4$, $D_{calcd} = 1.471$ g cm⁻³, $T = -147$ °C, $R = 0.085$, and $R_w = 0.086$ for 2783 unique reflections with $I > 3\sigma(I)$.

2.5. Analytical and spectroscopic data for **8a** and **8b**

For **8a**. Anal. Found: C, 52.22; H, 3.86; N, 1.40. $C_{82}H_{76}F_{12}N_2P_8Pd_3$. Calc.: C, 52.26; H, 4.06; N, 1.48%. IR (nujol) cm^{-1} : 2139 (N≡C). 1H NMR (acetone- d_6): δ 1.71 (s, *o*-Me), 4.14, 4.65, 5.39 (m, CH_2), 6.9–8.0 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ -29.5 (m, $^2J_{PP'} = 365$ Hz, 2P), -25.5 (m, 2P), 12.9 (m, $^2J_{PP'} = 365$ Hz, 2P). UV-vis (CH_2Cl_2) nm: λ_{max} (log ϵ) 471 (3.59). Yield 66%.

For **8b**. Anal. Found: C, 52.52; H, 4.11; N, 1.43%. $C_{84}H_{80}F_{12}N_2P_8Pd_3$. Calc.: C, 52.75; H, 4.22; N, 1.46%. IR (nujol) cm^{-1} : 2137 (N≡C). 1H NMR (acetone- d_6): δ 1.76 (s, *o*-Me), 2.21 (s, *p*-Me), 4.50, 4.99, 5.73 (m, CH_2), 6.88–8.89 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ -28.9 (m, $^2J_{PP'} = 364$ Hz, 2P), -26.4 (m, 2P), 10.6 (M, $^2J_{PP'} = 364$ Hz, 2P). UV-vis (CH_2Cl_2) nm: λ_{max} (log ϵ) 470 (3.55). Yield 71%.

2.6. Crystal data for **8a**

$C_{82}H_{76}N_2P_8F_{12}Pd_3$, monoclinic, $C2/c$ (No. 15), $a = 15.383(2)$ Å, $b = 23.427(5)$ Å, $c = 23.056(7)$ Å, $\beta = 102.65(2)^\circ$, $V = 8107$ Å³, $Z = 4$, $D_{calcd} = 1.544$ g cm⁻³, $T = 23$ °C, $R = 0.069$, and $R_w = 0.063$ for 2489 unique reflections with $I > 2.5\sigma(I)$.

3. Discussion

The reaction of *anti*-[Pt₂(μ -dpmp)₂(RNC)₂](PF₆)₂ (**3**) with [Pt₃(RNC)₆], which is a good precursor of the d¹⁰ Pt(RNC)₂ fragment, gave yellow clusters formulated as *A-frame*-[Pt₃(μ -dpmp)₂(RNC)₂](PF₆)₂ (**6**; R = Xyl, 70%) (see Section 2.1). The IR and 1H NMR spectra indicated the presence of terminal isocyanide ligands. The $^{31}P\{^1H\}$ NMR spectrum of **6** exhibited three resonances at δ -34.0, 1.9, and 23.0 in an intensity ratio of 1:1:1, all being accompanied by satellite peaks due to coupling to ¹⁹⁵Pt with $^1J_{PtP} = 2581$ –2900 Hz (Fig. 1(a)). The two resonances at δ -34.0 and 23.0, in addition, are coupled to each other with $^2J_{PP'} = 412$ Hz. These spectral data suggested that the

