© 2002 The Chemical Society of Japan Bull. Chem. Soc. Jpn., **75**, 1407–1422 (2002) 1407

Accounts

Recent Development of Linearly Ordered Multinuclear Transition-Metal Complexes

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(Received August 6, 2001)

This paper reviews the recent development of linearly ordered multinuclear transition-metal complexes, which have been of increasing interest as potential nanostructured molecular units and their precursors. In particular, it focuses on our recent results of platinum-based homo- and heteromultimetallic complexes supported by the tridentate phosphine ligands, bis(diphenylphosphinomethyl)phenylphosphine (dpmp). The synthetic strategy involved the metal core expansion using the diplatinum precursors having two uncoordinated phosphine pendants, *syn*- and *anti*-$[Pt_2(\mu\text{-dpmp})_2(RNC)_2]^{2+}$ (**11** and **12**), which allowed us to gain access to versatile homo- and heterotrinuclear complexes with Pt_2M cores. Reactions of **11** with d^{10} and d^8 metal fragments afforded the Pt–Pt–M metal frameworks (M = Pt, Pd, Au, Ag, Cu, Ir, Rh), and in contrast, those of **12** gave the Pt–M–Pt ones (M = Pt, Pd, Rh). The inserted position of the additional metal interestingly depends on the two dpmp arrangement of the starting diplatinum complexes. The corresponding chemistry of palladium and gold complexes is also described. Since the metal–metal bonded triplatinum complex, *linear*-$[Pt_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (**16**), was regarded as a minimal model for the surface of metal catalysts, its reactions with various small organic molecules were examined. Further, the axial ligand exchange reactions of **16** with bulky aromatic bisisocyanide led to a one-dimensional assemblage of the linear Pt_3 units, resulting in rigid rod-like cluster polymers, and the reduction of **16** afforded the linearly ordered hexaplatinum cluster molecules supported by four dpmp ligands through a direct combination of the two linear Pt_3 fragments.

Multinuclear transition-metal complexes have attracted increasing attention in various chemical fields since they have the potential to act as new multifunctional materials thanks to their versatile chemical and physical properties.[1] In particular, linearly constrained, multimetallic cluster molecules have been promising precursors in developing nanostructured materials including molecular-scale electronic, optical, and chemical devices. In designing metal-metal bonded cluster cores and creating new metal assemblages, synthetic strategy and choice of polydentate supporting ligands for metals are very important. In the following parts, recent developments of linearly ordered multinuclear complexes with various supporting ligands are briefly surveyed. In general, synthetic methods using self-assembly of metal atoms often led to polyhedral cluster cores and thus, routes to linear metal aggregations have been extremely limited. Whereas a number of interesting structures and physical properties of solid-state compounds with one-dimensionally assembled metal chains have been reported,[2] the present account mainly focuses on discrete cluster molecules which involve linear multimetallic chains.

The well-known bridging ligand, bis(diphenylphosphino)methane (dppm), and its analogues have been extensively used to prepare metal-metal bonded dinuclear motives (Chart 1); the dinuclear Pt(I) and Pd(I) complexes (**1**) bridged by two dppm ligands have been studied as a minimal model of metal surfaces with regard to their ability to react with small molecules through additions across the metal-metal bond (Chart 2).[3–5] However, dppm was not a suitable ligand for linear multimetallic aggregations; instead, it supported the triangular trimetallic systems. Puddephatt et al. have reported the electron-deficient triplatinum complex, $[Pt_3(\mu\text{-dppm})_3(\mu_3\text{-CO})]^{2+}$ (**2**) (Chart 2), which could provide an unsaturated reaction site composed of three metal atoms, a variety of small molecules and metal fragments being introduced to the coordinatively unsaturated Pt_3 triangular face.[6–11]

The tridentate phosphine ligand, bis(diphenylphosphinomethyl)phenylphosphine (dpmp) (Chart 1), showed versatile bridging and chelating coordination behaviors for di- and trinuclear metal centers (Chart 1).[12–25] The chemistry of linearly ordered small-size clusters, mainly focused on rhodium and iridium, has systematically been studied by Balch and his coworkers; in particular, the trirhodium complex of $[Rh_3(\mu\text{-Cl})Cl(\mu\text{-dpmp})_2(CO)_3]^+$ (**3**) showed a variety of reactions with small molecules (Chart 2).[14–24] The analogous tridentate ligands, bis(diphenylphosphinomethyl)phenylarsine (dpma) and 2,6-bis(diphenylphosphino)pyridine (dppy), have been

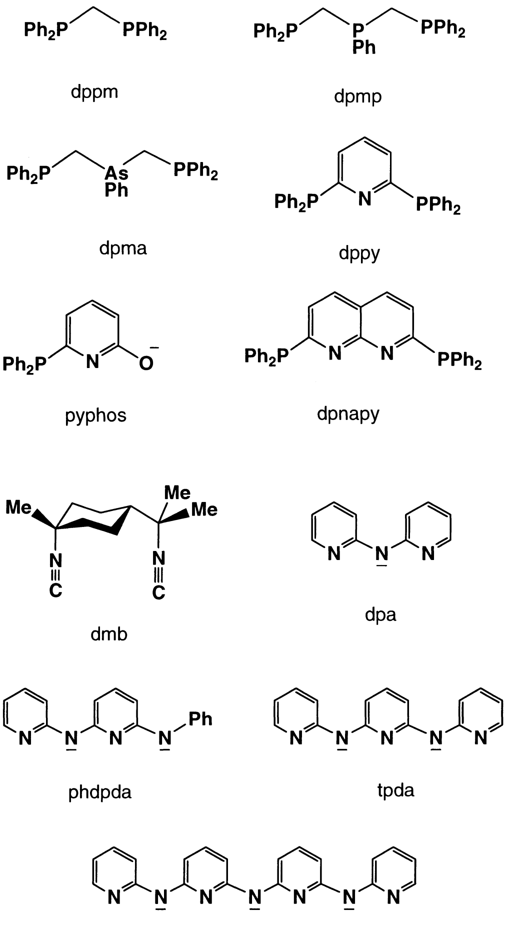
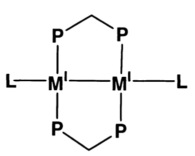
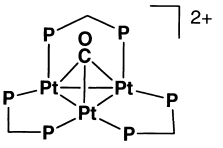


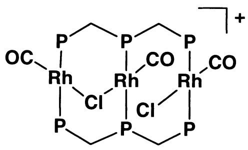
Chart 1. Supporting ligands and their abbreviation.



(**1**) M = Pt, Pd



(**2**)

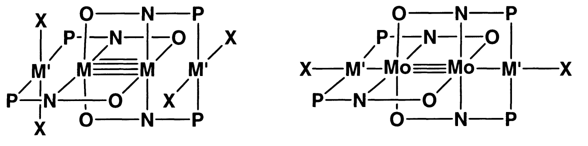


(**3**)

Chart 2.

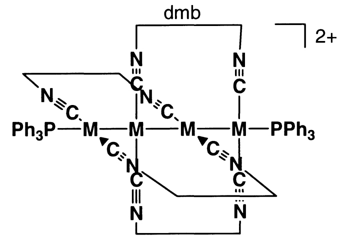
used in similar cluster chemistry, which has also been reviewed by Balch (Chart 1).[12,13] The rigid mixed-donor dppy ligand can stabilize Rh and Ir-based linear heterotrimetallic aggregations in which the heteroatom sits in the central position. In contrast, the corresponding chemistry of Pt and Pd has largely been unexplored. Recently, Mashima et al. have developed an anionic rigid PNO ligand, 6-diphenylphosphino-2-pyridonate (pyphos) (Chart 1), and have successfully synthesized the linear tetrametallic complexes involving M′-M-M-M′ cores (M = Mo, Cr, M′ = Pt, Pd) (**4**), by reactions of the quadruply bonded dinuclear complexes of pyphos, $[M_2(\text{pyphos})_4]$, with the heterometal complexes; the representative complexes are depicted in Chart 3.[26] The linearly constrained tetradentate PNNP ligand, 2,7-bis(diphenylphosphino)-1,8-naphthylidine (dpnapy), has also been assumed to support linearly ordered metallic frameworks. Its cluster chemistry has not been fruitful thus far, examples being $[\text{Au}_2\text{K}(\mu\text{-dpnapy})_3]^{3+}$, $[\text{Ag}_3(\mu\text{-dpnapy})_3]^{3+}$, and *cis*- and *trans*-$[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-dpnapy})_2]^{2+}$.[27]

By utilizing polydentate ligands other than phosphines, several groups have recently presented excellent studies on linearly ordered cluster molecules. Harvey and his co-workers have prepared the linear tetraplatium and palladium cluster molecules by using a bisisocyanide, 1,8-diisocyano-*p*-menthan (dmb) (Chart 1), formulated as $[\text{M}_4(\mu\text{-dmb})_4(\text{PPh}_3)_2]^{2+}$ (**5**) (Chart 4).[28] The axial phosphine ligands of **5** (M = Pt) were replaced by diphosphines to afford the cluster polymers in which the tetraplatinum fragments, $\{\text{Pt}_4(\mu\text{-dmb})_4\}^{2+}$, were connected by $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (n = 4–6). Kurosawa et al. have synthesized the tri-, tetra-, and pentanuclear palladium complexes by using the polyene ligands $\text{Ph}(\text{CH})_n\text{Ph}$ (n = 8, 12).[29] The linear cationic clusters, $[\text{Pd}_4(\text{Ph}(\text{CH})_8\text{Ph})_2]^{2+}$ and

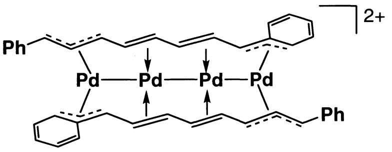


(**4a**) M = Mo; M = Pt, Pd; X = Cl, Br, I (**4c**) M′ = Pt, Pd; X = Cl, Br, I
(**4b**) M = Cr; M′ = Pt; X = Cl, Me

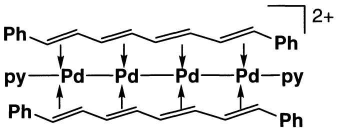
Chart 3. P–N–O = pyphos.



(**5**) M = Pt, Pd

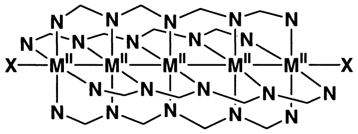


(**6a**)

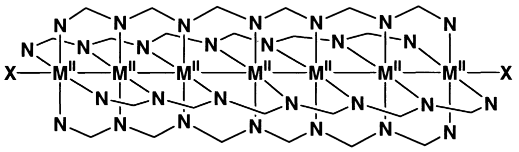


(**6b**)

Chart 4.



