Inorg. Chem. **1996,** *35,* 4114−4119

Asymmetrical A-Frame Triplatinum Clusters Bridged by Small Organic Molecules and Bis((diphenylphosphino)methyl)phenylphosphine

Tomoaki Tanase,* Hirokazu Ukaji, Toshiaki Igoshi, and Yasuhiro Yamamoto*

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

Received September 8, 1995[⊗]

Reactions of the linear triplatinum complex $[Pt_3(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$ (**3**) with small organic molecules led to formation of asymmetrical A-frame triplatinum complexes with an additional bridge across one of the metal−metal bonds, where dpmp is bis((diphenylphosphino)methyl)phenylphosphine. Reaction of complex **3** with electron deficient alkynes ($R^1C{\equiv}CR^2$: $R^1 = R^2 = CO_2Me$; $R^1 = H$, $R^2 = CO_2Me$; $R^1 = R^2 = CO_2Et$) afforded a new series of triplatinum clusters formulated as $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^1CCR^2)(XylNC)_2](PF_6)_2$ (**5a**, $R^1 = R^2 = CO_2Me$; **5b**, $R^1 = H$, $R^2 = CO_2Me$; **5c**, $R^1 = R^2 = CO_2Et$) in good yields. The complex cation of **5b** was characterized by X-ray crystallography to have an asymmetrical A-frame structure comprising three Pt atoms bridged by two dpmp ligands, in which an acetylene molecule was inserted into one of the Pt−Pt bonds (triclinic, $P\bar{1}$, $a = 19.507(3)$ Å, $b = 20.327(4)$ Å, $c = 14.499(4)$ Å, $\alpha = 107.69(2)°$, $\beta = 102.08(2)°$, $\gamma = 71.30(1)°$, $V = 5148$ Å^3, $Z = 2$, $R = 0.070$, and $R_w = 0.084$). The Pt−Pt bond length is 2.718(1) Å and the Pt···Pt nonbonded distance is 3.582(1) Å. Treatment of **3** with an excess of $HBF_4{\cdot}Et_2O$ gave the asymmetrical cluster $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-H})(XylNC)_2](BF_4)_3{\cdot}CH_2Cl_2$ ($\mathbf{6}{\cdot}CH_2Cl_2$), in 61% yield, and a similar reaction with $p\text{-}NO_2C_6H_4NC$ led to the formation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^3NC)(XylNC)_2](PF_6)_2{\cdot}CH_2Cl_2$ ($\mathbf{7}{\cdot}CH_2Cl_2$) in 94% yield ($R^3 = p\text{-}NO_2C_6H_4$). Complexes **6** and **7** are assumed to have a single atom-bridged, asymmetrical A-frame structures. Reaction of the complex *syn*-$[Pt_2(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$ (**1**) with $[MCl_2(cod)]$ (M = Pt, Pd) gave the dimer−monomer combined trinuclear cluster $[Pt_2MCl_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (**8a**, M = Pt, 89%; **8b**, M = Pd, 55%). The structure of **8a** was determined by X-ray crystallography to be comprised of a metal−metal-bonded diplatinum core and a monomeric platinum center bridged by two dpmp ligands with a face-to-face arrangement (triclinic, $P\bar{1}$, $a = 18.082(7)$ Å, $b = 19.765(6)$ Å, $c = 15.662(4)$ Å, $\alpha = 98.51(2)°$, $\beta = 94.24(3)°$, $\gamma = 109.82(2)°$, $V = 5161$ Å^3, $Z = 2$, $R = 0.069$, and $R_w = 0.080$). The Pt−Pt bond length is 2.681(2) Å and the Pt···Pt nonbonded distance is 3.219(2) Å. The heteronuclear complex **8b** was transformed to an A-frame trinuclear cluster, $[Pt_2PdCl(\mu\text{-Cl})(\mu\text{-dpmp})_2(XylNC)](PF_6)_2$ (**9**), which was characterized by X-ray crystallography (monoclinic, $C2/c$, $a = 33.750(9)$ Å, $b = 28.289(9)$ Å, $c = 23.845(8)$ Å, $\beta = 118.19(4)°$, $V = 20066$ Å^3, $Z = 8$, $R = 0.082$, and $R_w = 0.077$). The diplatinum unit (Pt−Pt = 2.606(2) Å) is connected to the mononuclear Pd center by a chloride bridge (Pt···Pd = 3.103(3) Å, Pt−Cl−Pd = 79.6(3)°).

Introduction

Metal−metal-bonded small-size clusters of platinum and palladium have been of increasing interest as minimal models for the surface of heterogeneous catalysts; structures, properties, and reactivities are able to be modified by varying the synthetic strategy and the choice of organic ligands. The first model extensively studied is the dppm-bridged dinuclear platinum and palladium complexes which have the ability to coordinate small molecules *via* additions across the metal−metal bond, resulting in so-called “A-frame” complexes, where dppm is bis(diphenylphosphino)methane.[1] The synthetic interests have then shifted to trinuclear clusters, examples being the dppm-bridged triangular clusters, such as $[Pt_3(\mu\text{-dppm})_3(\mu^3\text{-CO})]^{2+}$ and its derivatives.[2]

We have systematically prepared and characterized metal−metal-bonded di- and trinuclear platinum and palladium complexes supported by bidentate phosphine ligands.[3] Recently, the tridentate phosphine ligand, bis((diphenylphosphino)methyl)phenylphosphine (dpmp), has attracted our attention. The dpmp ligand has versatile bridging and chelating coordination behaviors for di- and mononuclear metal centers, and linear coordination mode for trinuclear metal centers.[4] Chemistry on linearly-ordered rhodium complexes has systematically been studied by Balch and his co-workers,[4] whereas the corresponding chemistry of Pt and Pd has been largely unexplored. Earlier we demonstrated that the reaction of $[Pt_2(XylNC)_6]^{2+}$ (Xyl = 2,6-dimethylphenyl) with 2 equiv of dpmp afforded a mixture of isomeric diplatinum complexes, *syn*- and *anti*-$[Pt_2(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$ (**1** and **2**), where the central P atoms of dpmp ligands bind to the same metal center in **1** (*syn*-type) and to the different metal centers in **2** (*anti*-type) (Scheme 1).[5] Complexes