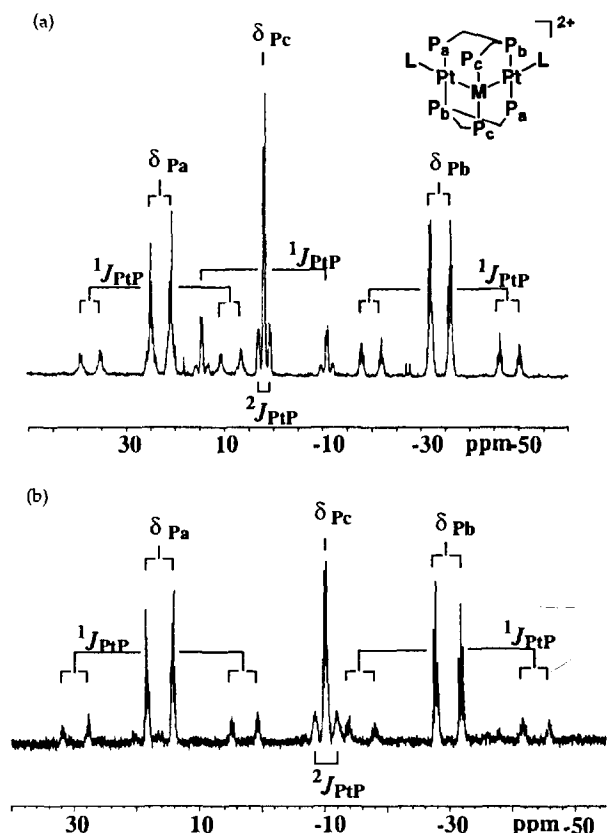


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of (a) *A-frame*- $[\text{Pt}_3(\mu\text{-dpmp})_2(\text{XylNC})_2](\text{PF}_6)_2$ (**6**) and (b) *A-frame*- $[\text{Pt}_2\text{Pd}(\mu\text{-dpmp})_2(\text{MesNC})_2](\text{PF}_6)_2$ (**7**), measured at 100 MHz in acetone- d_6 .

three phosphorus atoms of dpmp are in three environmentally different sites around a symmetrical triplatinum aggregation. An X-ray crystallographic analysis revealed that complex **6** comprises an A-frame triplatinum core bridged by two dpmp ligands as shown in Fig. 2 (see Section 2.2). The complex cation has a crystallographically imposed C_2 symmetry. The core

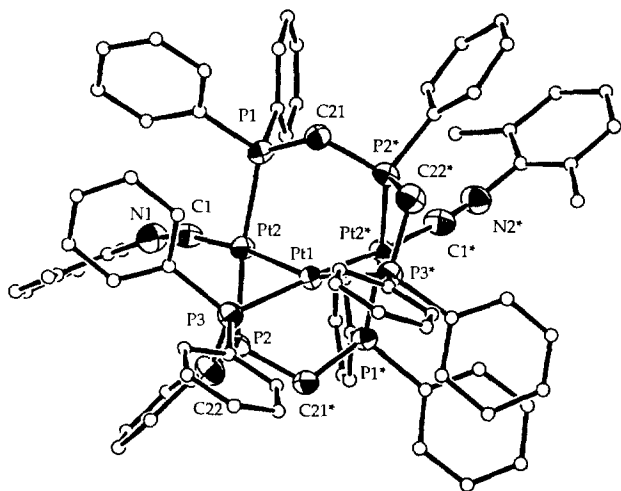


Fig. 2. ORTEP diagram of the complex cation of *A-frame*- $[\text{Pt}_3(\mu\text{-dpmp})_2(\text{XylNC})_2](\text{PF}_6)_2$ (**6**).

geometry is quite similar to that of $[\text{Pt}_3(\mu\text{-dpmp})_2(\text{XylNC})_4](\text{PF}_6)_2$ (**1**) [5] except for the geometry around the central Pt atom, which is fairly distorted from a square planar structure. The dihedral angle between the planes $[\text{Pt}(1)\text{Pt}(2)\text{Pt}(2)^*]$ and $[\text{Pt}(1)\text{P}(3)\text{P}(3)^*]$ is 16° . The dpmp ligand bridges over the Pt(2) and Pt(2)* atoms with a pair of the outer and inner P atoms and between the Pt(1) and Pt(2) atoms with the other pair. The double bridging system of dpmp results in thermal stability of complex **6**. The Pt(1)–Pt(2) bond distance is $2.6309(7)\text{ \AA}$ and the interatomic Pt(2) \cdots Pt(2)* distance is $3.2333(9)\text{ \AA}$. The former corresponds to a Pt–Pt σ -bond and the latter indicates the absence of bonding interaction between the two terminal Pt atoms. The Pt(1)–Pt(2)–Pt(1)* angle is $76.76(3)^\circ$.

The similar reaction of **3** (R = Mes) with $[\text{Pd}_3(\text{MesNC})_6]$ afforded a heterotrimetallic A-frame cluster, *A-frame*- $[\text{Pt}_2\text{Pd}(\mu\text{-dpmp})_2(\text{MesNC})_2](\text{PF}_6)_2$ (**7**) in 31% yield (see Section 2.3). The IR and ^1H NMR spectra were similar to those of **6**, whereas a new band appeared at a longer wavelength (396 nm) than that of **6** in the electronic absorption spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed the presence of three non-equivalent phosphorus atoms at $\delta -29.8$, -10.2 , and 16.2 (Fig. 1(b)). The spectral pattern was similar to that of **6**, except for the fact that the central peak ($\delta -10.2$) did not have satellites due to one-bond coupling to ^{195}Pt . The structure of **7** was confirmed by X-ray crystallography to have a symmetrical Pt_2Pd A-frame assembly (Fig. 3) (see Section 2.4). The Pd atom occupies the central position between the two Pt atoms. The Pt(1)–Pd(1) bond length of $2.599(3)\text{ \AA}$ is shorter by 0.031 \AA than the Pt–Pt bond length of **6**, and the Pt(1) \cdots Pt(1)* interatomic distance of $3.290(3)\text{ \AA}$ is out of bonding range. The Pt(1)–Pd(1)–Pt(1)* angles is $78.5(1)^\circ$. The