(**8**) M = Ni, Co, Cr; X = Cl, CN, N_3, NCS



(**10**) M = Ni, Cr; X = Cl, NCS

Chart 5.

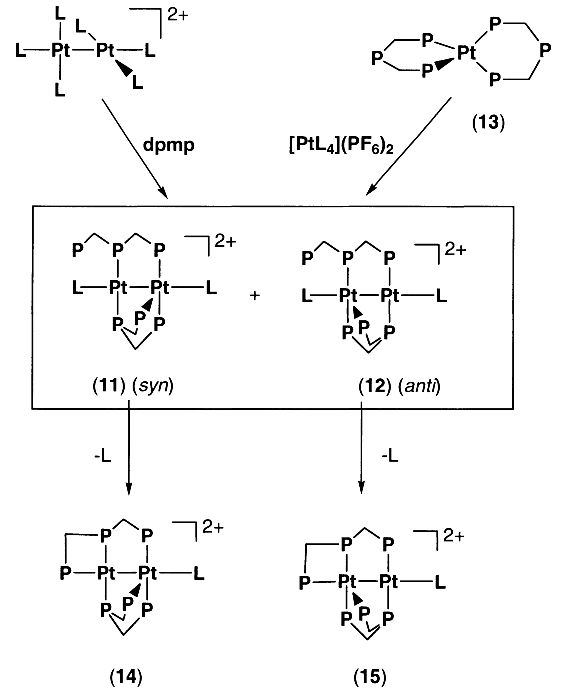
$[Pd_4(Ph(CH)_8Ph)_2(pyridine)_2]^{2+}$ (**6**), were unambiguously characterized by X-ray crystallography to comprise a linear tetrapalladium chain sandwiched by two linearly π-conjugated polyene ligands (Chart 4). These studies suggested that the linear metallic chains with general $M^I(M^0)_nM^I$ (M = Pt, Pd) configurations could be stabilized by utilizing appropriately designed supporting ligands.

Peng and Cotton have independently developed the linearly ordered multinuclear complexes of Ni, Co, Cr, Cu, Ru, and Rh with oligo(2-pyridyl)amido ligands, $[2\text{-py}(N\text{-}2\text{-py})_n]^{n-}$, which were systematically prepared (Chart 1). A number of trimetallic cores were stabilized with four bis(2-pyridyl)amido anions (dpa),[30,31] which further fixed the linear Cu_4 and Mo_2Cu_2 aggregations.[32] The tetra-, penta-, and heptametallic strings were successfully constructed using tris(2-pyridyl)diamido (tpda), *N*-phenyldi(2-pyridyl)diamido (phdpda), and tetra(2-pyridyl) triamido (teptra) ligands (Chart 1), as observed in the X-ray characterized compounds, $[Ni_4(\mu\text{-phdpda})_4]$ (**7**),[33a] $[M_5(\mu\text{-tpda})_4X_2]$ (M = Ni, Cr, Co; X = Cl, CN, N_3, NCS) (**8**),[33] $[Ni_5(\mu\text{-tpda})_4(CH_3CN)_2]^{2+}$ (**9**), $[M_7(\mu\text{-teptra})_4X_2]$ (M = Ni, Cr, X = Cl, NCS) (**10**) (Chart 5).[33] These compounds are in a hot topic with regard to molecular designed metallic wires.

We have studied the structurally constrained multinuclear complexes with a variety of organic ligands.[34] Recently, we found strategic synthetic routes by utilizing dpmp ligands to the linear Pt-Pt-M (M = Pt, Pd, Ir, Rh, Au, Ag) and Pt-Pt-M-M-Pt-Pt (M = Pt, Pd) clusters; such routes are described in the following chapters.

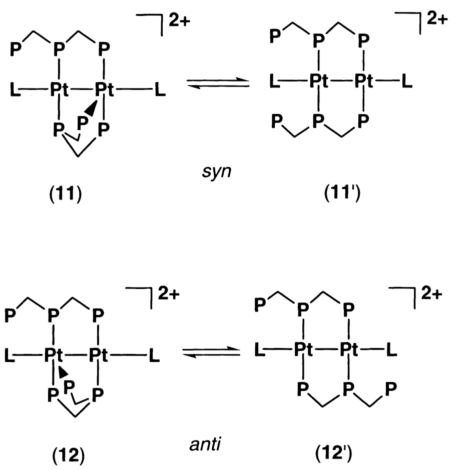
1. Linearly Ordered Pt_2M Trinuclear Complexes with Tridentate Phosphine Ligands

1-1. Diplatinum Precursors.[35,40] When the homoleptic diplatinum(I) isocyanide complexes, $[Pt_2(RNC)_6](PF_6)_2$,[36,37] were treated with 2 equivs of dpmp, isomeric diplatinum complexes, **11** (*syn*) and **12** (*anti*), formulated as $[Pt_2(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (R = 2,6-dimethylphenyl (Xyl) (**11a**, **12a**), 2,4,6-trimethylphenyl (Mes) (**11b**, **12b**)) were obtained as pure forms (Scheme 1).[35] The structures of **11a** and **12a** were determined by X-ray crystallography to consist of asymmetrical diplatinum(I) centers bridged by two dpmp ligands and terminally coordinated by two isocyanide molecules. The Pt–Pt distances are 2.7094(8) Å (**11a**) and 2.683(2) Å (**12a**), which are considerably longer than those for typical Pt(I)–Pt(I) σ-bond lengths.[3–5] From the geometrical assumption with 32 valence electrons, it is resulted from a contribution of the Pt(II)←Pt(0) dative bonded structure which is mixed into the main Pt(I)–Pt(I) σ-bonded nature. Since the central P atoms of two dpmp ligands bind to the same metal center in **11a**, we denote this arrangement as *syn*-form. In contrast, the central P atoms of two dpmp ligands bind to the different Pt centers in **12a**, which is denoted as *anti*-form. Cotton et al. have predicted the presence of *syn*- and *anti*-isomers in the dirhenium complex $[Re_2Cl_3(\mu\text{-dpmp})_2]^+$, although only the *anti*-form has been isolated and characterized.[38] Whereas the diplatinum complexes **11** and **12** are asymmetrical in their crystalline forms, the ^1H and $^{31}P\{^1H\}$ NMR spectra strongly suggested a fluxional behavior of dpmp ligands via the symmetrical intermediates, *syn*-**11′** and *anti*- **12′**, as indicated in Scheme 2.[35b] Complexes **11** and **12** can be good precursors of tri- and higher-nuclear clusters, since they possess two uncoordinate phosphine units in solution. We have extensively studied reactions of **11** and **12** with various metal fragments to expand the multimetallic cores in a step-wise fashion, as described in the following chapters.



Scheme 1. L = XylNC (**a**), MesNC (**b**).

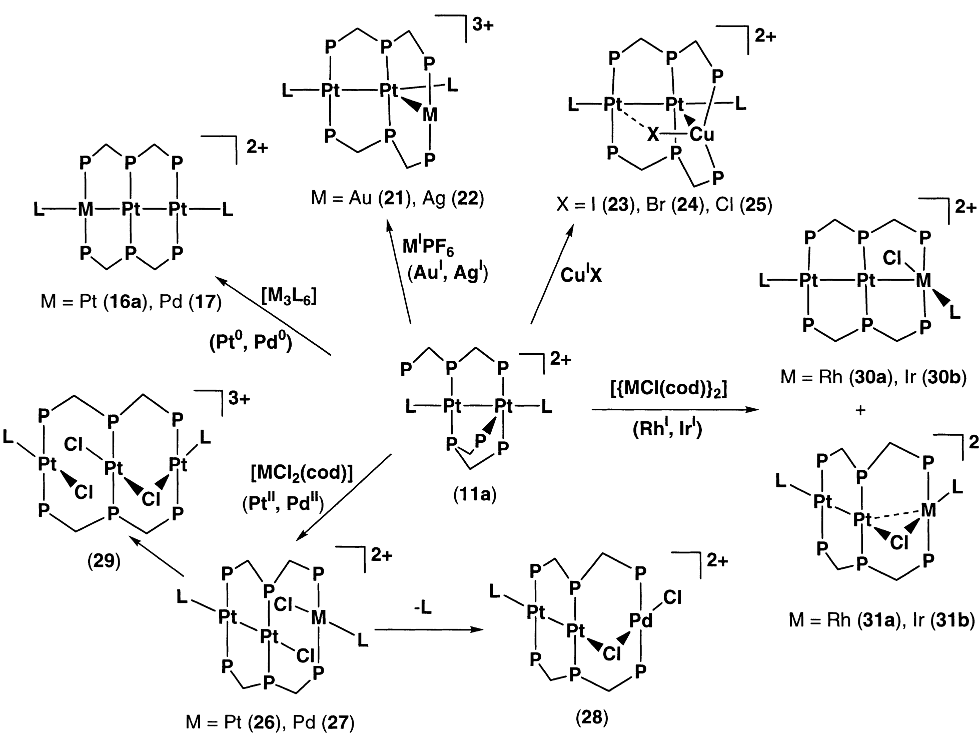
In the above reactions, the starting complex $[Pt_2(RNC)_6](PF_6)_2$ was prepared only by a potentiostatic electrolysis of the Pt(II) monomer of isocyanide, $[Pt(RNC)_4](PF_6)_2$;[36,37,39] the synthetic procedure was not suitable for large-scale preparation. We have also developed another route[40] to the *syn*- and *anti*-platinum dimers (**11** and **12**) by using the comproportionation reaction between the zero-valent platinum complex with dpmp, $[Pt(dpmp)_2]$ (**13**), and the divalent platinum complex with isocyanide, $[Pt(RNC)_4](PF_6)_2$.[41] (Scheme 1). Complex **13** was prepared by reduction of $[PtCl_2(dpmp)]$[19] with $NaBH_4$ in the presence of dpmp.[40] The analogous zero-valent complexes of Pd and Ni, $[M(dpmp)_2]$ (M = Pd, Ni), were also prepared by



Scheme 2. L = RNC.

similar procedures.[40] Complexes **11** and **12** were not interconverted at room temperature. They were likely to lose one isocyanide molecule at heating, resulting in the formation of *syn*-[Pt$_2$(μ-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (**14**) and *anti*-[Pt$_2$(μ-dpmp)$_2$(XylNC)](PF$_6$)$_2$ (**15**), respectively. Similar coordination structures of dpmp were observed in [PtIrCl(CO)(μ-dpmp)$_2$]$^{2+}$, [PdIrCl(CO)(μ-dpmp)$_2$]$^{2+}$,[42] and [Re$_2$Cl$_3$(μ-dpmp)$_2$]$^{+}$.[38]