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

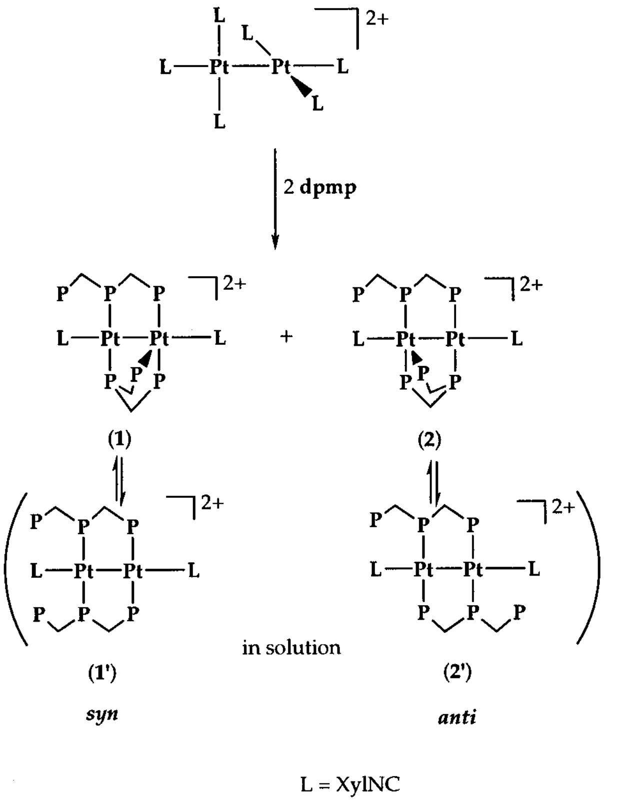
(1) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Balch, A. P. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 167.

(2) (a) Manojlovic-Muir, Lj.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1336. (b) Lloyd, B. R.; Puddephatt, R. J. *Inorg. Chim. Acta* **1984**, *90*, L77. (c) Manojlovic-Muir, Lj.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 536. (d) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344. (e) Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767, and references cited therein.

(3) (a) Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2458. (b) Yamamoto, Y.; Yamazaki, H. *Organometallics* **1993**, *12*, 933. (c) Tanase, T.; Kudo, Y.; Ohno, M.; Kobayashi, K.; Yamamoto, Y. *Nature* **1990**, *344*, 526. (d) Tanase, T.; Horiuchi, T.; Kobayashi, K.; Yamamoto, Y. *J. Organomet. Chem.* **1992**, *440*, 1. (e) Tanase, T.; Kawahara, K.; Ukaji, H.; Kobayashi, K.; Yamazaki, H.; Yamamoto, Y. *Inorg. Chem.* **1993**, *32*, 3682. (f) Tanase, T.; Ukaji, H.; Kudo, Y.; Ohno, M.; Kobayashi, K.; Yamamoto, Y. *Organometallics* **1994**, *13*, 1301. (g) Tanase, T.; Yamamoto, Y.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 1502.

S0020-1669(95)01186-4 CCC: $12.00

Scheme 1



1 and **2** are fluxional in solution *via* the symmetrical structures **1′** and **2′**. Further, the *syn*-type dimer **1** was readily transformed, by treatment with d^{10} $M(XylNC)_2$ fragments, to novel homo and hetero trinuclear clusters, $[Pt_2M(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$ (**3**: M = Pt, **4**: M = Pd) (Scheme 2).[5] Versatile reactions of compounds **3** and **4** can be expected from analogy to those of the dppm-bridged diplatinum complexes.

We wish to describe herein the reactions of the linear trinuclear complex **3** with small organic molecules, leading to formation of asymmetrical A-frame triplatinum complexes with an additional bridge across one of the metal−metal bonds. An alternative route to an asymmetrical A-frame complex was also established by utilizing the reaction of **1** (*syn*-type) with d^8 $[MCl_2(cod)]$ (M = Pt, Pd).

Experimental Section

Dichloromethane, chloroform, and acetone were distilled over calcium hydride and diethyl ether was distilled over lithium aluminum hydride prior to use. Other reagents were of the best commercial grade and were used as received. *syn*-$[Pt_2(dpmp)_2(XylNC)_2](PF_6)_2$ (**1**) and *linear*-$[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2\cdot(CH_3)_2CO$ (**3**) were prepared by the methods already reported.[5] All reactions were carried out under a nitrogen atmosphere with standard Schlenk and vacuum line techniques.

Measurements. ^1H NMR spectra were measured on a Bruker AC250 instrument at 250 MHz. Chemical shifts were calibrated to tetramethylsilane as an external reference. $^{31}P\{^1H\}$ NMR spectra were recorded by the same instrument at 101 MHz, chemical shifts being calibrated to 85% H_3PO_4 as an external reference. Infrared and electronic absorption spectra were recorded with Jasco FT/IR-5300 and Ubest-30 spectrometers, respectively.

