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# Platinum-Based Heterotrinuclear Complexes Involving a Group 9 Metal Ion: MCl(isocyanide)-Fragment-Capped Pt$_2$M T-Shaped Clusters (M = Rh(I), Ir(I))

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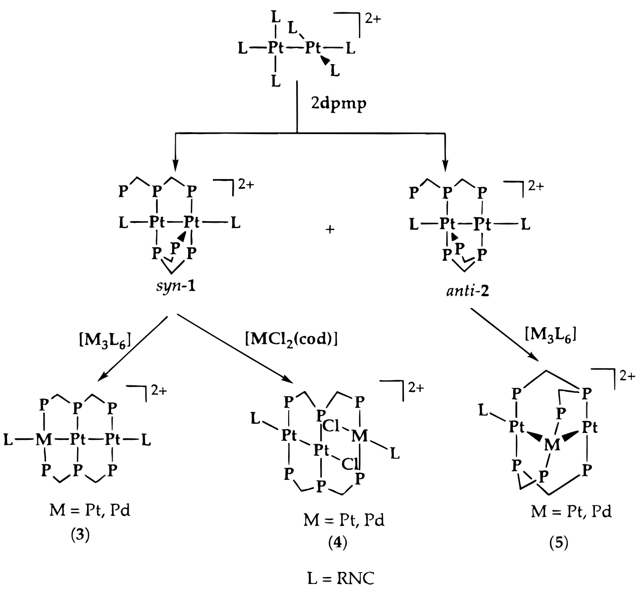
*Summary:* Reactions of *syn*-[Pt$_2$($\mu$-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**1**), where dpmp = bis((diphenylphosphino)methyl)phenylphosphine and Xyl = 2,6-xylyl, with [MCl(cod)]$_2$ (M = Rh, Ir) afforded the linearly ordered Pt−Pt−M clusters [Pt$_2${MCl(XylNC)}($\mu$-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (**6a**, M = Rh; **6b**, M = Ir) and the asymmetrical A-frame clusters [Pt$_2${M(XylNC)}($\mu$-Cl)($\mu$-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (**7a**, M = Rh; **7b**, M = Ir). The structures of **6a** and **6b** as well as that of **7a** were determined by X-ray crystallography to reveal that the trinuclear core of the linearly ordered clusters **6** is joined by two metal−metal bonds in which the Pt−Pt and Pt−M bonds can be viewed, respectively, as d$^9$−d$^9$ covalent and a d$^9$←d$^8$ dative interactions.

Construction of a new transition-metal assembly is a significant subject because small metal−metal-bonded clusters could serve as minimal models for the surface of heterogeneous catalysts and have the potential to promote new homogeneous catalytic reactions which are not established by mononuclear centers. In designing such cluster cores, one of the most significant problems is how to stabilize the cluster aggregation to resist cluster fragmentation during chemical reactions. The choice of supporting ligands such as multidentate phosphines is thus important in developing new metal assemblages, hopefully coordinatively unsaturated ones.[1−4] In this respect, the tridentate phosphine ligand bis((diphenylphosphino)methyl)phenylphosphine (dpmp) has attracted our attention because the dpmp ligand has versatile bridging and chelating coordination behavior toward di- and trinuclear metal centers.[5] We have recently established a new strategic synthetic route to homo- and heterotrimetallic clusters with Pt$_2$M metal cores by using the isomeric diplatinum complexes *syn*- and *anti*-[Pt$_2$($\mu$-dpmp)$_2$(isocyanide)$_2$]$^{2+}$ (*syn*-**1**, *anti*-**2**) as precursors (Scheme 1).[6] The *syn*-type dimer was readily transformed by treatment with d$^{10}$ M(isocyanide)$_2$ fragments and d$^8$ metal species [MCl$_2$(cod)] (cod = cyclooctadiene) to the novel linear homo- and heterotrinuclear clusters *linear*-[Pt$_2$M($\mu$-dpmp)$_2$(isocyanide)$_2$]$^{2+}$ (**3**: M = Pt, Pd)[6] and combined dimer−monomer complexes [PtMCl$_2$($\mu$-dpmp)$_2$(isocyanide)$_2$]$^{2+}$ (**4**),[7] respectively, and the *anti*-type dimer was transformed with the d$^{10}$ M(isocyanide) fragment to the A-frame trinuclear clusters *A-frame*-[Pt$_2$M($\mu$-dpmp)$_2$(isocyanide)$_2$]$^{2+}$ (**5**)[8] (Scheme 1). Interestingly, the inserted position of the additional metal depends on the diplatinum precursors used. We applied this synthetic methodology to group 9 metal ions and wish to report herein the new linear clusters of [Pt$_2${MCl(XylNC)}($\mu$-dpmp)$_2$(XylNC)]$^{2+}$ (M = Rh(I), Ir(I)) together with an isomeric cluster with a Pt−Pt−M A-frame array, *A-frame*-[Pt$_2${M($\mu$-Cl)(XylNC)}($\mu$-dpmp)$_2$(XylNC)]$^{2+}$.