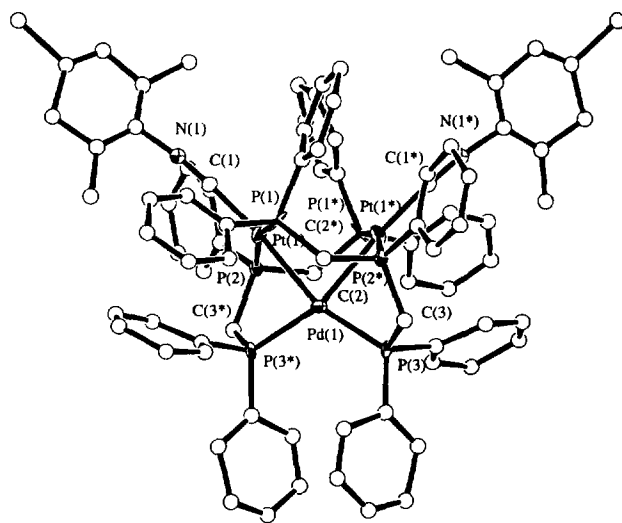


Fig. 3. ORTEP diagram of the complex cation of *A-frame*- $[\text{Pt}_2\text{Pd}(\mu\text{-dpmp})_2(\text{MesNC})_2](\text{PF}_6)_2$ (**7**).

structure of **7** suggests a formation mechanism which involves an insertion of a d^{10} $M(\text{RNC})_2$ fragment into the Pt–Pt bond in **3'** supported by the ligation of the two uncoordinated P atoms. The position of the trapped metal atom in **7** (central position) is interestingly contrasted with that in *linear*- $[\text{Pt}_2\text{Pd}(\mu\text{-dpmp})_2(\text{XylNC})_2]^{2+}$ (**5**) derived from the reaction of *syn*- $[\text{Pt}_2(\mu\text{-dpmp})_2(\text{XylNC})_2]^{2+}$ (**2**) with the $\text{Pd}(\text{XylNC})_2$ fragment (terminal position). The arrangement of the two free phosphorus atoms in **2'** and **3'** may play a critical role in determining the direction of the d^{10} metal-inserted position.

The similar homotrimeric A-frame complexes of palladium, *A-frame*- $[\text{Pd}_3(\mu\text{-dpmp})_2(\text{RNC})_2](\text{PF}_6)_2$ (**8a**: R = Xyl; **8b**: R = Mes), were also prepared in good yields (66–71%) by the reaction of $[\text{Pd}_3(\text{RNC})_8](\text{PF}_6)_2$ with two equivalents of dpmp (see Section 2.5). The structure of **8a** was shown by X-ray crystallography (see Section 2.6) to have an isomorphous structure with that of **6**. The Pd–Pd bond length is 2.592(2) Å, which is slightly shorter than the Pt–Pd distance in **7**. The corresponding reaction with $[\text{Pt}_3(\text{RNC})_8](\text{PF}_6)_2$, notably, did not lead to the A-frame triplatinum cluster **6**; instead, it resulted in an exclusive formation of the non-bridged linear triplatinum complex with chelating dpmp ligands, $[\text{Pt}_3(\text{dpmp})_2(\text{RNC})_4]^{2+}$, which was confirmed by the electronic absorption spectra.

4. Conclusion

In this study, it was revealed that the diplatinum complex, *anti*- $[\text{Pt}_2(\mu\text{-dpmp})_2(\text{RNC})_2]^{2+}$ (**3**), readily

traps a d^{10} Pt or Pd atom into the Pt–Pt σ -bond to form homo- and heterotrimeric A-frame clusters. Reactions of **3** with other d^{10} and d^8 metal ions are now under investigation.

5. Supplementary material available

Tabulations of crystallographic data, and positional and thermal parameters for **6**, **7**, and **8a** (21 pages) and an ORTEP plot of **8a** are available from TT on request.

Acknowledgements

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