Preparation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^1CCR^2)(XylNC)_2](PF_6)_2$ (5a, $R^1 = R^2 = CO_2Me$; 5b, R^1 = H, $R^2 = CO_2Me$; 5c, $R^1 = R^2 = CO_2Et$). To a dichloromethane solution (20 mL) containing *linear*-$[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2\cdot(CH_3)_2CO$ (**3**) (103 mg, 4.67×10^{-2} mmol) was added $R^1C{\equiv}CR^2$ ($R^1 = R^2 = CO_2Me$) (20 mg, 1.41×10^{-1} mmol). The solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether, followed by recrystallization from dichloromethane/diethyl ether mixed solvent, to give red crystals of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}MeO_2CC_2CO_2Me)(XylNC)_2](PF_6)_2$ (**5a**), which were separated by filtration, washed with diethyl ether, and dried in vacuo (89 mg, yield 83%). Anal Calcd for $C_{88}H_{82}N_2Pt_3P_8F_{12}O_4$: C, 46.10; H, 3.61; N, 1.22. Found: C, 45.61; H, 3.63; N, 1.32. IR (Nujol): $\nu(N{\equiv}C)$ 2166, 2128, $\nu(C{=}O)$ 1684, $\nu(C{=}C)$ 1572 cm^{-1}. ^1H NMR (in $CDCl_3$): δ 1.29, 1.65 (s, *o*-Me), 2.42, 3.11 (s, OMe), 3.2−5.8 (m, CH_2), 6.5−8.3 (m, Ar). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ −7.6 (m, 1P, $^1J_{PtP}$ = 2777 Hz), 1.1 (m, 1P, $^1J_{PtP}$ = 2946 Hz), 5.9 (m, 1P, $^1J_{PtP}$ = 2946 Hz). Orange crystals of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}HC_2CO_2Me)(XylNC)_2](PF_6)_2\cdot CH_2Cl_2$ (**5b**$\cdot CH_2Cl_2$) were obtained in 60% yield (63 mg) by a procedure similar to that described above from the reaction of **3** (100 mg, 4.53×10^{-2} mmol) with $HC{\equiv}CCO_2Me$ (80 mg, 9.52×10^{-1} mmol) for 3 days. Anal Calcd for $C_{86}H_{80}N_2Pt_3P_8F_{12}O_2\cdot CH_2Cl_2$: C, 45.05; H, 3.56; N, 1.21. Found: C, 45.20; H, 3.63; N, 1.17. IR (Nujol): $\nu(N{\equiv}C)$ 2155 (sh), 2130, $\nu(C{=}O)$ 1672, $\nu(C{=}C)$ 1539 cm^{-1}. ^1H NMR (in acetone-d_6): δ 1.58, 1.80 (s, *o*-Me), 2.49 (s, OMe), 3.3−6.3 (m, CH_2), 5.63 (s, CH_2Cl_2), 6.3−8.7 (m, Ar), 11.15 (br, $HC{\equiv}C$). Reddish orange crystals of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}EtO_2CC_2CO_2Et)(XylNC)_2](PF_6)_2$ (**5c**) were obtained in 90% yield (97 mg) by a procedure similar to that described above from the reaction of **3** (102 mg, 4.62×10^{-2} mmol) with $EtO_2CC{\equiv}CCO_2Et$ (60 mg, 3.53×10^{-1} mmol) for 6 h. Anal Calcd for $C_{90}H_{86}N_2Pt_3P_8F_{12}O_4$: C, 46.58; H, 3.74; N, 1.21. Found: C, 46.00; H, 3.54; N, 1.01. IR (Nujol): $\nu(N{\equiv}C)$ 2145, $\nu(C{=}O)$ 1696, 1670, $\nu(C{=}C)$ 1572 cm^{-1}. ^1H NMR (in $CDCl_3$): δ 0.36, 0.73 (t, OCH_2CH_3), 1.36, 1.65 (s, *o*-Me), 2.47, 3.00 (m, OCH_2CH_3), 3.41, 3.68 (m, OCH_2CH_3), 2.6−5.8 (m, CH_2), 6.5−8.3 (m, Ar). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ −5.8 (m, 1P, $^1J_{PtP}$ = 2870 Hz), 0.4 (m, 1P, $^1J_{PtP}$ = 3056 Hz), 4.1 (m, 1P, $^1J_{PtP}$ = 3034 Hz).

Preparation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}H)(XylNC)_2](BF_4)_3\cdot CH_2Cl_2$ (6$\cdot CH_2Cl_2$). To a $CHCl_3$ solution (10 mL) containing *linear*-$[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2\cdot(CH_3)_2CO$ (**3**) (51 mg, 2.31×10^{-2} mmol) was added $HBF_4\cdot(C_2H_5)_2O$ (20 mg, 1.24×10^{-1} mmol). The solution was stirred at room temperature for 15 min. The solvent was removed under reduced pressure and the residue was washed with *n*-hexane, followed by recrystallization from dichloromethane/methanol/diethyl ether mixed solvent, to give pale yellow crystals of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}H)(XylNC)_2](BF_4)_3\cdot CH_2Cl_2$ (**6**$\cdot CH_2Cl_2$), which were collected by filtration, washed with diethyl ether, and dried in vacuo (31 mg, yield 61%). Analytical and spectral data for **6**$\cdot CH_2Cl_2$ follow. Anal Calcd for $C_{82}H_{77}N_2Pt_3P_6F_{12}B_3\cdot CH_2Cl_2$: C, 45.17; H, 3.61; N, 1.27. Found: C, 45.15; H, 3.55; N, 1.43. IR (Nujol): $\nu(N{\equiv}C)$ 2205, 2162 cm^{-1}. ^1H NMR (in CD_2Cl_2): δ 1.28, 1.46 (s, *o*-Me), 4.7−5.7 (m, CH_2), 5.32 (s, CH_2Cl_2), 6.7−8.3 (m, Ar), −7.09 (br, μ-H, $^1J_{PtH}$ = 675, 529 Hz). $^{31}P\{^1H\}$ NMR (in CD_2Cl_2): δ −5.9 (m, 1P, $^1J_{PtP}$ = 2371 Hz), −1.2 (m, 1P, $^1J_{PtP}$ = 2613 Hz), 12.6 (m, 1P, $^1J_{PtP}$ = 2235 Hz).