**Scheme 1**



The *syn*-type diplatinum complex *syn*-[Pt$_2$($\mu$-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**1**) was treated with [RhCl(cod)]$_2$ to afford two reddish orange complexes formulated as [Pt$_2$RhCl(dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**6a** and **7a**) (Scheme 2).[9] Compounds **6a** and **7a** did not interconvert with each other at room temperature and were isolated by recrystallization in 58% and 32% yields, respectively. The IR and $^1$H NMR spectra of both **6a** and **7a** indicated the presence of two nonequivalent terminal isocyanide ligands, presumably one coordinating to a Pt atom and

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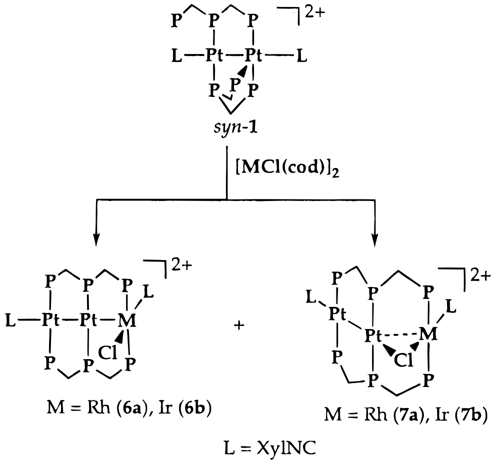
**Scheme 2**



the other to a Rh center on the basis of their N−C stretching energies. The electronic absorption spectra of **6a** and **7a** are quite different; that of **6a** showed a characteristic band centered at 416 nm and that of **7a** at 463 nm. The $^{31}P\{^1H\}$ NMR spectrum of **6a** exhibited two multiplets from phosphorus atoms bound to platinum atoms ($^1J_{PtP} = 2466$ and 2800 Hz) and a doublet of doublets of multiplets due to phosphorus atoms coordinated to the rhodium center ($^1J_{RhP} = 106-108$ Hz and $^2J_{PP'} = 428$ Hz), whereas that of **7a** consisted of two multiplets ($^1J_{PtP} = 2466$ and 2810 Hz) and a doublet of multiplets ($^1J_{RhP} = 122$ Hz). A similar reaction with $[IrCl(cod)]_2$ gave the analogous clusters **6b** and **7b**, formulated as $[Pt_2IrCl(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$, in 36% and 34% yields, respectively. The spectroscopic features of **6b** and **7b** are similar to those of the corresponding $Pt_2Rh$ clusters (Scheme 2).[10]