1-2. Platinum-Based Homo- and Heterotrimetallic Complexes Involving d^9-d^{10}-d^9 Pt$_2$M Cores (M = Pt, Pd).[35b] When the diplatinum complex, *syn*-[Pt$_2$(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**11a**), was treated with [Pt$_3$(XylNC)$_6$] which was a good precursor of d^{10} Pt^0(XylNC)$_2$ fragment, the linear triplatinum complex, *linear*-[Pt$_3$(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**16a**), was obtained in high yield (Scheme 3).[35b] A similar treatment of **11a** with [Pd$_3$(XylNC)$_6$] afforded the analogous heterotrinuclear complex, *linear*-[Pt$_2$Pd(μ-dpmp)$_2$(XylNC)$_2$](PF$_6$)$_2$ (**17**). The complex cation of **16a** has a metal-metal bonded linear triplatinum structure symmetrically bridged by two dpmp ligands. The Pt–Pt bond lengths of 2.723(2) Å and 2.724(2) Å are significantly longer than those of the dppm bridged dimer [Pt$_2$Cl$_2$(μ-dppm)$_2$] (2.652 Å)[43] and the unbridged trinuclear complex [Pt$_3$(dppen)$_2$(RNC)$_4$]$^{2+}$ (2.655 Å),[33d] but still demonstrated the presence of covalent bonds between them. The L-Pt-Pt-Pt-L core is almost linear with the Pt–Pt–Pt angle of 178.66(8) °. The three square-planar coordination planes around the Pt atoms are in a somewhat twisted side-by-side arrangement with the dihedral angles of 29–34 °. The pseudo centro symmetrical structure of **16a** suggested that the apparent oxidation state of the three Pt atoms is Pt(I)-Pt(0)-Pt(I) with 44 cluster valence electrons. The similar trinuclear framework was observed in [Au$_3$(dpmp)$_2$]$^{3+}$ [25] and [Rh$_3$Cl$_2$(dpmp)$_2$(CO)$_3$]$^{+}$,[12,14] but there is no direct bonding interaction between Au^{I} or Rh^{I} ions. Complex **17** is isostructural with **16a**, the Pd atom occupying a terminal position of the trimetallic centers. The crystal structure of the complex cation is refined with a disordered model in which the terminal metal site is occupied by a Pt atom with 0.5 multiplicity and a Pd atom with 0.5 multiplicity. The average metal-metal bond length of 2.690(1) Å is shorter than the Pt–Pt distances in **16a** due to an incorporation of a palladium atom into the cluster core. The asymmetrical Pt-Pt-Pd structure of **17** clearly indicated a formation mechanism where a d^{10} M(RNC)$_2$ fragment is trapped by the two uncoordinated P atoms of **11′** to be incorporated in a terminal position of the trinuclear array, followed by formation of metal-metal bond and dissociation of isocyanide ligands. One electron transfer from the terminal Pd atom to

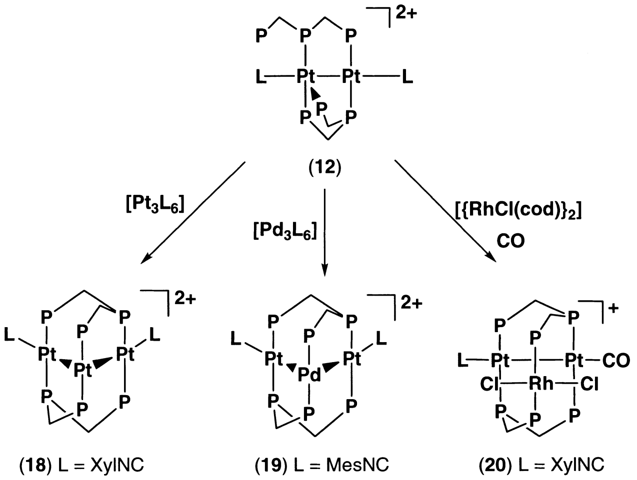


Scheme 3. L = XylNC.

the central Pt atom resulted in a formation of Pt(I)-Pt(0)-Pd(I) cluster core. The mechanistic aspect is quite interesting, in contrast with that for the A-frame triplatinum cluster from the reaction of the *anti*-dimer **12** (vide infra).

The electronic structure of the linear triplatinum complex **16a** was investigated by molecular orbital calculations with EHMO on a model compound, $[Pt_3(PH_3)_6(HNC)_2]^{2+}$, and with DFT methods (B3LYP) on the crystal structure of **16a**.[35b] There are two significant σ-bonding interactions between the three Pt atoms, suggesting that the three Pt atoms are joined by two covalent bonds, although the observed Pt–Pt bond lengths are relatively long. The HOMO is a σ-bonding orbital between the three Pt atoms and the next LUMO is a σ-antibonding orbital between them. Notably, the LUMO is stabilized and is a widely delocalized π-bonding orbital generated from the dπ and pπ orbitals of the terminal and central Pt atoms, respectively, and the π* orbitals of two RNC ligands. The HOMO–LUMO gap is considerably smaller than that of the dppm bridged diplatinum complex, $[Pt_2(dppm)_2(RNC)_2]^{2+}$.

The *anti*-dimer **12a** (R = Xyl) readily reacted with $[Pt_3(RNC)_6]$ to afford the trimetallic A-frame complex, *A-frame*-$[Pt_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (**18**: R = Xyl) (Scheme 4).[35b] Similar treatment of **12b** (R = Mes) with $[Pd_3(MesNC)_6]$ also yielded a heterotrimetallic cluster, *A-frame*-$[Pt_2Pd(\mu\text{-dpmp})_2(MesNC)_2](PF_6)_2$ (**19**).[35b] The complex cations of **18** and **19** have symmetrical Pt_3 and Pt_2Pd A-frame assemblies, respectively, and are quite similar to $[Pt_3(\mu\text{-dppm})_2(XylNC)_4](PF_6)_2$ [39] except for the geometry around the central Pt atom, which is rather distorted from a square planar structure. The Pt–Pt bond distance of **18** is 2.6309(7) Å and the interatomic Pt···Pt distance between the terminal Pt atoms is 3.2333(9) Å with a Pt–Pt–Pt angle of 76.76(3) °. The Pt–Pd bond length of **19** is 2.599(3) Å, which is shorter by 0.031 Å than the Pt–Pt bond length of **18**. The structure of **19** suggested a formation mechanism which involves an insertion of d^{10} $M(RNC)_2$ fragment into the Pt–Pt bond in **12′** supported by ligation of the two uncoordinated P atoms. Since Hoffmann et al. theoretically predicted the existence of A-frame trinuclear complexes on the basis of isolobal analogy between CH_2 and d^{10} ML_2 and d^8 ML_4 fragments,[44] several synthetic examples have been prepared through insertion of metal fragments into Pd–Pd and Pt–Pt σ-bonds bridged by diphosphines such as dppm and dmpm (bis(dimethylphosphino)methane); e.g. $[Pt_2(\mu\text{-PtL}_2)(\mu\text{-dppm})_2L_2]^{2+}$ (L = isocyanide),[39] $[Pt_2Cl_2(\mu\text{-HgCl}_2)(\mu\text{-dppm})_2]$,[45] $[Pt_2(\mu\text{-AuI})(C_2t\text{-Bu})_2(\mu\text{-dppm})_2]$,[46] and $[Pd_2Cl_2(\mu\text{-Pt(PPh}_3)_2)(\mu\text{-dmpm})_2]$.[47] On the basis of these examples, the formation of **19** from **12** can be accommodated within the context of an insertion of a d^{10} ML_2 fragment into the metal-metal σ-bond. An insertion of a $M(RNC)_2$ fragment into the Pt(I)-Pt(I) σ-bond is followed by a replacement of isocyanide ligands with the terminal phosphine units. The position of the trapped metal atom in **19** (central position) is interestingly contrasted with that in the linear Pt_2Pd complex **17** (terminal position) derived from the reaction of *syn*-dimer **11a**. The arrangement of the two free phosphorus atoms in **11′** and **12′** may play a critical role in determining the direction of the d^{10} metal-inserted position. Reaction of complex **12a** with $[\{RhCl(cod)\}_2]$ under CO atmosphere gave the Pt_2Rh complex of $[Pt_2(RhCl_2)(\mu\text{-dpmp})_2(XylNC)(CO)](PF_6)$ (**20**), in which the Rh center is just trapped by the two uncoordinated phosphines of **12′** without bond formation between the Rh and Pt centers.[48]



Scheme 4.

1-3. Platinum-Based Heterotrimetallic Complexes Involving d^9-d^9-d^{10} Pt_2M Cores (M = Au, Ag, Cu).[49] Reactions of the *syn*-dimer **11a** with $AuPF_6$ and $AgPF_6$ afforded the Pt_2Au and Pt_2Ag trinuclear complexes, $[Pt_2M(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_3$ (M = Au (**21**), Ag (**22**)) in good yields (Scheme 3).[49] The complex cations of **21** and **22** involve a Pt_2M trinuclear core bridged by two dpmp ligands. The additional M(I) ion is trapped by two uncoordinated phosphine units of **11′**, resulting in a deformed Pt–Pt···M aggregation, and the two isocyanide molecules are terminally coordinated to the Pt_2 unit in a linear array. The two Pt atoms are connected by a single bond (Pt–Pt = 2.708(2) Å (**21**) 2.657(2) Å (**22**)), but the Pt···M interaction was estimated to be very weak (Pt···Au = 3.045(2) Å (**21**), Pt···Ag = 3.118(3) Å (**22**). The Pt···Au interatomic distance of **21** is quite close to that of the d^{10}-d^8 mixed metal dimer, $[AuPt(CN)_2(\mu\text{-dppm})_2]^+$ (3.046(2) Å),[50a] somewhat longer than that found in $[AuPt(C{\equiv}CPh)_2(\mu\text{-dppm})_2]^+$ (2.910(1) Å),[50b] and is considerably longer than those found in Pt^I-Au^I-Pt^I A-frame clusters: $[Pt_2(C{\equiv}C\text{-}t\text{-Bu})_2(\mu\text{-AuI})(\mu\text{-dppm})_2]$ (av 2.659 Å),[46] $[Pt_2(CN)_2(\mu\text{-AuCl})(\mu\text{-dppm})_2]$ (av 2.641 Å),[51] and $[Pt_2(\mu\text{-AuPPh}_3)\{C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]BF_4$ (av 2.710 Å),[52] which were considered as typical bonding interactions. The Pt···Ag distance of **22** is comparable to that of $[PtAgI(\mu\text{-dppm})_2(C{\equiv}CPh)_2]$ (3.146(3) Å),[53] and is longer than the Pt–Au distance in **21**. This difference may be due to the lanthanide contraction and relativistic effects, although the covalent radii of Au and Ag are almost identical (~1.34 Å).[54] The Pt–Pt···M angles are 110.68(5) ° (**21**) and 136.36(8) ° (**22**)), resulting in a Y-shaped LPt_2ML structure, which is interesting to compare with the linear LPt_2PdL structure of **17** derived from the reaction of **11** with the d^{10} Pd(0) isocyanide complex.[35b] In the latter case, one electron transfer from the d^{10} metal center to the d^9-d^9 diplatinum center led to a d^9-d^{10}-d^9 Pt_2Pd aggregation joined by two metal-metal covalent bonds. In the present case, the d^{10} M(I) ion (M = Au, Ag) is trapped, and separated from the Pt_2 dinuclear center owing to its electronic stability.