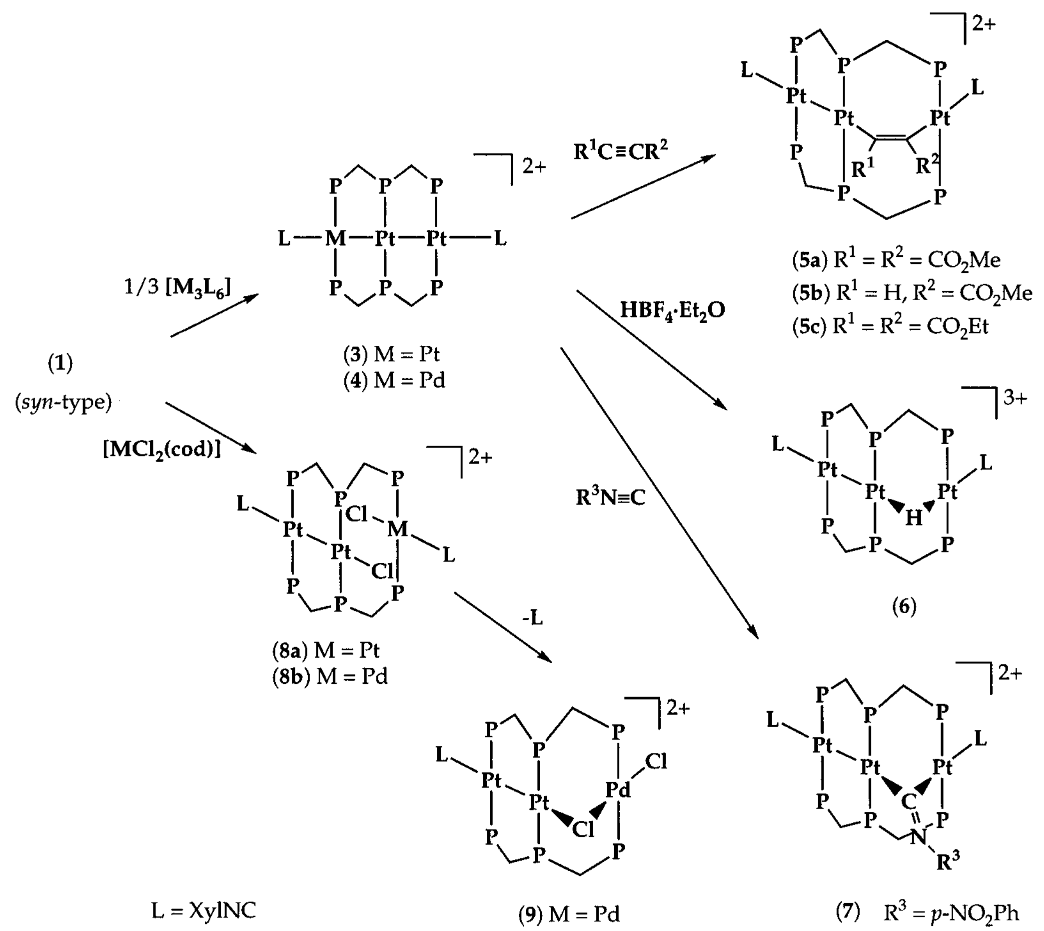
Preparation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}p\text{-}NO_2C_6H_4NC)(XylNC)_2](PF_6)_2\cdot CH_2Cl_2$ (7$\cdot CH_2Cl_2$). To a dichloromethane solution (20 mL) containing *linear*-$[Pt_3(dpmp)_2(XylNC)_2](PF_6)_2\cdot(CH_3)_2CO$ (**3**) (104 mg, 4.71×10^{-2} mmol) was added *p*-$NO_2C_6H_4NC$ (7.5 mg, 5.06×10^{-2} mmol). The solution was stirred at room temperature for 5 min. The solvent was removed under reduced pressure and the residue was washed with diethyl ether, followed by recrystallization from dichloromethane/diethyl ether mixed solvent, to give dark green microcrystals of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}p\text{-}NO_2C_6H_4NC)(XylNC)_2](PF_6)_2\cdot CH_2Cl_2$ (**7**$\cdot CH_2Cl_2$), which were separated by filtration, washed with diethyl ether, and dried in vacuo (105 mg, yield 94%). Anal Calcd for $C_{89}H_{80}N_4Pt_3P_8F_{12}O_2\cdot CH_2Cl_2$: C, 45.35; H, 3.47; N, 2.35 (%). Found: C, 45.57; H, 3.35; N,

---

(4) (a) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677. (b) Olmstead, M. M.; Guimerans, R. R.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 2473. (c) Balch, A. L.; Guimerans, R. R.; Olmstead, M. M. *J. Organomet. Chem.* **1984**, *268*, C38. (d) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M. *Organometallics* **1985**, *4*, 781. (e) Balch, A. L.; Linehan, J. C.; Olmstead, M. M. *Inorg. Chem.* **1986**, *25*, 3937. (f) Balch, A. L.; Davis, B. J.; Olmstead, M. M. *Inorg. Chem.* **1990**, *29*, 3066. (g) Balch, A. L.; Guimerans, R. R.; Linehan, J. *Inorg. Chem.* **1985**, *24*, 290. (h) Olmstead, M. M.; Guimerans, R. R.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta.* **1983**, *75*, 199. (i) Balch, A. L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; 1994; Vol. 42, p 239 and references cited therein. (j) Li, P.; Che, C.-M.; Peng, S.-M.; Liu, S.-T.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1993**, 189.

(5) Yamamoto, Y.; Tanase, T.; Ukaji, H.; Hasegawa, M.; Igoshi, T.; Yoshimura, K. *J. Organomet. Chem.* **1995**, *498*, C23.

Scheme 2



2.32 (%). IR (Nujol): ν(N≡C) 2159, 2133, ν(C=N) 1554 (br) cm^{-1}. ^{1}H NMR (in CDCl$_3$): δ 1.28, 1.46 (s, *o*-Me), 2.3−5.5 (m, CH$_2$), 5.27 (s, CH$_2$Cl$_2$), 6.2−8.4 (m, Ar).

Preparations of [Pt$_2$MCl$_2$(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (8a, M = Pt; 8b, M = Pd) and [Pt$_2$PdCl(μ-Cl)(μ-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (9). To a dichloromethane solution (20 mL) containing *syn*-[Pt$_2$(dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**1**) (371 mg, 1.90 × 10^{-1} mmol) was added [PtCl$_2$(cod)] (107 mg, 2.86 × 10^{-1} mmol). The solution was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether, followed by recrystallization from acetone/diethyl ether mixed solvent, to give yellow crystals of [Pt$_3$Cl$_2$(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**8a**), which were separated by filtration, washed with diethyl ether, and dried in vacuo (374 mg, yield 89%). Anal Calcd for C$_{82}$H$_{76}$N$_2$Pt$_3$P$_8$F$_{12}$Cl$_2$: C, 44.34; H, 3.45; N, 1.26. Found: C, 43.38; H, 3.55; N, 1.13. IR (Nujol): ν(N≡C) 2199, 2166 cm^{-1}. ^{1}H NMR (in acetone-*d*$_6$): δ 1.51, 1.71 (s, *o*-Me), 4.0−5.7 (m, CH$_2$), 6.6−8.3 (m, Ar). ^{31}P{^{1}H} NMR (in acetone-*d*$_6$): δ −7.6 (m, 1P, $^1J_{\mathrm{PtP}}$ = 3111 Hz), −5.4 (m, 1P, $^1J_{\mathrm{PtP}}$ = 2476 Hz), 1.1 (m, 1P, $^1J_{\mathrm{PtP}}$ = 2276 Hz). A portion of [PdCl$_2$(cod)] (16 mg, 5.60 × 10^{-2} mmol) was added to a dichloromethane solution (20 mL) containing *syn*-[Pt$_2$(dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**1**) (107 mg, 5.47 × 10^{-2} mmol). The solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure to ~5 mL and addition of diethyl ether gave yellow micro crystals of [Pt$_2$PdCl$_2$(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$·1.5CH$_2$Cl$_2$ (**8b**·1.5CH$_2$Cl$_2$), which were separated by filtration, washed with diethyl ether, and dried in vacuo (68 mg, yield 55%). Anal Calcd for C$_{82}$H$_{76}$N$_2$Pt$_2$PdP$_8$F$_{12}$Cl$_2$·$^3/_2$CH$_2$Cl$_2$: C, 44.37; H, 3.52; N, 1.24. Found: C, 44.21; H, 3.72; N, 1.19. IR (Nujol): ν(N≡C) 2199, 2160 cm^{-1}. When the crystallization took few days, complex **9** described below was obtained instead of **8b**·1.5CH$_2$Cl$_2$. Slow recrystallization of **8b**·1.5CH$_2$Cl$_2$ (80 mg, 3.54 × 10^{-2} mmol) from a acetone or dichloromethane/diethyl ether mixed solvent at 2 °C for 2 days afforded block-shaped red crystals of [Pt$_2$PdCl(μ-Cl)(μ-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (**9**) in 41% yield (29 mg). Anal Calcd for C$_{73}$H$_{67}$NPt$_2$PdP$_8$F$_{12}$Cl$_2$: C, 43.81; H, 3.37; N, 0.70. Found: C, 43.37; H, 3.23; N, 0.64. IR (Nujol): ν(N≡C) 2173 cm^{-1}. ^{1}H NMR (in acetone-*d*$_6$): δ 1.43 (s, *o*-Me), 4.0−5.4 (m, CH$_2$), 6.5−8.4 (m, Ar). ^{31}P{^{1}H} NMR (in acetone-*d*$_6$): δ −1.7 (m, 1P, $^1J_{\mathrm{PtP}}$ = 2365 Hz), 6.5 (m, 1P, $^1J_{\mathrm{PtP}}$ = 2801 Hz), 10.0 (m, 1P).