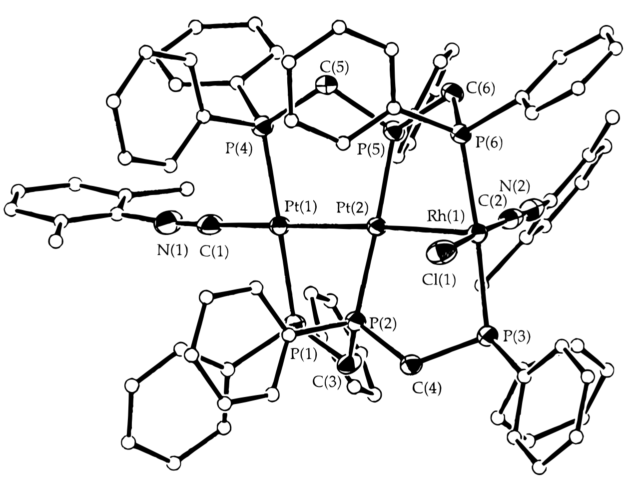


**Figure 1.** ORTEP view of the complex cation of $\mathbf{6a}\cdot 2CH_2Cl_2$, $[Pt_2\{RhCl(XylNC)\}(\mu\text{-dpmp})_2(XylNC)]^{2+}$. Carbon atoms of the phenyl and xylyl groups are drawn with arbitrary circles, and hydrogen atoms are omitted for clarity. Some selected bond distances (Å) and angles (deg) are as follows: Pt(1)−Pt(2) = 2.6588(3), Pt(2)−Rh(1) = 2.7537(5), Pt(1)−P(1) = 2.309(1), Pt(1)−P(4) = 2.322(1), Pt(1)−C(1) = 1.947(6), Pt(2)−P(2) = 2.262(1), Pt(2)−P(5) = 2.269(1), Rh(1)−P(3) = 2.334(1), Rh(1)−P(6) = 2.293(1), Rh(1)−Cl(1) = 2.358(1), Rh(1)−C(2) = 1.884(6); Pt(1)−Pt(2)−Rh(1) = 177.13(1), Pt(2)−Pt(1)−C(1) = 178.1(2), Pt(2)−Rh(1)−C(2) = 77.8(2), Pt(2)−Rh(1)−Cl(1) = 105.72(4), C(2)−Rh(1)−Cl(1) = 176.5(2).

The structures of **6a** and **6b** were determined by X-ray crystallography to consist of a linearly ordered $Pt_2M$ core bridged by two dpmp ligands. The structures of **6a** and **6b** are isomorphous, and an ORTEP plot of the complex cation of **6a** is given in Figure 1.[11,12] The terminal platinum is three-coordinated with two terminal P atoms of dpmp and an isocyanide molecule, and the central platinum is two-coordinated with two central P atoms of dpmp. The additional metal (Rh, Ir) is four-coordinated with the other two terminal P atoms of dpmp, an isocyanide, and a chloride anion. The three metal units are joined by metal−metal bonds. The Pt−Pt vector is almost perpendicular to the square plane of the M(I) ion. In other words, the $Pt^I_2$ dinuclear core is terminally capped by the M(I) square plane, resulting in a T-shaped LPtPtMClL (L = XylNC) structure linearly bridged by the two triphosphine ligands. The Pt−Pt distances are 2.6588(3) Å (**6a**) and 2.652(2) Å (**6b**), and the Pt−M distances are 2.7537(5) Å (**6a**) and 2.765(2) Å (**6b**). The former values are in the range of $Pt^I-Pt^I$ single-bond distances and the latter slightly longer than the $Pt^{II}-Rh^I$ (2.688(2)−2.709(2) Å) and the $Pt^{II}-Ir^I$ (2.730(2) Å) distances found in the 3:5 type dinuclear complexes of $[PtRh(\mu\text{-dppm})_2(CH_3NC)_4]^{3+}$, $[PtRh(\mu\text{-dppm})_2(CH_3NC)_3X]^{2+}$ (dppm = bis(diphenylphosphino)methane, X = Cl, I),[13] and $[PtIr(CO)Cl(\mu\text{-dpmp})_2]^{2+}$.[14] The Pt−M bond can be viewed as a dative bond with the $d^8$ Rh(I) or Ir(I) acting as a two-electron donor to the Pt(I) atom and the Pt−Pt bond as a typical covalent bond with two $d^9$ electronic configurations. The total valence electron count for the trinuclear core is