When **11a** was treated with CuX, a series of Pt_2CuX clusters, $[Pt_2CuX(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (X = I (**23**), Br (**24**), Cl (**25**)), were obtained (Scheme 3).[49] The solid state structures were determined by X-ray crystallographic analyses to reveal that complexes **23**–**25** are isomorphous to each other. The complex cation of **24** (X = Br) consists of two Pt and one Cu atoms bridged by two dpmp ligands, and has a pseudo C_s symmetry with a mirror plane comprised of the Pt_2CuBr atoms. The Pt_2CuBr assembly forms a rhombic structure, with the Pt–Pt, Pt···Cu, Cu–Br, and Pt···Br distances being 2.7180(5) Å, 2.857(1) Å, 2.412(2) Å, and 3.088(1) Å, respectively. Although the Pt···Cu interatomic distance of **24** (2.857(1) Å) is considerably shorter than the corresponding values of Pt···Au (3.045(2) Å (**21**)) and Pt···Ag (3.118(3) Å (**22**)) distances, no typical bonding interaction between the Pt and Cu atoms is estimated on the basis of small covalent radius of Cu(I) (~1.17 Å).[54] The Cu atom is ligated by two P atoms and a bromide anion to form a distorted three-coordinate structure. The coordination plane around the Cu atom is approximately parallel to the Pt_2 coordination plane, in a face-to-face arrangement. The Pt···Cu–Br angle (85.94(4) °) is less than 90 °, resulting in a relatively short interatomic distance between the terminal Pt and Br atoms (3.088(1) Å). The Pt···X distances of **23**–**25** fall within the narrow range (3.088(1)–3.130(2) Å), independent of the Cu–X bond lengths (2.276(3)–2.597(2) Å).

1-4. Platinum-Based Homo- and Heterotrimetallic Complexes Involving d^9-d^9-d^8 Pt_2M Cores (M = Pt, Pd).[55] The same strategy for the expansion of multimetallic core could be applied for d^8 additional metal fragments. The *syn*-type diplatinum complex **11a** readily reacted with $[PtCl_2(cod)]$ or $[PdCl_2(cod)]$ to afford $[Pt_2MCl_2(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$ (M = Pt (**26**), Pd (**27**)) (Scheme 3).[55] The complex cation of **26** contains a metal-metal bonded diplatinum(I) core and a mononmeric platinum(II) center bridged by two dpmp ligands (Pt–Pt = 2.681(2) Å, Pt···Pt = 3.219(2) Å). There is no bonding interaction between the d^9-d^9 Pt^I_2 fragment and d^8 Pt^{II} mononuclear center and their coordination planes are located in a face-to-face arrangement.

In the heterometallic complex **27**, the additional Pd(II) ion was incorporated into the mononuclear site on the basis of spectroscopic analyses. Complex **27** slowly lost one terminal isocyanide in solution and was converted into a chloride-bridged complex, $[Pt_2PdCl(\mu\text{-Cl})(\mu\text{-dpmp})_2(XylNC)](PF_6)_2$ (**28**).[55] The complex cation of **28** has an asymmetrical A-frame structure of Pt_2Pd aggregation (Pt–Pt = 2.606(2) Å, Pt···Pd = 3.103(3) Å, Pt–Cl–Pd = 79.6(3) °). The similar Cl-bridged asymmetrical A-frame structure, Rh(μ-Cl)PdRh, has also been reported in $[Rh_2Pd(CO)_2(\mu\text{-Cl})Cl_2(\mu\text{-dpma})_2]^{2+}$.[56]

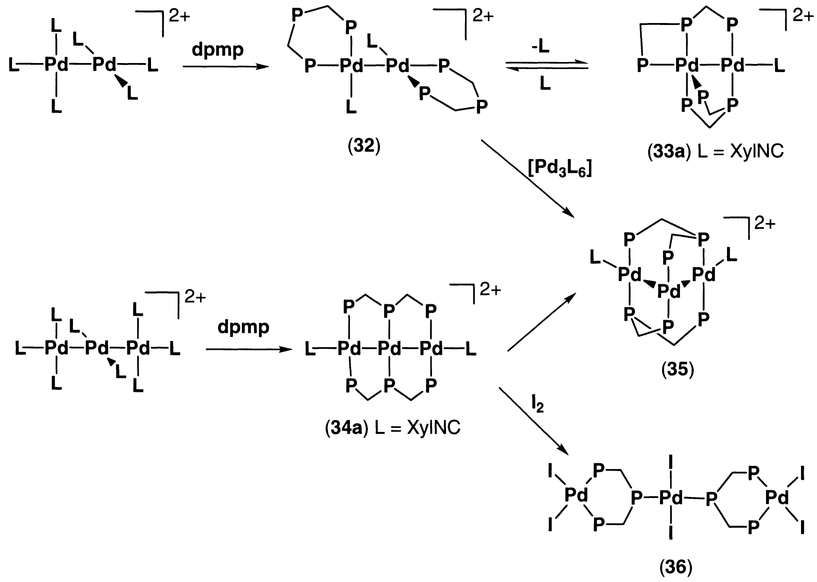
When complex **26** was treated with $[NO][BF_4]$, oxidation and subsequent disproportionation occured to yield the d^8-d^8-d^8 Pt^{II}_3 complex, $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-Cl})Cl_2(XylNC)_2](BF_4)_3$ (**29**), in which no metal–metal bonding interaction was observed (Pt···Pt = 3.1948(8) Å, 3.2626(8) Å).[57]

1-5. Platinum-Based Heterotrimetallic Complexes Involving d^9-d^9-d^8 Pt_2M Cores (M = Ir, Rh).[58] The *syn*-dimer **11a** reacted with $[\{RhCl(cod)\}_2]$ (0.5 equiv) to afford two isomeric Pt_2Rh complexes formulated as $[Pt_2RhCl(dpmp)_2(XylNC)_2](PF_6)_2$ (**30a** and **31a**) (Scheme 3).[58] Compounds **30a** and **31a** were not interconverted to each other at room temperature. A similar reaction with $[\{IrCl(cod)\}_2]$ gave the analogous clusters **30b** and **31b** formulated as $[Pt_2IrCl(\mu\text{-dpmp})_2(XylNC)_2](PF_6)_2$. The structures of **30a** and **30b** were determined by X-ray crystallography to consist of a linearly ordered Pt_2M core bridged by two dpmp ligands.[58] The three metal units are joined by metal–metal bonds and the Pt–Pt axis is almost vertical to the square plane of the M(I) ion, resulting in a T-shaped LPtPtMClL (L = XylNC) structure. The Pt–Pt distances are 2.6588(3) Å (**30a**) and 2.652(2) Å (**30b**), and the Pt–M distances are 2.7537(5) Å (**30a**) and 2.765(2) Å (**30b**). The former values are in the range of Pt(I)–Pt(I) single bond distances and the latter are 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 $[PtRh(\mu\text{-dppm})_2(CH_3NC)_4]^{3+}$, $[PtRh(\mu\text{-dppm})_2(CH_3NC)_3X]^{2+}$ (X = Cl, I),[59] and $[PtIr(CO)Cl(\mu\text{-dpmp})_2]^{2+}$.[42] 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 44 with 16 apparent valence electrons for each metal. In contrast, the cluster core of **31a** involves two platinum and one rhodium atoms bridged by two dpmp ligands and a chloride anion. The Cl atom is located at the vertex of an asymmetrical A-frame trinuclear structure between the Pt and Rh atoms. The Pt–Pt distance of 2.644(1) Å showed the presence of a typical metal–metal σ-bond and the Pt and Rh atoms are spanned by a chloride bridge of 2.967(2) Å, which is longer by ~0.31 Å than that of **30a**.

2. Tripalladium Complexes with Tridentate Phosphine Ligands.[60]

Reaction of $[Pd_2(RNC)_6](PF_6)_2$ [39b] with 2 equiv of dpmp readily afforded $[Pd_2(dpmp)_2(RNC)_2](PF_6)_2$ (R = Xyl (**32a**), Mes (**32b**)) (Scheme 5).[60] The complex cation of **32a** comprises two Pd(I) ions joined by a Pd–Pd σ-bond which is not supported by any bridging ligands (Pd–Pd = 2.607(2) Å). The coordination mode of dpmp in **32a** is close to that observed in the mononuclear Pd(II) complex, $[PdCl_2(dpmp)]$.[16] Unlike the diplatinum complexes of dpmp,[35b] the dpmp-bridged dipalladium complexes corresponding to *syn*-**11** and *anti*-**12** were not obtained. Complex **32a** dissolving in acetonitrile slowly lost one isocyanide ligand to lead to *anti*-$[Pd_2(\mu\text{-dpmp})_2(XylNC)](PF_6)_2$ (**33a**), which was monitored by electronic absorption spectroscopy. The electronic absorption band maximum shifted to the lower energy side (λ_{max} 454 nm) compared with **32a** (λ_{max} 430 nm), suggesting that the metal–metal covalent interaction in **33a** is weaker than that in **32a**. Reaction of **33a** with an excess amount of XylNC regenerated complex **32a**. The structure of **33a** is close to that of the diplatinum complex **15**. The Pd–Pd bond length of 2.702(1) Å is longer than that found in **32a** and falls within the longer values reported for Pd(I)–Pd(I) dinuclear complexes.[34i,61–66] The value is, however, smaller than being found in the d^{10}-d^{10} palladium(0) dimer, $[Pd_2(Cy_2PCH_2CH_2PCy_2)_2]$ (2.7611(5) Å).[67]

When $[Pd_3(RNC)_8](PF_6)_2$ [39b] was treated with 2 equiv of dpmp, the color of the solution immediately changed to violet, and this gradually turned to dark red. From the initial violet solution, the linear tripalladium complex formulated as *linear*-

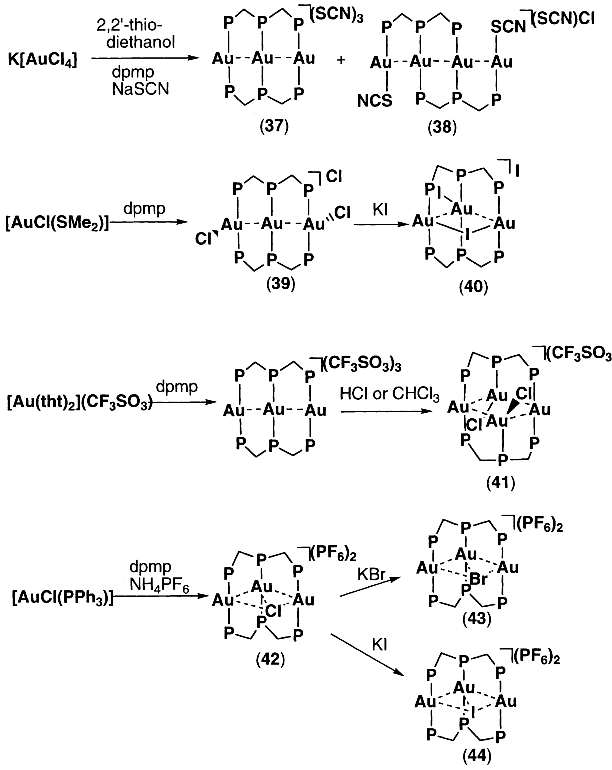


Scheme 5. L = XylNC (**a**), MesNC (**b**).