Crystal Data and Intensity Measurements for 5b, 8a, and 9. The crystals used in data collection were sealed into a glass tube capillary (0.7 mm o.d.) with a droplet of mother liquor. Crystal data and experimental conditions are summarized in Table 1. All data were collected on a Rigaku AFC5S diffractometer equipped with graphite monochromatized Mo Kα (λ = 0.710 69 Å) radiation. The cell constants were obtained from least squares refinement of 20−25 reflections with 20 < 2θ < 30°. Three standard reflections were monitored every 150 reflections and showed no systematic decrease in intensity. Reflection data were corrected for Lorentz−polarization and absorption effects (ψ-scan method).

Structure Solution and Refinement. The structure of **5b** was solved by Patterson method with DIRDIF.[6] The three platinum atoms were located initially, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of all hydrogen atoms were calculated at ideal positions with a C−H distance of 0.95 Å and were not refined. The structure was refined with the full-matrix least-squares techniques minimizing $\sum w(|F_o| - |F_c|)^2$. Final refinement was carried out with anisotropic thermal parameters for Pt and P(1)−P(6) atoms and with isotropic ones for other non-hydrogen atoms. The C(221)−C(226) atoms and the P(11) and F(11)−F(16) atoms were treated as rigid groups of C$_6$H$_5$ and PF$_6$, respectively. The structures of **8a** was solved and refined by the similar procedures described for **5b**. Final full-matrix least-squares refinement was carried out with anisotropic thermal parameters for the Pt, Cl, P, and F atoms and with isotropic ones for other non-hydrogen atoms. The structure of **9** was solved by direct methods with MITHRIL.[7] The two platinum and one

---

(6) Parthasarathi, V.; Beurskens, P. T.; Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860.

(7) Gilmore, G. J. *J. Appl. Crystallogr.* **1984**, *17*, 42

Table 1. Crystallographic and Experimental Data for $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}HC_2CO_2Me)(XylNC)_2](PF_6)_2$ (**5b**), $[Pt_3Cl_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (**8a**), and $[Pt_2PdCl(\mu\text{-}Cl)(\mu\text{-dpmp})_2(XylNC)](PF_6)_2$ (**9**)

	5b	8a	9
formula	$C_{86}H_{84}N_2O_2P_8F_{12}Pt_3$	$C_{82}H_{76}N_2P_8F_{12}Pt_3Cl_2$	$C_{73}H_{67}NP_8F_{12}Pt_2PdCl_2$
fw	2238.66	2221.46	2001.60
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	19.507(3)	18.082(7)	33.750(9)
b, Å	20.327(4)	19.765(6)	28.289(9)
c, Å	14.499(4)	15.662(4)	23.845(8)
α, deg	107.69(2)	98.51(2)	
β, deg	102.08(2)	94.24(3)	118.19(4)
γ, deg	71.30(1)	109.82(2)	
V, Å^3	5148	5161	20066
Z	2	2	8
T, °C	23	23	23
D_{calcd}, g cm^{-1}	1.444	1.429	1.325
abs coeff, cm^{-1}	42.90	43.28	32.18
transm factor	0.69−1.00	0.88−1.00	0.84−1.00
2θ range, deg	$3 < 2\theta < 50$	$3 < 2\theta < 50$	$3 < 2\theta < 45$
no. of unique data	18 781	18 104	13 455
no. of obsd data	9131 ($I > 3\sigma(I)$)	5443 ($I > 3\sigma(I)$)	4247 ($I > 3\sigma(I)$)
no. of variables	460	562	352
R^a	0.070	0.069	0.082
$R_w{}^a$	0.084	0.080	0.077

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).

palladium atoms were located in the initial E-map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of all hydrogen atoms were calculated at ideal positions with a C−H distance of 0.95 Å and were not refined. Final refinement was carried out with anisotropic thermal parameters for the Pt, Pd, Cl, P, and F atoms and with isotropic ones for other non-hydrogen atoms. Phenyl groups were treated as rigid groups by using TEXSAN.

Atomic scattering factors and values of f' and f'' for Pt, Pd, Cl, P, F, N, and C were taken from the literature.[8] All calculations were carried out on a Digital VAX Station 3100 with the TEXSAN Program System.[9] The perspective views were drawn by using the programs ORTEP-II.[10] Compilation of final atomic parameters for all non-hydrogen atoms is supplied as supplementary material.