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[9] To a dichloromethane solution (50 mL) containing *syn*-$[Pt_2(dpmp)_2(XylNC)_2](PF_6)_2$ (1.00 g, $5.12 \times 10^{-1}$ mmol) was added a dichloromethane solution (10 mL) of $[RhCl(cod)]_2$ (0.130 g, $2.64 \times 10^{-1}$ mmol). The reaction mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, and the residue was crystallized from a $CH_2Cl_2/Et_2O$ mixed solvent to give orange crystals of **6a** (0.620 g, 58%). Addition of $Et_2O$ to the mother liquor afforded dark orange crystals of **7a** (0.339 g, 32%). Analytical and spectroscopic data are as follows. **6a**: Anal. Calcd for $C_{82}H_{76}N_2F_{12}P_8ClPt_2Rh$: C, 47.04; H, 3.66; N, 1.34. Found: C, 47.30; H, 3.65; N, 1.09. IR (Nujol): 2160, 2120 (N≡C) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.39 (s, *o*-Me), 1.48 (s, *o*-Me), 3.3−5.2 (m, $CH_2$), 6.5−8.4 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −4.66 (m, $^1J_{PtP} = 2466$ Hz, 2P), 4.64 (m, $^1J_{PtP} = 2800$ Hz, 2P), 17.65 (d × d × m, $^1J_{RhP} = 108$ Hz, $^2J_{PP} = 428$ Hz, 1P), 27.79 (d × d × m, $^1J_{RhP} = 106$ Hz, $^2J_{PP} = 428$ Hz, 1P). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\epsilon$) 416 (4.00), 375 (4.02) nm. **7a**: Anal. Calcd for $C_{82}H_{76}N_2F_{12}P_8ClPt_2Rh$: C, 47.04; H, 3.66; N, 1.34. Found: C, 46.94; H, 3.62; N, 1.29. IR (Nujol): 2176, 2091 (N≡C) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.67 (s, *o*-Me), 1.84 (s, *o*-Me), 3.6−5.6 (m, $CH_2$), 6.9−8.4 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −0.25 (m, $^1J_{PtP} = 2466$ Hz, 2P), 1.64 (m, $^1J_{PtP} = 2810$ Hz, 2P), 19.80 (d × m, $^1J_{RhP} = 122$ Hz, $^2$P). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\epsilon$) 463 (3.72) nm.

[10] Analytical and spectroscopic data are as follows. $\mathbf{6b}\cdot 0.5CH_2Cl_2$: Anal. Calcd for $C_{82.5}H_{77}N_2F_{12}P_8Cl_2Pt_2Ir$: C, 44.52; H, 3.49; N, 1.26. Found: C, 44.18; H, 3.63; N, 1.37. IR (Nujol): 2164, 2099 (N≡C) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.36 (s, *o*-Me), 1.50 (s, *o*-Me), 3.3−5.2 (m, $CH_2$), 6.5−8.4 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ −4.46 (m, $^1J_{PtP} = 2475$ Hz, 2P), 0.18 (m, $^1J_{PtP} = 2774$ Hz, 2P), 15.10 (d × m, $^2J_{PP} = 393$ Hz, 1P), 25.88 (d × m, $^2J_{PP} = 393$ Hz, 1P). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\epsilon$) 461 (3.44), 373 (4.09) nm. **7b**: Anal. Calcd for $C_{82}H_{76}N_2F_{12}P_8ClPt_2Ir$: C, 45.11; H, 3.51; N, 1.28. Found: C, 44.65; H, 3.31; N, 1.21. IR (Nujol): 2160, 2056 (N≡C) $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 1.00 (s, *o*-Me), 1.65 (s, *o*-Me), 3.4−5.5 (m, $CH_2$), 6.6−8.3 (m, Ar). $^{31}P\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 1.26 (m, $^1J_{PtP} = 2466$ Hz, 2P), 6.33 (m, $^1J_{PtP} = 2837$ Hz, 2P), 19.20 (m, 2P). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ 569, 397, 322 nm.