$[Pd_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (**34a**: R = Xyl) was isolated and was characterized by spectroscopic techniques (Scheme 5).[60] From the final dark red solution, the trimetallic A-frame complexes, *A-frame*-$[Pd_3(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (R = Xyl (**35a**), Mes (**35b**)), were isolated in good yields (Scheme 5).[60] The core structure of **35a** is identical to those in the Pt_3 and Pt_2Pd trimetallic A-frame complexes **18** and **19**.[35b] Complex **35a** was also obtained by reaction of **32a** with $[Pd_3(XylNC)_6]$. Although complex **35** was fairly stable towards thermal, photochemical, and chemical reactions, it reacted with an excess amount of I_2 to be oxidized into the tripalladium complex $[Pd_3I_6(dpmp)_2]$ (**36**), where two *cis*-$PdI_2(dpmp)$ units are joined by a *trans*-PdI_2 fragment to produce a dpmp-spanned trinuclear Pd(II) structure. The structure of **36** is identical to a structure predicted for $[Pd_3Cl_6(\mu\text{-dpmp})_2]$ by Balch et al.[16] and similar to that of $[(CH_3CN)PdCl_2(\mu\text{-dpmp})PdCl_2]$.[16]

3. Tri- and Tetranuclear Gold(I) Complexes with Tridentate Phosphine Ligands

The dpmp-bridged gold(I) clusters have also attracted attention in relation to photochemical materials. The tri- and tetragold(I) complexes, $[Au_3(\mu\text{-dpmp})_2](SCN)_3$ (**37**) and $[Au_4(\mu\text{-dpmp})_2(SCN)_2](SCN)Cl$ (**38**),[68] were prepared by Che and his co-workers, both involving almost linearly ordered multimetallic cores (Au–Au–Au = 167.21(2) ° (**37**), av 163.6 ° (**38**)) (Scheme 6). The same group has also reported the trigold(I) complexes of $[Au_3(\mu\text{-dpmp})_2X_2]X$ (X = Cl (**39**), I (**40**)), in which the Au_3X_2 cluster core is dramatically changed from a zigzag $ClAu_3Cl$ structure to a rhombic $Au_3(\mu\text{-I})I$ one depending on the halide ligand used.[69] The rhombic tetragold(I) cluster with dpmp ligands, $[Au_4(\mu\text{-dpmp})_2Cl_2](CF_3SO_3)_2$ (**41**),[70] was also reported by another group (Scheme 6). The structures and properties of dpmp-bridged trigold(I) complexes were interestingly influenced by the halide anions used. By the use of other tridentate supporting ligands, in contrast, considerably bending cluster cores, with the Au–Au–Au angles ranging from 88.0(1) ° to 136.26(4) °, have been observed in $[Au_3(\mu\text{-dmmp})_2](ClO_4)_3$ (dmmp = bis(dimethylphosphinomethyl)methylphosphine),[71] $[Au_3Cl_3(\mu\text{-dpma})]$ and $[Au_4Cl_2(\mu\text{-dpma})_2]^{2+}$.[72] These observations demonstrated that the gold(I) cluster frameworks can be varied by a choice of supporting ligands and counter anions. We have independently tried to prepare Au(I) clusters with dpmp ligands.[73] Reaction of $[AuCl(PPh_3)]$ with dpmp with a 3:2 ratio in the presence of NH_4PF_6 afforded the trinuclear gold(I) complex, $[Au_3(\mu\text{-dpmp})_2Cl](PF_6)_2$ (**42**). Complex **42** was readily transformed



Scheme 6. tht = tetrahydrothiophene.

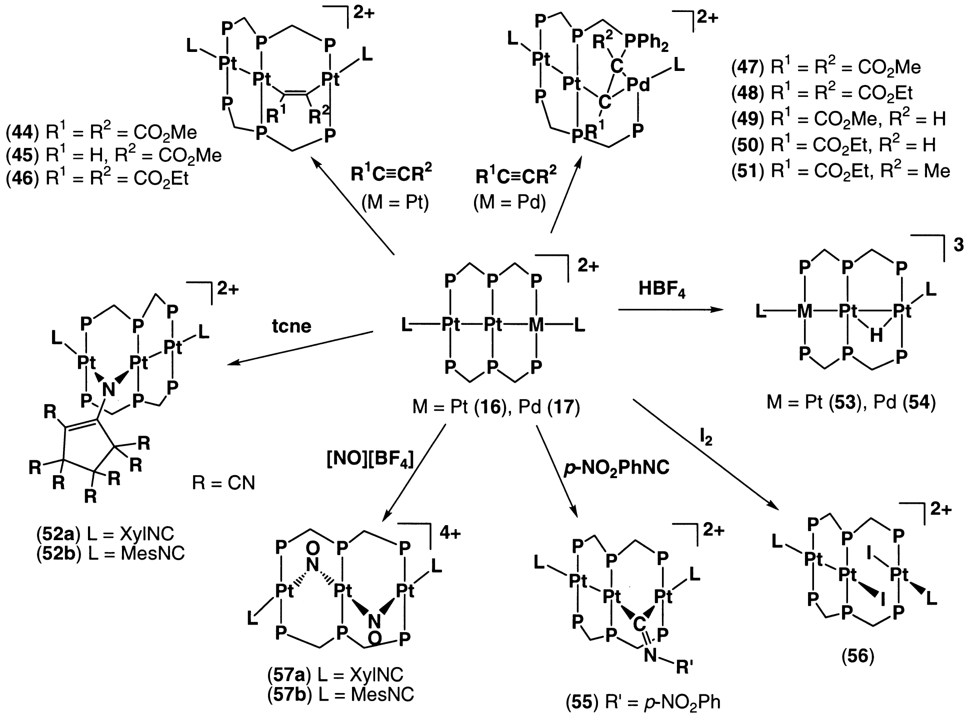
by treatment with KX (X = Br, I) into the analogous complexes, [Au$_3$(μ-dpmp)$_2$X](PF$_6$)$_2$ (X = Br (**43**), I (**44**)) (Scheme 6).[73] Complexes **42**–**44** consist of three Au(I) ions bridged by two dpmp ligands (av Au–Au = 2.934–2.950 Å), which further interacted with a halide anion to lead to a significantly bent trinuclear core with Au–Au–Au angles ranging 141.12(6)–143.46(4) °. The bent trimetallic core is assumed to be retained even in solution on the basis of their spectral data.

4. Reactions of Linearly Ordered Trinuclear Complexes

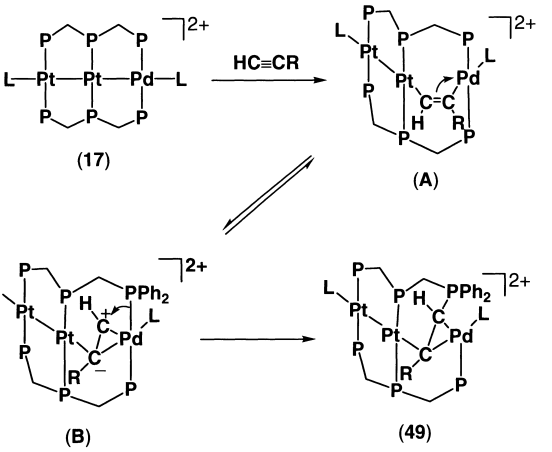
4-1. Reactions of Linear Pt$_3$ and Pt$_2$Pd Complexes (16a, 17) with Small Molecules. The linear triplatinum complex **16** is an important expansion of the well-known chemistry on dppm-bridged diplatinum complexes, in which a number of small molecules were oxidatively inserted into the metal–metal bond.[3–5] The two conjugated Pt–Pt bonds in **16** could serve as a minimal model of the metal surface of heterogeneous catalysts and also as a scaffold for metal-surface mimic homogeneous chemistry. In this regard, we have studied the reactivity of **16** and **17** toward small molecules such as alkynes, alkenes, isocyanides as well as H$^+$, NO$^+$, and I$_2$ (Scheme 7).[55,74–76]

Complex **16a** easily reacted at room temperature with an excess of electron deficient alkynes (R^{1}C≡CR^2: R^1 = R^2= CO$_2$Me; R^1 = H, R^2 = CO$_2$Me; R^1 = R^2 = CO$_2$Et) to be transfered into the triplatinum adducts of [Pt$_3$(μ-dpmp)$_2$(μ-R^{1}C=CR^2)(XylNC)$_2$](PF$_6$)$_2$ (R^1 = R^2 = CO$_2$Me (**44**), R^1 = H, R^2 = CO$_2$Me (**45**), R^1 = R^2 = CO$_2$Et (**46**)) (Scheme 7).[55] The structure of **45** was determined by an X-ray analysis to contain an asymmetrical A-frame structure comprised of three Pt atoms bridged by two dpmp ligands, in which an acetylene molecule was inserted into one of the Pt–Pt bonds (Pt–Pt = 2.718(1) Å, Pt···Pt = 3.582(1) Å). The C–C bond length of the inserted acetylene unit is 1.39(3) Å and corresponds to the usual C–C double bond. The remaining Pt–Pt σ-bond of **44**–**46** did not react even in the case being treated with an excess of the activated alkynes at higher temperature. Non-functional alkynes, such as phenyl- and diphenyl acetylene, did not react with **16a**. Similar reactions were investigated with the Pt$_2$Pd heterotrimetallic complex **17** and some significantly different adducts were isolated, the Pd heterometal interestingly altering the reactivity of the linear trimetallic system.[74] Complex **17** was readily reacted with electron-deficient alkynes, RC≡CR′, and converted to the unsymmetrical A-frame clusters of [Pt$_2$Pd(μ-dpmp)(μ-Ph$_2$PCH$_2$P(Ph)CH$_2$P(Ph)$_2$CRCR′)(XylNC)$_2$](PF$_6$)$_2$ (R = R′ = CO$_2$Me (**47**); R = R′ = CO$_2$Et (**48**); R = H, R′ = CO$_2$Me (**49**); R = H, R′ = CO$_2$Et (**50**); R = CH$_3$, R′ = CO$_2$Et (**51**)), which were characterized by spectroscopic techniques and X-ray crystallography. In complexes **47**–**51**, the alkyne molecule was site-selectively inserted into the Pt–Pd bond over the Pt–Pt one and was further reacted with a phosphine unit of dpmp ligand through double bond breaking of the C≡C unit (Scheme 7).[74] In complexes **49** and **50**, the P–C bond formation occurred regioselectively between the terminal alkyne carbon and the phosphine unit of dpmp, resulting in a μ-2κC : 3(η^2)-phosphorus ylide bridging structure. The reaction mechanism for the apparent double insertion of the acetylene into the Pt–Pd and Pd–P bonds was estimated to involve the site-selective insertion and the zwitter ionic activation of the acetylene unit (Scheme 8).[74] The presence of the intermediate, [PtPt(μ-HC=CHCO$_2$Me)Pd(μ-dpmp)$_2$(XylNC)$_2$]$^{2+}$ (**A**), was confirmed by low-temperature ^{31}P{^{1}H} NMR spectroscopy.