Results and Discussion

Reaction of *linear*-$[Pt_3(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ with Small Organic Molecules Leading to Asymmetrical A-Frame Complexes. The reaction of complex **3**, $[Pt_3(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$, with an excess of electron deficient alkynes ($R^1C{\equiv}CR^2$: $R^1 = R^2 = CO_2Me$; $R^1 = H$, $R^2 = CO_2Me$; $R^1 = R^2 = CO_2Et$) in dichloromethane at room temperature afforded a new series of triplatinum complexes formulated as $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^1CCR^2)(XylNC)_2](PF_6)_2$ (**5a**: $R^1 = R^2 = CO_2Me$; **5b**: $R^1 = H$, $R^2 = CO_2Me$; **5c**: $R^1 = R^2 = CO_2Et$) in good yields (Scheme 2), although phenylacetylene and diphenylacetylene did not react. The IR and ^1H NMR spectra of **5a** indicated the presence of two environmentally different terminal isocyanides and carboxymethyl groups. In the $^{31}P\{^1H\}$ NMR spectrum of **5a**, three resonances were observed at δ −7.6, 1.1, and 5.9 accompanied by satellite peaks due to coupling to ^{195}Pt ($^1J_{PtP}$ = 2777−2946 Hz). The spectral data of **5b** and **5c** were similar to those of **5a**. The structure of **5b** was elucidated by an X-ray analysis. An ORTEP plot of the complex cation of **5b** with the atomic numbering scheme is shown in Figure 1 and some selected bond lengths and angles are given in Table 2. The complex cation has an asymmetrical A-frame structure comprising three Pt atoms bridged by two dpmp ligands, in which an acetylene molecule was inserted into one of the Pt−Pt bonds. The Pt(1)−Pt(2) bond length is 2.718(1) Å and the Pt(2)···Pt(3) distance is 3.582(1) Å; the former is slightly shorter than that found in **3** (average 2.737 Å) and the latter is out of bonding range. The C(31)−C(32) bond length of 1.39(3) Å corresponds to the usual C−C double bond and those of Pt(2)−C(31) (2.03(2) Å) and Pt(3)−C(32) (2.02(2) Å), to the Pt−C σ-bond. The structure of **5b** clearly demonstrated that the linearly-ordered triplatinum platform is well supported by dpmp ligands during the reaction.

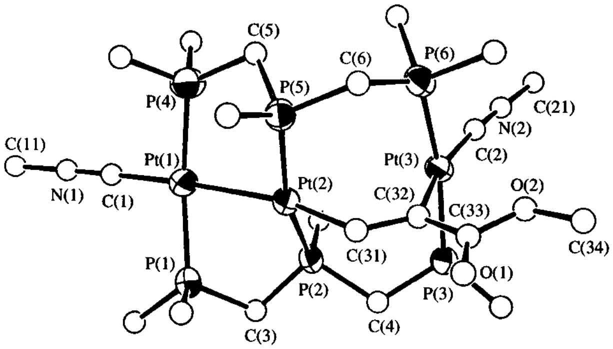


Figure 1. ORTEP plot of the complex cation of **5b,** $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}HCCCO_2Me)(XylNC)_2]^{2+}$, phenyl and xylyl rings being omitted for clarity.

Treatment of **3** with an excess of $HBF_4{\cdot}Et_2O$ gave the asymmetrical trinuclear complex $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}H)(XylNC)_2](BF_4)_3{\cdot}CH_2Cl_2$ (**6**$\cdot CH_2Cl_2$) in 61% yield. In the ^1H NMR spectrum, two singlets for the methyl groups of isocyanides were observed at δ 1.28 and 1.46, and the hydride peak was observed at δ −7.09 with two sets of satellite peaks due to coupling to two adjacent ^{195}Pt atoms ($^1J_{PtH}$ = 529 and 675 Hz) (Figure 2). The $^{31}P\{^1H\}$ NMR spectrum of **6** exhibited three multiplets with a 1:1:1 ratio, all being accompanied by ^{195}Pt satellites with $^1J_{PtP}$ = 2235−2613 Hz. Complex **6** is unstable in organic solvents and is likely to regenerate the linear trinuclear complex **3** by a loss of H atom. The similar reaction of **3** with 1 equiv of $p\text{-}NO_2C_6H_4NC$ led to the formation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^3NC)(XylNC)_2](PF_6)_2{\cdot}CH_2Cl_2$ (**7**$\cdot CH_2Cl_2$) in 94% yield ($R^3 = p\text{-}NO_2C_6H_4$). The IR spectrum of **7** showed bands correspond-

---

(8) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV. (b) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(9) *TEXSAN Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

(10) Johnson, C. K. *ORTEP-II*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}HC_2CO_2Me)(XylNC)_2](PF_6)_2$ (**5b**)[a]

Bond Distances			
Pt(1)−Pt(2)	2.718(1)	Pt(2)···Pt(3)	3.582(1)
Pt(1)−P(1)	2.293(6)	Pt(1)−P(4)	2.307(7)
Pt(1)−C(1)	1.97(2)	Pt(2)−P(2)	2.250(8
Pt(2)−P(5)	2.238(7)	Pt(2)−C(31)	2.03(2)
Pt(3)−P(3)	2.317(7)	Pt(3)−P(6)	2.323(8)
Pt(3)−C(2)	1.92(2)	Pt(3)−C(32)	2.02(2)
O(1)−C(33)	1.22(3)	O(2)−C(33)	1.35(2)
O(2)−C(34)	1.42(3)	N(1)−C(1)	1.19(2)
N(1)−C(11)	1.43(3)	N(2)−C(2)	1.18(3)
N(2)−C(21)	1.47(3)	C(31)−C(32)	1.39(3)
C(32)−C(33)	1.46(3)		
Bond Angles			
Pt(2)−Pt(1)−P(1)	78.3(1)	Pt(2)−Pt(1)−P(4)	88.4(1)
Pt(2)−Pt(1)−C(1)	176.8(6)	P(1)−Pt(1)−P(4)	163.0(2)
P(1)−Pt(1)−C(1)	98.8(6)	P(4)−Pt(1)−C(1)	94.3(7)
Pt(1)−Pt(2)−P(2)	87.8(1)	Pt(1)−Pt(2)−P(5)	95.4(1)
Pt(1)−Pt(2)−C(31)	166.2(6)	P(2)−Pt(2)−P(5)	160.0(2)
P(2)−Pt(2)−C(31)	94.8(8)	P(5)−Pt(2)−C(31)	86.7(7)
P(3)−Pt(3)−P(6)	166.6(2)	P(3)−Pt(3)−C(2)	96.9(7)
P(3)−Pt(3)−C(32)	82.5(7)	P(6)−Pt(3)−C(2)	96.4(7)
P(6)−Pt(3)−C(32)	84.9(7)	C(2)−Pt(3)−C(32)	167.1(7)
C(33)−O(2)−C(34)	117(2)	C(1)−N(1)−C(11)	179(3)
C(2)−N(2)−C(21)	178(2)	Pt(1)−C(1)−N(1)	174(2)
Pt(3)−C(2)−N(2)	172(2)	Pt(2)−C(31)−C(32)	124(2)
Pt(3)−C(32)−C(31)	121(1)	Pt(3)−C(32)−C(33)	121(1)
C(31)−C(32)−C(33)	117(2)	O(1)−C(33)−O(2)	123(2)
O(1)−C(33)−C(32)	128(2)	O(2)−C(33)−C(32)	110(2)

[a] Estimated standard deviations are given in parentheses.

