Electrochemical Preparations and Reactions of Linear Di- and Trinuclear Complexes of Platinum and Palladium[§]

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Electrochemical reduction of $[M(RNC)_4]^{2+}$ (1) (M = Pd, Pt; R = $2.6\text{-}Me_2C_6H_3$(Xyl), $2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2$) and $[M(RNC)_2(dppm)]^{2+}$ (**1f**, **1h**) (M = Pt, Pd; R = $2,6\text{-}Me_2C_6H_3$) produced $[M_2(RNC)_6]^{2+}$ (**2**), $[M_3(RNC)_8]^{2+}$ (**3**), $[HgPt_6(RNC)_{12}]$, $[M_2(RNC)_2(dppm)_2]^{2+}$ (**2f**, **2h**), and $[M_3(RNC)_4(dppm)_2]^{2+}$ (**5**), depending on the charge consumed and reduction potential. Reaction of **3** with PPh_3 gave a linear axially-substituted complex $[Pt_3(RNC)_6(PPh_3)_2]^{2+}$ (**4**). The reaction with dppm gave an A-frame complex, $[Pt_3(RNC)_4(dppm)_2]^{2+}$ (**5**), in which the structure was confirmed by an X-ray analysis. Complex **5** contains CH_2Cl_2 as a solvated molecule, and the crystals are orthorhombic with the space group $P2_12_12_1$, with $a = 21.861(7)$ Å, $b = 21.822(8)$ Å, $c = 18.146(8)$ Å, $\alpha = \beta = \gamma = 90.0°$, $V = 8656(6)$ Å^3, and Z = 4 ($R = 0.084$ and $R_w = 0.095$ for 4899 independent reflections with $F_o > 3\sigma(F_o)$). This complex was also prepared by the reaction of **2f** (M = Pt) with a $Pt(RNC)_2$ fragment. Treatment of the complex **2f**, **2h** with 4-nitrophenyl isocyanide in a 1:1 molar ratio led to an insertion of isocyanide into a metal–metal bond to produce an A-frame complex, $[(RNC)M(\mu\text{-dppm})_2(\mu\text{-CNC}_6H_4\text{-}4\text{-}NO_2)M(RNC)]^{2+}$, and the reaction in a 1:2 molar ratio gave $[(RNC)M(\mu\text{-dppm})_2(\mu\text{-CNC}_6H_4\text{-}NO_2)M(4\text{-}NO_2C_6H_4NC)]^{2+}$, but the reaction with 2,6-xylyl isocyanide did not proceed due to steric hindrance. In the electronic spectra of $[M_n(RNC)_{2n+2}]^{2+}$ (n = 1–3), transition of the lower energy shifted to a longer wavelength with the number of metal, related to an increase of the HOMO energy level of their complexes.

A variety of bridged metal–metal-bonded transition metal complexes are well documented in the literature.[1] These complexes are of particular interest since they are an important means to study the interactions between two metals. A-frame complexes have also been increasing attention on the systematic cooperative binding and activation of substrates. The electrochemical method can be used for selective preparation of transition metal complexes by control of potentials and coulometric electrolysis. We have investigated the preparation of metal–metal-bonded complexes by means of electrochemical methods. Recently, we reported the electrochemical reduction of $[MCl_2(RNC)_2]$ (M = Pd or Pt) to give dimeric complexes containing a metal–metal bond.[2-4] We found that the electrochemical reduction of cationic complex $[Pt(RNC)_4]^{2+}$, at a mercury electrode, produced the linear triplatinum complex and then that they reacted with bis(diphenylphosphino)methane (dppm) to be transformed to an A-frame complex. This type of A-frame complex was also obtained by insertion of a d^{10} $Pt(RNC)_2$ fragment into a metal–metal bond in the dimeric platinum complex, $[Pt_2(RNC)_2(dppm)_2]^{2+}$. This reaction is evidence that Hoffman and Hoffmann[5] predicted the existence of an A-frame complex containing a bridged ML_2 moiety on the basis of the isolobal analogy between CH_2 and d^{10} ML_2 fragments. We report a new aspect of the chemistry that led to the electrochemical preparation and structure of linear di- and trinuclear and A-frame platinum and palladium complexes. A preliminary account has been described previously.[6]

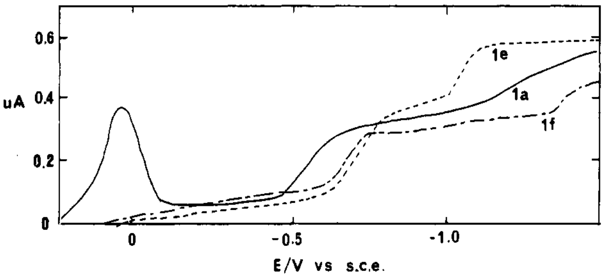

Figure 1. Polarograms of platinum complexes in a $[n\text{-}Bu_4N][ClO_4]$–MeCN solution: $[Pt(XylNC)_4][PF_6]_2$ (**1a**), $[Pt(XylNC)_2(PPh_3)_2][PF_6]_2$ (**1e**), $[Pt(XylNC)_2(dppm)][PF_6]_2$ (**1f**) [concentration: ca. 1 mM for **1a** and **1e**; saturated solution for **1f** (<1.0 mM)].