Complex **16** was readily reacted with an excess of the strongly electron-deficient olefin, tetracyanoethylene (tcne), to

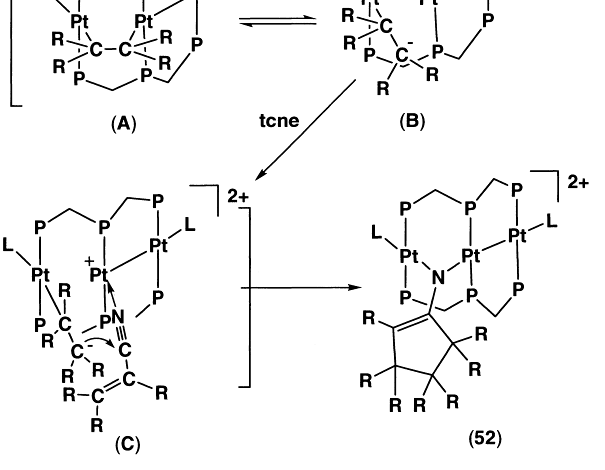


Scheme 7. L = XylNC (or MesNC).



Scheme 8. R = CO_2Me, L = XylNC.

give a pale-green complex, $[Pt_3(\mu\text{-dpmp})_2\{\mu\text{-}C_{12}N_8\}(XylNC)_2](PF_6)_2$ (R = Xyl (**52a**), Mes (**52b**)) (Scheme 7).[75] The complex cation of **52a** has a mono-atom-bridged asymmetrical A-frame structure supported by two dpmp ligands, in which two tcne molecules are coupled to form a cyclopentene imide moiety being inserted into one of the metal–metal bonds (Pt–Pt = 2.6446(8) Å, Pt···Pt = 3.2150(8) Å). The imido nitrogen atom bridges the two platinum atoms in a rather asymmetrical manner with Pt–N = 2.18(1) or 2.05(1) Å, Pt–N–Pt = 98.9(6) °, and Pt–N–C = 138(1) ° or 123(1) °. This type of tcne cyclic dimerization was very rare, and the relative compound has been reported only as *N*-(heptacyanocyclopent-1-enyl)triphenylphosphoranimine.[77] A plausible reaction mechanism was proposed, as shown in Scheme 9. The 1 : 1 tcne adduct (**A**) might be formed at the initial step by analogy with reaction of **16** with electron-deficient alkynes (Scheme 7). The strong *trans* influence of the Pt–Pt bond may cause the zwitter ionic Pt–C bond breaking (**B**), and the nucleophilic attack of the carbanion on the electron-deficient nitrile carbon of the second tcne molecule (**C**) was inferred as a key step for the coupling. The coupling reaction of tcne should be unique feature of the linear triplatinum complex **16**, since it was not promoted by the diplatinum complex $[Pt_2(\mu\text{-dppm})_2(XylNC)_2](PF_6)_2$.[39b]



Scheme 9. L = isocyanide, R = CN.

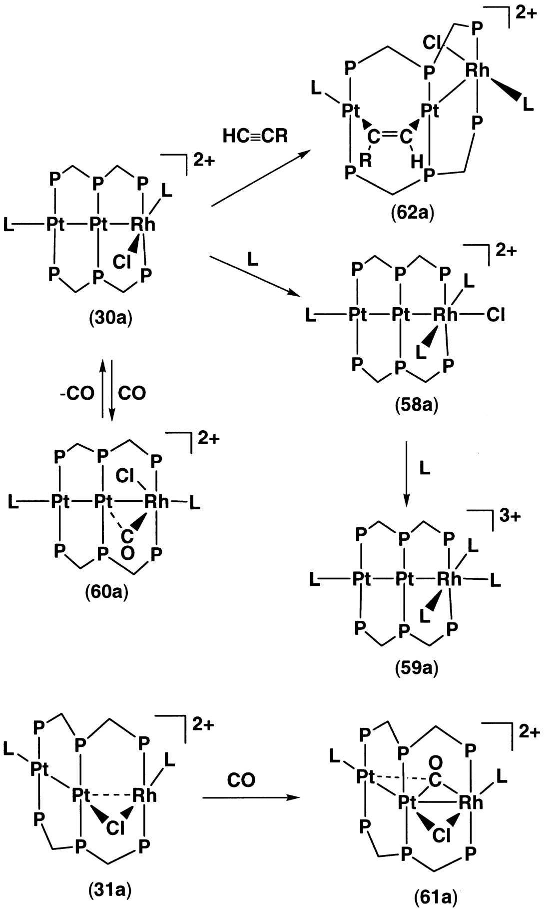
Treatment of **16a** with an excess of $HBF_4{\cdot}Et_2O$ gave the asymmetrical trinuclear complex, $[Pt_3(\mu\text{-H})(\mu\text{-dpmp})_2(XylNC)_2](BF_4)_3$ (**53**), and the same reaction of **17** afforded $[Pt_2Pd(\mu\text{-H})(\mu\text{-dpmp})_2(XylNC)_2](BF_4)_3$ (**54**) (Scheme 7).[55,74] Complex **54** was characterized by X-ray crystallography to reveal that a proton was oxidatively added to the Pt–Pt bond vs the Pt–Pd one site-selectively, accompanied by small structural changes with elongation of the Pt–Pt bond from 2.690(1) Å (**17**) to 2.867(2) Å (**54**) and tilting of the terminal isocyanide.[74] The slight but appreciable structural change can be monitored by electronic absorption spectroscopy. Reaction of **16** with 1 equiv of an electron-deficient isocyanide, *p*-$NO_2C_6H_4NC$, led to the formation of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-}R^3NC)(XylNC)_2](PF_6)_2$ (**55**) (R^3 = *p*-$NO_2C_6H_4$) and that with I_2 resulted in two-electron oxidation of **16**, leading to the dimer-monomer combined complex, $[Pt_3I_2(\mu\text{-dpmp})_2(XylNC)_2]I_2$ (**56**) (Scheme 7).[55]

By treatment with an excess of $[NO][BF_4]$, complex **16** immediately converted to the pale green adducts of $[Pt_3(\mu\text{-dpmp})_2(\mu\text{-NO})_2(RNC)_2](BF_4)_4$ (R = Xyl (**57a**), Mes (**57b**)) (Scheme 7).[76] The complex cation of **57a** retains the linear triplatinum core supported by two dpmp ligands, in which two nitrosyl groups are inserted into the two Pt–Pt bonds in an almost symmetrical manner. The Pt–Pt separation of 3.0962(4) Å, indicating the absence of Pt–Pt bond, is shorter than those for the A-frame diplatinum complexes with dppm ligands, e.g. $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2](BPh_4)$ (3.246 Å),[78] $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2](BF_4)$ (3.186 Å),[79] $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$ (3.151 Å),[80] and is comparable to that of $[Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-dppm})_2]$ (3.094 Å).[81] The N-O bond length of 1.09(1) Å corresponds to values for neutral N-O triple bonds rather than N-O double bonds.[82] This nitrosyl-bridging structure is quite different from that of $[Pt_2Cl_2(\mu\text{-NO})(\mu\text{-dppm})_2]^+$ which involves a NO^- unit with a N-O bond length of 1.20(2) Å.[78,79] The present reaction can be regarded as a novel three-center oxidative addition proceeding on a linear triplatinum center, involving an apparent two electron transfer from the triplatinum core to two NO^+ ions.

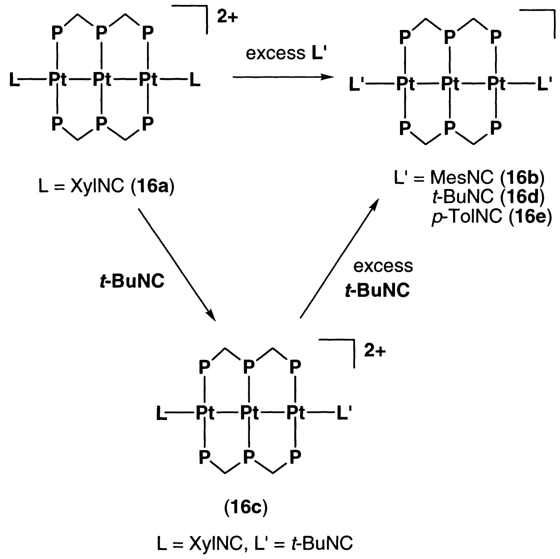
4-2. Reactions of Linearly Ordered Pt_2Rh, Pt_2Ir Heterotrimetallic Complexes with Small Molecules.[58] Heterometallic clusters could have the potential to promote new homogeneous catalytic reactions which are not established by mononuclear centers. In particular, Pt/Rh and Pt/Ir mixed-metal systems are quite important as tunable models of industrial heterogeneous catalysts used in scrubbing of automobile exhaust gases and in petroleum refining.[1c,83]

We have examined the reactivity of the linearly ordered Pt_2Rh mixed-metal complex **30a** in contrast with that of the triplatinum complex **16**.[58b] Reaction of **30a** with 1 equiv of xylyl isocyanide (L) afforded $[Pt_2\{RhClL_2\}(\mu\text{-dpmp})_2L](PF_6)_2$ (**58a**) and that with an excess of L led to $[Pt_2\{RhL_3\}(\mu\text{-dpmp})_2$-