[11] Crystal data for $\mathbf{6a}\cdot 2CH_2Cl_2$: $C_{84}H_{80}N_2P_8F_{12}Cl_5Pt_2Rh$, monoclinic, $P2_1/c$ (No. 14), $a = 24.951(2)$ Å, $b = 15.772(1)$ Å, $c = 25.526(4)$ Å, $\beta = 119.20(1)°$, $V = 8769$ Å$^3$, $Z = 4$, $D_{calcd} = 1.714$ g cm$^{-3}$, $T = -80$ °C, $R = 0.027$, and $R_w = 0.040$ for 10 013 unique reflections with $I > 3\sigma(I)$.

[12] Crystal data for **6b**: $C_{82}H_{76}N_2P_8F_{12}ClPt_2Ir$, triclinic, $P\bar{1}$ (No. 2), $a = 15.987(6)$ Å, $b = 22.041(6)$ Å, $c = 15.145(7)$ Å, $\alpha = 103.31(3)°$, $\beta = 95.86(4)°$, $\gamma = 74.68(2)°$, $V = 5004$ Å$^3$, $Z = 2$, $D_{calcd} = 1.449$ g cm$^{-3}$, $T = 23$ °C, $R = 0.062$, and $R_w = 0.069$ for 6574 unique reflections with $I > 3\sigma(I)$.

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[14] Balch, A. L.; Catalano, V. J. *Inorg. Chem.* **1992**, *31*, 2569.

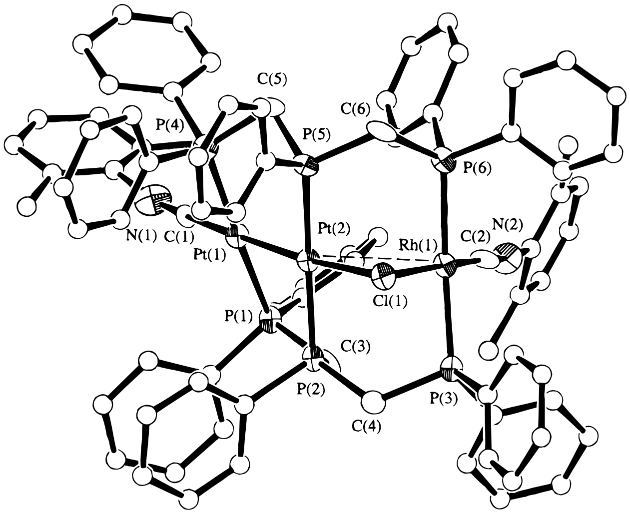

**Figure 2.** ORTEP plot of the complex cation of **7a**·$4CH_2Cl_2$, $[Pt_2\{Rh(XylNC)\}(\mu\text{-}Cl)(\mu\text{-dpmp})_2(XylNC)]^{2+}$. Carbon atoms of the phenyl and xylyl groups are drawn with arbitrary circles, and hydrogen atoms are omitted for clarity. Some selected bond distances (Å) and angles (deg) are as follows: Pt(1)−Pt(2) = 2.644(1), Pt(2)−Rh(1) = 2.967(2), Pt(1)−P(1) = 2.289(5), Pt(1)−P(4) = 2.330(5), Pt(1)−C(1) = 1.85(1), Pt(2)−Cl(1) = 2.563(4), Pt(2)−P(2) = 2.248(5), Pt(2)−P(5) = 2.283(5), Rh(1)−P(3) = 2.283(5), Rh(1)−P(6) = 2.323(6), Rh(1)−Cl(1) = 2.406(4), Rh(1)−C(2) = 1.86(1); Pt(1)−Pt(2)−Rh(1) = 125.21(4), Pt(1)−Pt(2)−Cl(1) = 174.9(1), Pt(2)−Pt(1)−C(1) = 177.8(6), Pt(2)−Rh(1)−C(2) = 118.5(6), Pt(2)−Cl(1)−Rh(1) = 73.3(1), C(2)−Rh(1)−Cl(1) = 173.8(6).