Results and Discussion

Polarograms of the Platinum(II) Complexes. Polarograms of $[Pt(XylNC)_4][PF_6]_2$ (**1a**) (XylNC = $2,6\text{-}Me_2C_6H_3NC$), $[Pt(XylNC)_2(PPh_3)_2][PF_6]_2$ (**1e**), and $[Pt(XylNC)_2(dppm)][PF_6]_2$ (**1f**) (dppm = $Ph_2PCH_2PPh_2$) in 0.1 mol dm^{-3} $[n\text{-}Bu_4N][ClO_4]$–MeCN solution were measured at a dropping mercury electrode (dme) to investigate the conditions of a macroscopic electrochemical reduction. These complexes are polarographically irreversible. The polarogram of **1a** showed three waves (Figure 1). The wave at about 0 V is assumed to be reduction of an adsorbed

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[§] Electrochemical studies of organometallic compounds. 8. Part 7: Yamamoto, Y.; Ehara, K.; Takahashi, K. *Bull. Chem. Soc. Jpn.*, in press.

(1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(2) Yamamoto, Y.; Takahashi, K., Yamazaki, H. *Chem. Lett.* **1985**, 201. Yamamoto, Y.; Takahashi, K.; Matsuda, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1987**, 1833.

(3) Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2665.

(4) Takahashi, K.; Yamamoto, Y.; Matsuda, K.; Yamazaki, H. *Electrochim. Acta* **1988**, *33*, 1489.

(5) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

(6) Yamamoto, Y.; Takahashi, K.; Yamazaki, K. *J. Am. Chem. Soc.* **1986**, *108*, 2458.

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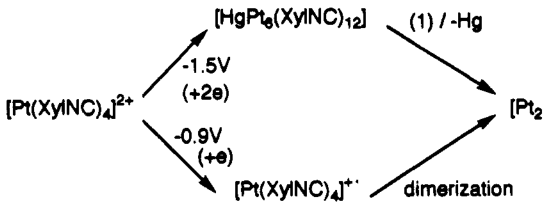
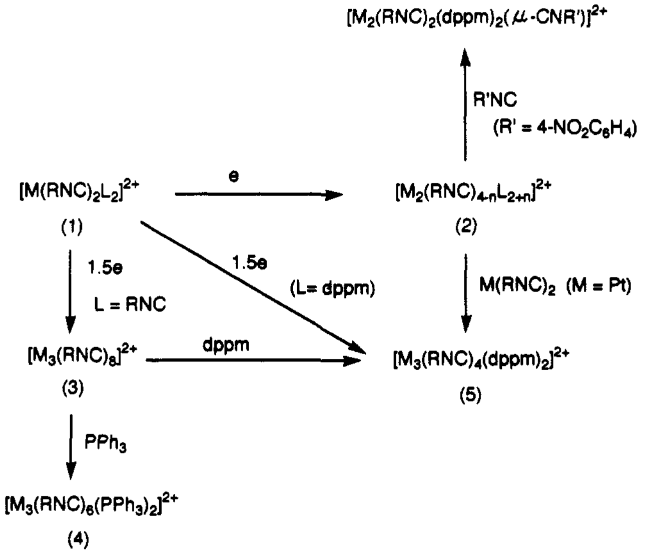
Scheme I. Electrochemical Reactions of $[Pt(XylNC)_4]^{2+}$



Scheme II. Overall Reactions of $[M(RNC)_2L_2]^{2+}$ (M = Pd, Pt) [(1) L_2 = $2PPh_3$, dppm; (2) n = 2, L_2 = dppm, n = 0, L = PPh_3, RNC]



species of the complex on the Hg electrode, in which a similar adsorbed wave has been observed in $PtCl_2(RNC)_2$.[2] The other waves showed apparently a one-electron two-step process. On the polarograms of **1e** and **1f** no adsorption wave was observed and two reductive waves appeared, probably corresponding to a one-electron two-step process similar to that of **1a**.

$$[Pt(RNC)_2(L_2)]^{2+} \xrightarrow{e} \text{“}[Pt(RNC)_2(L_2)]^{+\cdot}\text{”} \xrightarrow{e} \text{“}[Pt(RNC)_2(L_2)]^{0}\text{”}$$

$$L_2 = 2RNC,\ 2PPh_3,\ \text{and dppm}$$

Preparation and Some Reactions of Dinuclear Complexes. We have reported in the previous paper that a 14-electron species, $Pt(RNC)_2$, generated by a two-electron reduction of $PtCl_2(RNC)_2$ led to comproportionation with $PtCl_2(RNC)_2$ to produce a dinuclear complex $Pt_2Cl_2(RNC)_4$ containing a metal–metal bond.[2] A similar mechanism for the cationic complexes is expected. The reduction of **1a** consumed 1 F (F = 96.5 kC) of charge per mole of the complex at −1.50 V, giving the yellow complex **2a**, $[Pt_2(XylNC)_6][PF_6]_2$, in a 63% yield. In this reductive reaction, the solution on the surface of the mercury pool electrode changed from yellow to green, and the green color rapidly changed back to yellow by diffusion of the green color toward the bulk with stirring. Since appearance of the green color suggests the formation of $[HgPt_6(XylNC)_{12}]$,[2,7] a two-electron reduction occurred and was followed by a subsequent comproportionation of a platinum–mercury cluster with **1a** (Scheme I). When the reduction was carried out at −0.9 V, the green color was not observed and **2a** was an isolated complex, showing a one-electron transfer. This reaction is slower than that at −1.5 V, and the yield (32%) is low, due to the low current efficiency.