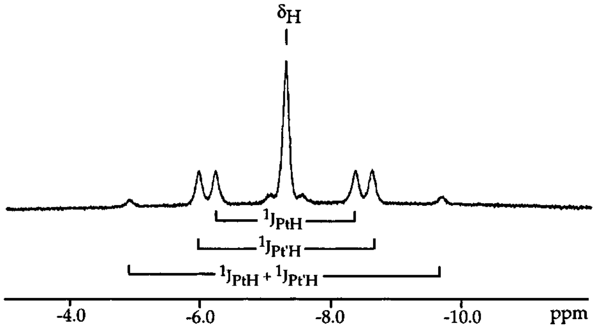


Figure 2. ^1H NMR spectrum of **6** showing a set of resonances for the bridging hydride.

ing to N≡C and C═N stretchings and the ^1H NMR spectrum indicated the presence of two kinds of xylyl isocyanides at δ 1.28 and 1.46 for *o*-methyl groups. On the basis of the spectroscopic data and the structure of **5b**, complexes **6** and **7** were assumed to have the asymmetrical A-frame structures as depicted in Scheme 2.

Reaction of *syn*-$[Pt_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (1) with $[MCl_2(cod)]$ (M = Pt, Pd). The reaction of the *syn*-type diplatinum complex **1** with $[MCl_2(cod)]$ gave yellow complexes formulated as $[Pt_2MCl_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (**8a**: M = Pt, 89%; **8b**: M = Pd, 55%). The IR spectrum of **8a** showed two N≡C stretching bands at 2199 and 2166 cm^{-1}, which were assigned to terminal isocyanide ligands. The ^1H NMR indicated the presence of two kinds of isocyanides at δ 1.51 and 1.71 for *o*-methyl protons. In the $^{31}P\{^1H\}$ NMR of **8a**, three resonances were observed at δ −7.6, −5.4, and 1.1 accompanied by satellite peaks due to coupling to ^{195}Pt ($^1J_{PtP}$ = 2276−3111 Hz). The structure of **8a** was determined by X-ray crystallography. An ORTEP diagram of the complex cation of **8a** with the atomic numbering scheme is illustrated in Figure 3 and some selected bond lengths and angles are listed in Table 3. The complex cation is comprised of a metal−metal-bonded diplatinum(I) core and a monomeric platinum(II) center bridged by two dpmp ligands. The Pt(1)−Pt(2) bond length of 2.681(2) Å is comparable to that of the dppm-bridged diplatinum(I) complex, $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (2.652 Å).[11] There is no bonding interaction between the Pt(2) and Pt(3) atoms (Pt(2)···Pt(3) = 3.219(2) Å). The two coordination planes around the Pt(2) and Pt(3) atom

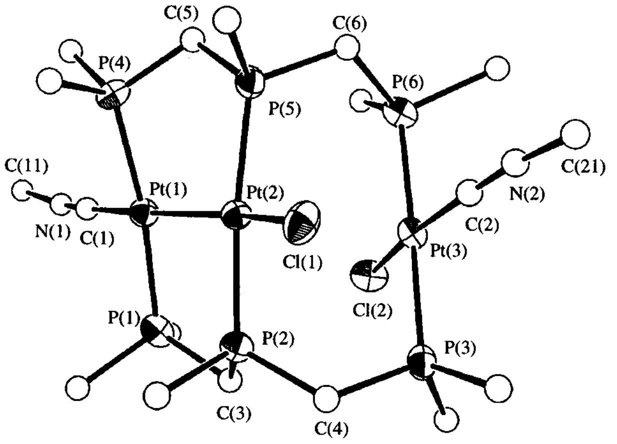


Figure 3. ORTEP diagram of the complex cation of **8a,** $[Pt_3Cl_2(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$, phenyl and xylyl rings being omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Pt_3Cl_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (**8a**)[a]

Bond Distances			
Pt(1)−Pt(2)	2.681(2)	Pt(2)···Pt(3)	3.219(2)
Pt(1)−P(1)	2.32(1)	Pt(1)−P(4)	2.30(1)
Pt(1)−C(1)	1.88(4)	Pt(2)−Cl(1)	2.430(9)
Pt(2)−P(2)	2.28(1)	Pt(2)−P(5)	2.29(1)
Pt(3)−Cl(2)	2.314(9)	Pt(3)−P(3)	2.36(1)
Pt(3)−P(6)	2.32(1)	Pt(3)−C(2)	1.85(4)
N(1)−C(1)	1.20(4)	N(1)−C(11)	1.52(5)
N(2)−C(2)	1.19(4)	N(2)−C(21)	1.45(4)
Bond Angles			
Pt(2)−Pt(1)−P(1)	94.7(3)	Pt(2)−Pt(1)−P(4)	88.0(2)
Pt(2)−Pt(1)−C(1)	178(1)	P(1)−Pt(1)−P(4)	171.9(4)
P(1)−Pt(1)−C(1)	87(1)	P(4)−Pt(1)−C(1)	90(1)
Pt(1)−Pt(2)−Cl(1)	165.0(2)	Pt(1)−Pt(2)−P(2)	90.6(2)
Pt(1)−Pt(2)−P(5)	94.1(3)	Cl(1)−Pt(2)−P(2)	87.7(3)
Cl(1)−Pt(2)−P(5)	88.8(3)	P(2)−Pt(2)−P(5)	173.8(4)
Cl(2)−Pt(3)−P(3)	88.6(3)	Cl(2)−Pt(3)−P(6)	92.4(3)
Cl(2)−Pt(3)−C(2)	170(1)	P(3)−Pt(3)−P(6)	177.6(4)
P(3)−Pt(3)−C(2)	93(1)	P(6)−Pt(3)−C(2)	86(1)
C(1)−N(1)−C(11)	169(4)	C(2)−N(2)−C(21)	172(3)
Pt(1)−C(1)−N(1)	172(4)	Pt(3)−C(2)−N(2)	175(3)

[a] Estimated standard deviations are given in parentheses.