44, with 16 apparent valence electrons for each metal. An $Au_2Pt$ cluster with a $d^9-d^8-d^9$ metal−metal-bonded system has already been reported.[15]

A perspective drawing of the complex cation of **7a** is illustrated in Figure 2.[16] The cluster core involves two platinum atoms and one rhodium atom bridged by two dpmp ligands, and a chloride anion occupies the vertex of an asymmetrical A-frame trinuclear structure. The Pt(1)−Pt(2) distance of 2.644(1) Å confirmed the presence of a typical metal−metal σ-bond between them. The Pt(2) and Rh(1) atoms are spanned by a chloride bridge (Pt(2)−Cl(1)−Rh(1) = 73.3(1)°); the distance between them 2.967(2) Å, is longer by ~0.31 Å than that of **6a** but still indicates a weak bonding interaction in comparison with the corresponding parameters (Pt···Pd = 3.103(3) Å, Pt−Cl−Pd = 79.6(3)°) found in *A-frame*-$[Pt_2(PdCl)(\mu\text{-}Cl)(\mu\text{-dpmp})_2(XylNC)]^{2+}$ (**8**),[7] which possesses an analogous $Pt_2M$ trimetallic core. The donation from Cl(1) to Pt(2) is estimated to be weak on the basis of the long distance of 2.563(4) Å.

The present study reports a synthetic route to new Pt−Pt−M (M = Rh, Ir) heterotrimetallic clusters with a $d^9-d^9-d^8$ metal combination, the structures of which can be interestingly compared with those of *linear*-$[Pt_2M(\mu\text{-dpmp})_2(XylNC)_2]^{2+}$ (M = Pt(I), Pd(I); $d^9-d^{10}-d^9$),[6] $[Pt_2Cl\{MCl(XylNC)\}(\mu\text{-dpmp})_2(XylNC)]^{2+}$ (M = Pt(II), Pd(II); $d^9-d^9-d^8$),[7] and $[Pt_2M(\mu\text{-dpmp})_2(XylNC)_2]^{3+}$ (M = Au(I), Ag(I); $d^9-d^9-d^{10}$).[17] These homo- and heterotrimetallic families could provide a systematic platform to explore new catalytic functions.

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**Supporting Information Available:** Tables of crystallographic data, positional and thermal parameters, and bond distances and angles for **6a**·$2CH_2Cl_2$, **7a**·$4CH_2Cl_2$, and **6b** and an ORTEP diagram of the complex cation of **6b** (31 pages). Ordering information is given on any current masthead page.

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[15] Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992.

[16] Crystal data for **7a**·$4CH_2Cl_2$: $C_{86}H_{84}N_2P_8F_{12}Cl_9Pt_2Rh$, monoclinic, *Pn* (No. 7), $a = 14.892(7)$ Å, $b = 20.813(6)$ Å, $c = 16.742(3)$ Å, $\beta = 113.50(2)°$, $V = 4758$ Å$^3$, $Z = 2$, $D_{calcd} = 1.698$ g cm$^{-3}$, $T = -95$ °C, $R = 0.049$, and $R_w = 0.052$ for 6509 unique reflections with $I > 3\sigma(I)$.

[17] Tanase, T.; Toda, H.; Yamamoto, Y. Submitted for publication.