L]$(PF_6)_3$ (**59a**) (Scheme 10). The analogous Pt_2Ir complex, $[Pt_2\{IrL'_3\}(\mu\text{-dpmp})_2L'](PF_6)_3$ (**59b**), was obtained from reaction of **30b** with an excess of mesityl isocyanide (L′). Complexes **58a** and **59b** were characterized by X-ray crystallography and the results demonstrated that the additional isocyanide molecules are attached exclusively to the Rh (or Ir) center. Complex **30a** was readily converted by treatment with CO into a CO adduct, $[Pt_2\{RhClL(\mu\text{-CO})\}(\mu\text{-dpmp})_2L](PF_6)_2$ (**60a**), which easily regenerated **30a** when dinitrogen passed through its solution. The structure of **60a** was determined by X-ray analysis to show that a carbon monoxide molecule was added to the Pt–Rh bond (2.762(2) Å), resulting in an asymmetrical, semi-bridging CO structure (Rh–C = 1.90(2) Å, Pt–C = 1.94(2) Å, C–O = 1.18(2) Å, Rh–C–O = 152(2) °, Pt–C–O = 123(2) °). A similar reaction of the Pt_2Rh A-frame complex **31a** with CO yielded another kind of CO adduct, $[Pt_2\{Rh(\mu\text{-Cl})(\mu\text{-CO})L\}(\mu\text{-dpmp})_2L](PF_6)_2$ (**61a**), which was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopic techniques. Reaction of **30a** with an electron-deficient alkyne, $HC{\equiv}CCO_2Me$, afforded the alkyne inserted compound, $[Pt(\mu\text{-}HC{=}CCO_2Me)Pt\{RhClL\}(\mu\text{-dpmp})_2L](PF_6)_2$ (**62a**), in which the alkyne is site-selectively inserted into the Pt–Pt bond as found on the basis of the spectroscopic data. These results suggested that the Rh center in **30a** is electron-deficient and acts as an electrophilic part, and the Pt_2 unit acts as a nucleophilic site using the metal-metal bonding electrons.



Scheme 10. L = XylNC, R = CO_2Me.

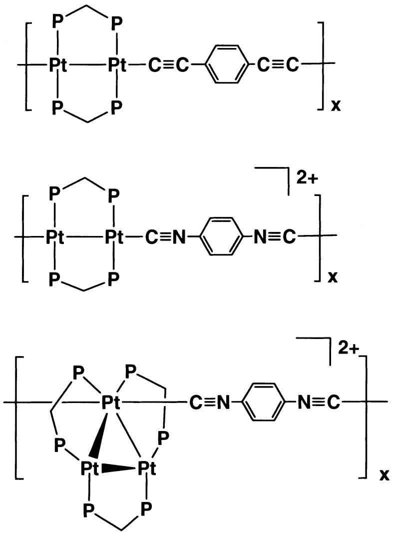


Scheme 11.

4-3. Axial Ligand Exchange Reactions of the Linear Triplatinum Complex 16a.[84] The axial XylNC ligands in **16a** were readily replaced by other RNC molecules to afford a series of linear triplatinum complexes, *linear*-$[Pt_3(dpmp)_2(RNC)_2](PF_6)_2$ (**16b**: R = 2,4,6-mesityl (Mes), **16d**: R = *t*-Bu, **16e**: R = 4-tolyl (Tol)) and *linear*-$[Pt_3(dpmp)_2(R^1NC)(R^2NC)](PF_6)_2$ (**16c**: R^1 = Xyl, R^2 = *t*-Bu) (Scheme 11).[84] Complexes **16b–16e** were characterized by elemental and spectroscopic analyses, X-ray crystallography (**16b–16d**), and EXAFS spectroscopy, to show that the metal-metal bonded linear triplatinum structure was retained during the reactions. In the crystal structure of **16c**, the Pt–Pt bond lengths trans to XylNC (2.728(2) Å) is longer than that to *t*-BuNC (2.696(2) Å), indicating the presence of trans π-influence of the terminal isocyanide. With increase of π-acidity of RNC, the metal–metal bonding electrons might partially migrate into the π^* orbital of the CN unit and, consequently, the Pt–Pt bond length increases. Complex **16e** with *p*-TolNC is green-colored and is extremely unstable in comparison with other orange complexes **16a–16d**. An EXAFS analysis of **16e** revealed that the Pt–Pt distance is 2.84(4) Å, which is considerably longer than those of **16a–16d** (2.696–2.724 Å). The Pt–Pt bonds of **16** were able to be tuned by varying the substituents of terminal isocyanide ligands, which suggests that the reactivity and physical properties of the linear Pt_3 complexes can be modified by changing axial ligands.

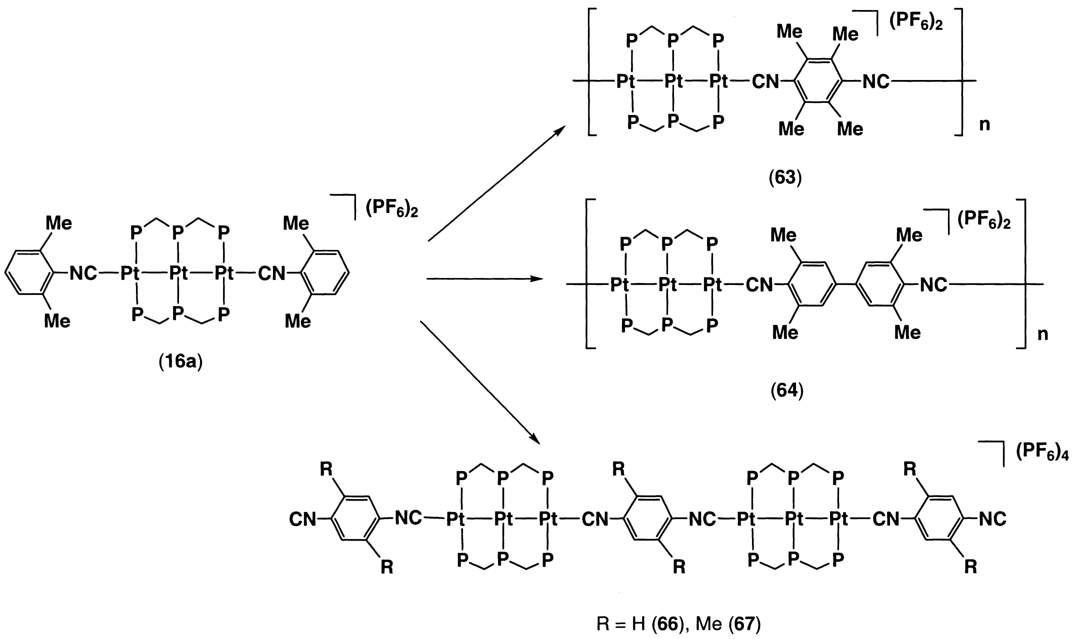
5. Ordered Assembling of Linear Triplatinum Clusters by Utilizing Organic Linkers[84]

Recently, development of ordered assemblies of transition-metal clusters with organic linkers has attracted growing attention to their use as multifunctional molecular devices and molecular scale electronics. Some rigid rod-like polymers that contain mononuclear transition-metal fragments connected by linear organic linkers, such as bisacetylide and bisisocyanide, have been reported and their photochemical and optical properties were investigated.[85] However, such polymers with di- and multimetallic cores have rarely been investigated, despite the fact that a variety of functions and reactivities with multimetallic systems can be introduced to the materials. Puddephatt et al. have reported the oligomers of di- and triplatinum complexes connected by phenylene-1,4-bisacetylide and phenylen-1,4-bisisocyanide, $\{Pt_2(\mu\text{-dppm})_2(C{\equiv}C(C_6H_4)C{\equiv}C)\}_n$, $\{[Pt_2(\mu\text{-dppm})_2(C{\equiv}N(C_6H_4)N{\equiv}C)]^{2+}\}_n$, and $\{[Pt_3(\mu\text{-dppm})_2(C{\equiv}N\text{-}(C_6H_4)N{\equiv}C)]^{2+}\}_n$ (n = 3–12), but they were poorly characterized owing to their low solubility (Scheme 12).[86] Recently, organometallo-oligomers (n = 2, 3) containing diruthenium cores connected by π-conjugated carbon chains have been explained.[87]



Scheme 12. x = 3–12 (Ref. 86).

By utilizing the axial ligand exchange reactions of **16** described above, we have tried to synthesize the rigid rod-like cluster polymers in which the linear triplatinum fragments, $\{Pt_3(\mu\text{-dpmp})_2\}^{2+}$, were connected by linear bisisocyanide linkers.[84] When complex **16** was treated with an excess of the bulky bis(isocyanide)s, 2,3,5,6-tetramethylphenylene-1,4-bisisocyanide, 2,2′,6,6′-tetramethylbisphenylene-1,1′-bisisocyanide, in dichloromethane, the desired Pt_3 cluster polymers formulated as $\{[Pt_3(dpmp)_2(CNRNC)](PF_6)_2\}_n$ (R = $C_6(Me)_4$ (**63**), $(C_6H_2Me_2)_2$ (**64**)) were deposited from the solution (Scheme 13).[84] The cluster polymer **63** was obtained as single crystals and was shown by X-ray crystallography to have a linearly ordered infinite-chain structure, $\{[Pt_3(dpmp)_2\text{-}(CN(C_6Me_4)NC)]^{2+}\}_n$, as illustrated in Fig. 1.[84] The metal–metal bonded triplatinum units of $\{Pt_3(\mu\text{-dpmp})_2\}^{2+}$ (av Pt–Pt = 2.692 Å) are covalently connected by the bisisocyanide ligands along the b axis. From the size of the crystal the molecular weight number n was estimated as ~10^5. The cluster polymer **63** is soluble in MeCN and DMF, although it is insol-



Scheme 13.