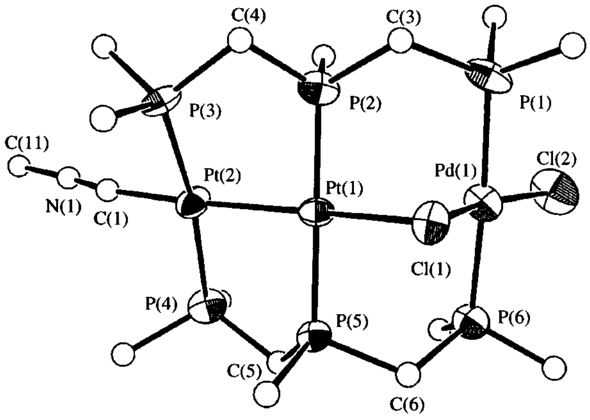


Figure 4. ORTEP view of the complex cation of **9,** $[Pt_2PdCl_2(\mu\text{-dpmp})_2(XylNC)]^{2+}$, phenyl and xylyl rings being omitted for clarity.

---

[11] Manojlovic-Muir, L.; Muir, K. M.; Solomun, T. *Acta Crystallogr.* **1979**, *B35*, 1237.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Pt_2PdCl(\mu\text{-}Cl)(\mu\text{-}dpmp)_2(XylNC)](PF_6)_2$ (**9**)[a]

Bond Distances			
Pt(1)−Pt(2)	2.606(2)	Pt(1)···Pd(1)	3.103(3)
Pt(1)−Cl(1)	2.494(9)	Pt(1)−P(2)	2.256(8)
Pt(1)−P(5)	2.252(8)	Pt(2)−P(3)	2.303(8)
Pt(2)−P(4)	2.292(8)	Pt(2)−C(1)	1.91(4)
Pd(1)−Cl(1)	2.349(9)	Pd(1)−Cl(2)	2.28(1)
Pd(1)−P(1)	2.339(8)	Pd(1)−P(6)	2.311(8)
N(1)−C(1)	1.15(6)	N(1)−C(11)	1.38(5)
Bond Angles			
Pt(2)−Pt(1)−Cl(1)	167.1(2)	Pt(2)−Pt(1)−P(2)	85.8(2)
Pt(2)−Pt(1)−P(5)	92.0(2)	Cl(1)−Pt(1)−P(2)	94.9(3)
Cl(1)−Pt(1)−P(5)	88.3(3)	P(2)−Pt(1)−P(5)	175.2(3)
Pt(1)−Pt(2)−P(3)	89.0(2)	Pt(1)−Pt(2)−P(4)	93.5(2)
Pt(1)−Pt(2)−C(1)	176.2(9)	P(3)−Pt(2)−P(4)	168.4(4)
P(3)−Pt(2)−C(1)	87.1(9)	P(4)−Pt(2)−C(1)	90.3(9)
Cl(1)−Pd(1)−Cl(2)	164.4(4)	Cl(1)−Pd(1)−P(1)	88.4(3)
Cl(1)−Pd(1)−P(6)	91.8(3)	Cl(2)−Pd(1)−P(1)	92.2(3)
Cl(2)−Pd(1)−P(6)	88.5(3)	P(1)−Pd(1)−P(6)	176.3(4)
Pt(1)−Cl(1)−Pd(1)	79.6(3)	C(1)−N(1)−C(11)	174(4)
Pt(2)−C(1)−N(1)	165(4)		

[a] Estimated standard deviations are given in parentheses.

are located in a face-to-face arrangement. Although the NMR spectroscopic data for **8b** were not obtained because of its instability in the solution state, a Pt_2Pd heterometallic structure similar to that of **8a** was deduced from the analytical and IR spectroscopic data as well as X-ray crystal structures of **9** (*vide infra*).

Structure of Asymmetrical A-Frame Pt_2Pd Complex. The heteronuclear complex **8b**, when it was kept in CH_2Cl_2 for 1−2 days, lost one terminal isocyanide to be converted into a chloride-bridged heterotrinuclear complex, $[Pt_2PdCl(\mu\text{-}Cl)(\mu\text{-}dpmp)_2(XylNC)_2](PF_6)_2$ (**9**), in 41% yield. The IR and ^1H NMR spectra suggested the presence of one terminal isocyanide ligand. In the $^{31}P\{^1H\}$ NMR spectrum, three resonances appeared at δ −1.7, 6.5, and 10.0 with an intensity ratio of 1:1:1; the former two are accompanied by satellite peaks due to coupling to ^{195}Pt ($^1J_{PtP} = 2365, 2801$ Hz, respectively) and the latter is without ^{195}Pt satellite peaks. The structure was characterized by an X-ray crystallographic analysis. An ORTEP view of the complex cation of **9** with the atomic numbering scheme is given in Figure 4, and some selected bond lengths and angles are summarized in Table 4. The complex cation exhibited an asymmetrical A-frame structure of the Pt_2Pd aggregation. The A-frame part is composed of a Pt(1)−Cl(1)−Pd(1) core with an angle of 79.6(3)° and a Pt(1)···Pd(1) distance of 3.103(3) Å. The Pt(1)−Pt(2) bond length is 2.606(2) Å, which is fairly shorter than is found in **8a**. A similar Cl-bridged asymmetrical A-frame aggregation, Rh(μ-Cl)PdRh, has already been observed in $[Rh_2Pd(CO)_2(\mu\text{-}Cl)Cl_2(\mu\text{-}dpma)_2]^{2+}$ (dpma = bis((diphenylphosphino)methyl)phenylarsine).[12]

Conclusion

The present reactions, insertions of small molecules into a metal−metal bond in the linear trinuclear complexes of platinum, can provide a new field of asymmetrical A-frame trinuclear complexes, which are of general interest as mimetic models for the interactions of the surfaces of heterogeneous catalysts with small molecules. Further, the synthetic methodology to heterotrinuclear complexes by utilizing *syn*-$[Pt_2(dpmp)_2(XylNC)_2]^{2+}$, which enables the heteroatom to sit in the terminal position of trinuclear array, is interestingly contrasted to the methods by using dinuclear complexes of dpma (bis((diphenylphosphino)methyl)phenylarsine) and $(Ph_2P)_2py$ (2,6-bis(diphenylphosphino)pyridine), which can house the heteroatom in the middle position,[4i] and may thus lead to a new class of heterotrimetallic systems.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

Supporting Information Available: Tabulations of crystallographic data, positional and thermal parameters, and bond lengths and angles of non-hydrogen atoms and perspective plots of complex cations for **5b**, **8a**, and **9** (30 pages). Ordering information is given on any current masthead page.

IC951186J

---

(12) Bailey, D. A.; Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.* **1987**, *26*, 2413.