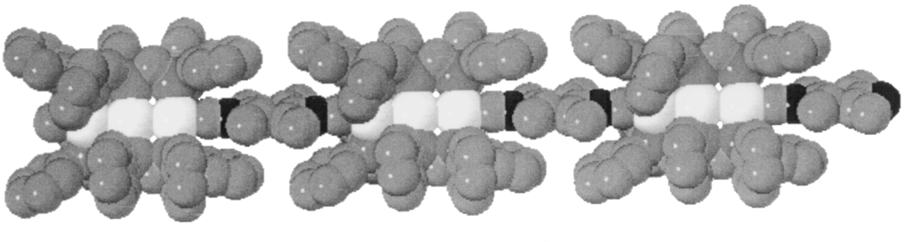
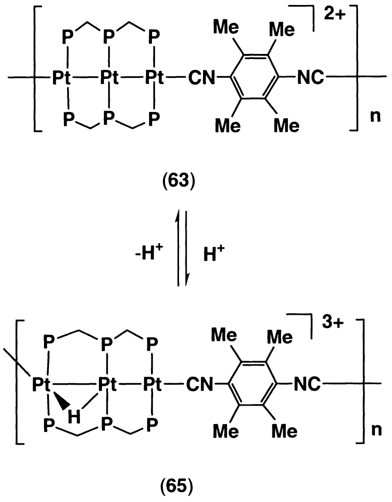


Fig. 1. A perspective view of $\{[Pt_3(dpmp)_2(CN(C_6Me_4)NC)]^{2+}\}_n$ (**63**) illustrated with Van der Waals radii.

uble in CH_2Cl_2 and acetone; it may exist as oligomers in solution, with an average molecular weight number of ~5 as suggested on the basis of the spectroscopic and osmometric analyses. The polymer **63** was very reactive with small molecules even in a heterogeneous system with CH_2Cl_2. For example, when a suspension of **63** in CH_2Cl_2 was treated with excess HPF_6, the yellow polymer of $\{[Pt_3(\mu\text{-}H)(\mu\text{-dpmp})_2(CN(C_6Me_4)NC)](PF_6)_3\}_n$ (**65**) was obtained quantitatively. The spectroscopic data were quite similar to those of $[Pt_2M(\mu\text{-}H)(\mu\text{-dpmp})_2(XylNC)_2](BF_4)_3$ (M = Pt (**53**), Pd (**54**)). On the basis of the crystal structure of **54**, the cluster polymer **65** was estimated to have a zigzag structure (Scheme 14). By treatment with an excess of Et_3N, the polymer **65** again became the rigid-rod polymer **63**. Reactions of **16** with less bulky bis(isocyanide)s, 2,5-dimethylphenylene- and phenylene-1,4-bisisocyanide, exclusively afforded the green cluster dimers formulated as $[(CNRNC)Pt_3(dpmp)_2(CNRNC)Pt_3(dpmp)_2(CNRNC)](PF_6)_4$ (R = C_6H_4 (**66**), $C_6H_2Me_2$ (**67**)) (Scheme 13). An EXAFS analysis suggested that compounds **66** and **67** involved the linear $Pt_3(\mu\text{-dpmp})_2$ cores with significantly longer Pt–Pt distances (2.85(4)–2.86(4) Å).



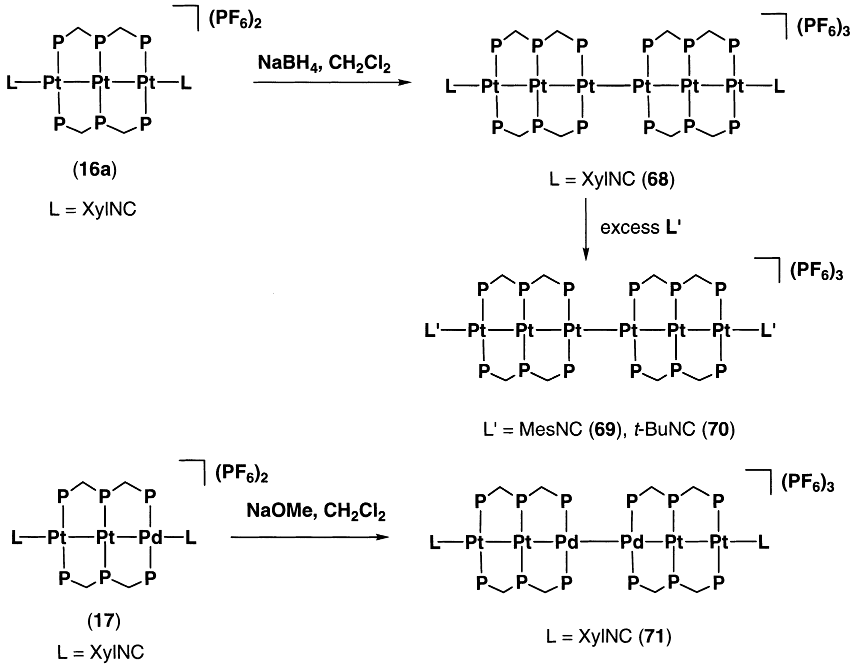
Scheme 14.

The present methodology may be applied to connect the linear Pt_3 units onto the self-assembled monolayer of bisisocyanides on metal surfaces.[88]

6. Linearly Ordered Platinum-Based Hexanuclear Clusters

Are the metal–metal bonded small-size clusters able to work as building blocks to construct further extended linear metallic chains? Recently, we announced a break-through in connecting the linear Pt_3 and Pt_2Pd units with direct metal-metal interaction.[89] When complex **16** was treated with $NaBH_4$ and the product was crystallized from a CH_2Cl_2/Et_2O mixed solvent, dark blue crystals of the hexaplatinum cluster, $[Pt_6(\mu\text{-dpmp})_4(XylNC)_2](PF_6)_3$ (**68**), was isolated in good yield (Scheme 15).[89] Complex **68** was also obtained in a very low yield from reaction of **16** with sodium methoxide. By treatment with an excess amount of MesNC or *t*-BuNC, the axial isocyanide ligands of **68** were replaced to generate $[Pt_6(\mu\text{-dpmp})_4(RNC)_2](PF_6)_3$ (R = Mes (**69**), *t*-Bu (**70**)) (Scheme 15).

The electronic absorption spectra of **68**–**70** in CH_2Cl_2 showed a very intense absorption around 580 nm, which is not observed with the Pt_3 cluster **16**. The characteristic absorption is assignable to intervalence (IT) charge transfer between the $[Pt_3^{2+}Pt_3^{+}]$ and $[Pt_3^{+}Pt_3^{2+}]$ mixed-valence states. From the energy of the band maxima, the binding energy between the two Pt_3 units is estimated as ~25 kcal mol^{-1}. The structure of **68** was determined by X-ray crystallography to consist of a metal–metal bonded hexaplatinum chain as shown in Fig. 2. The average oxidation state of Pt is 0.5 and the cluster valence elec-



Scheme 15.

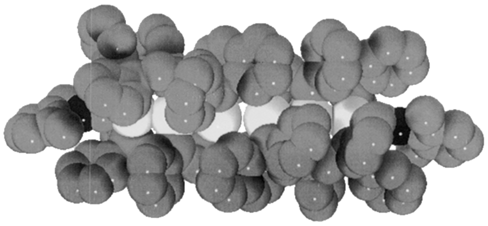


Fig. 2. A perspective view for the cluster cation of $[Pt_6(\mu\text{-dpmp})_4(XylNC)_2](PF_6)_3$ (**68**) illustrated with Van der Waals radii.

tron count is 85. The Pt–Pt distances are av 2.703 Å for the outer Pt–Pt bonds, av 2.723 Å for the inner Pt–Pt bonds, and 3.280(2) Å for the central Pt–Pt one. Although the central Pt–Pt bond is not supported by any bridging ligands and is much longer than those of normal Pt–Pt σ-bonds, it could be expected that a bonding interaction approximately corresponding to a half bond order exists between the two Pt_3 fragments in the light of the electronic absorption spectrum. Complexes **68–70** were paramagnetic and the ^1H NMR spectra showed appreciable upfield shifts of methylene and phenyl proton signals of dpmp ligands. The $^{31}P\{^1H\}$ NMR spectra were somewhat broad and indicated the presence of three unequivalent P atoms with ^{195}Pt satellite peaks in a 1:1:1 ratio. These results clearly demonstrated that complexes **68–70** were stable in solution and existed as linearly ordered molecules (~3 nm long) with a hexametallic chain.

When the linear Pt_2Pd complex **17** was treated with sodium methoxide, dark-green crystals of $[Pt_4Pd_2(\mu\text{-dpmp})_4(XylNC)_2](PF_6)_3$ (**71**) were obtained (Scheme 15). Complex **71** showed an intense and characteristic absorption around 670 nm in CH_2Cl_2 and was characterized by X-ray crystallography to consist of a Pt–Pt–Pd–Pd–Pt–Pt heterometallic chain.

7. Summary

The reactions of dinuclear platinum complexes bridged by dpmp ligands, $[Pt_2(\mu\text{-dpmp})_2(RNC)_2](PF_6)_2$ (**11** and **12**), with various metal fragments led to a variety of homo- and heterotrinuclear complexes. The arrangements, *syn* and *anti*, of the two uncoordinated phosphine units in the dimers play a critical role in determining the direction of additional metal-inserted position. The additional metal is incorporated into the terminal site of the trinuclear core from the *syn*-dimer **11** and into the central position from the *anti*-dimer **12**. The former systems afforded the linearly ordered Pt-Pt-M (M= Pt (**16**), Pd (**17**), Rh (**30a**), Ir (**30b**)) complexes which could be a useful platform to explore nanostructured functional devices. In fact, the Pt_3 complexes **16** were proved to be good precursors of the rigid rod-like cluster polymers, in which the Pt_3 units were linked by π-conjugated bisisocyanides (**63**, **64**), and of the linear hexaplatinum cluster molecules (**68–70**). On the basis of our recent results, we are now trying to develop more expanded linear metallic strings with respect to the three general concepts shown in Fig. 3.

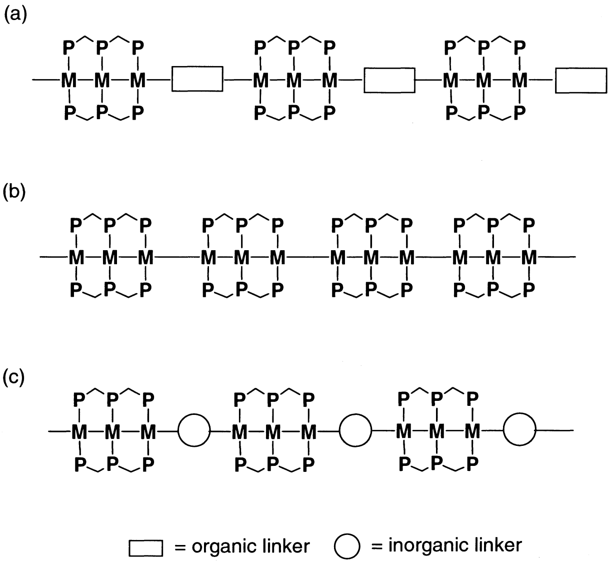


Fig. 3. Strategic concepts for expansion of linear metallic chains; (a) linear cluster fragments connected with organic linkers, (b) linear cluster fragments directly connected with metal-metal bonds, and (c) linear cluster fragments connected with inorganic (metallic) linkers.

The author would like warmly to acknowledge his graduate students of the last several years in Toho University and Nara Women's University. He also thanks Professors Yasuhiro Yamamoto of Toho University, Ken Sakai of Science University of Tokyo, Katsumi Tanigaki of Osaka City University, Shigenobu Yano of Nara Women's University, Dr. Shuzhong Zhan of the JSPS research associate, and Ms. Kimiko Kobayashi of the Institute of Physical and Chemical Research. The author would like to thank Rigaku Co. Ltd. for their kind help in obtaining CCD X-ray data. Finally, the author acknowledges financial support from the Ministry of Education, Science, and Culture, for Grants-in-Aid for Scientific Research.

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