Similar dinuclear complexes, $[Pt_2(RNC)_6][PF_6]_2$ (**2b**, R = 2,4-*t*-Bu_2-6-MeC_6H_2) were obtained by using an appropriate isocyanide. The perchlorate complex, $[Pt_2(XylNC)_6][ClO_4]_2$ (**2d**)[2] was prepared by electrolysis of a mixture of $PtCl_2(XylNC)_2$ and 2,6-xylyl isocyanide (XylNC) in an acetonitrile solution containing $NaClO_4$ as a supporting electrolyte. Electroreduction of $[Pt(XylNC)_2(PPh_3)_2][PF_6]_2$ (**1e**) consumed 1 F at ca −1.2 V, giving a pale yellow complex, $[Pt_2(XylNC)_4(PPh_3)_2][PF_6]_2$ (**2e**), in high yield, in which two PPh_3 ligands occupied the trans positions to the platinum atom. Complex **2e** was also obtained by replacement of **2a** with PPh_3. A similar reduction of $[Pd(XylNC)_2(dppm)][PF_6]_2$ (**1h**) at −1.0 V produced $[Pd_2(XylNC)_2(dppm)_2][PF_6]$ (**2h**). The ^1H NMR spectrum showed a singlet at δ 1.70, due to 2- and 6-methyl protons and a triplet centered at δ 4.80 due to the methylene protons of the dppm ligands, in which the two outer signals are not discernible. Complex **2h** was also obtained by the reaction of $Pd_2Cl_2(dppm)_2$ with 2,6-xylyl isocyanide in the presence of $[NH_4][PF_6]$.

Preparation and Some Reactions of Trinuclear Complexes. The electrolysis of **1a** consumed ca. 1.5 F at −1.5 V, giving two complexes, **2a** and $[Pt_3(XylNC)_8][PF_6]_2$ (**3a**) (yellow). Complex **3a** showed the presence of terminal isocyanides (2163 and 2149 cm^{-1}) in the infrared spectrum. The ^1H NMR spectrum showed three singlets due to the methyl groups at δ 2.30, 2.48, and 2.59, consisting of an intensity ratio of 2:1:1. The resonance at δ 2.30 is assigned to the equatorial isocyanide ligands bonded to the outer Pt atoms. The other two resonances are due to the axial isocyanides and isocyanides bonded to the central Pt atom. The perchlorate complex $[Pt_3(XylNC)_8][ClO_4]_2$ (**3d**) was prepared by the electrochemical reduction of $PtCl_2(XylNC)_2$ in the presence of 2,6-xylyl isocyanide, using $NaClO_4$ as a supporting electrolyte. The trinuclear complex having bulky isocyanide ligands, $[Pt_3(2,4\text{-t-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_8][PF_6]_2$ (**3b**), was also obtained by reduction of **1b**.

When $[Pd(XylNC)_4][PF_6]_2$ (**1g**) consumed ca. 1.5 F at −1.1 V, a trinuclear palladium complex, $[Pd_3(XylNC)_8][PF_6]_2$ (**3g**) was obtained in a 43% yield in addition to the dimer **2g** (4%).

The reactions of **3a** or **3d** with triphenylphosphine produced disubstituted products $[Pt_3(XylNC)_6(PPh_3)_2][X]_2$ (**4d**, X = ClO_4; **4e**, X = PF_6), showing the presence of only terminal isocyanide in the infrared spectrum (2144 and 2126 cm^{-1} for **4e** and 2146 and 2125 cm^{-1} for **4d**). Their ^1H NMR spectra showed two singlets at δ ca. 1.8 and 2.4 consisting of a 1:2 intensity ratio for methyl groups; the former was assigned to the two inner isocyanide ligands, and the latter, to four outer equatorial ones. An analogous palladium complex (**4g**), $[Pd_3(XylNC)_6(PPh_3)_2][PF_6]_2$, was readily prepared from **3g** and PPh_3. A similar complex containing methyl isocyanide ligands, $[Pd_3(MeCN)_6(PPh_3)_2]^{2+}$, has been previously described.[8]

In an attempt to confirm an accurate structure of **4**, an X-ray analysis of **4e** containing CH_2Cl_2 as a solvated molecule was undertaken.[6] X-ray analysis of the same complex without a solvated molecule was recently un-

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(7) (a) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329. (b) Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1989**, 2161.

(8) Balch, A. L.; Boehm, J. R.; Hope, H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1979**, *98*, 7431.

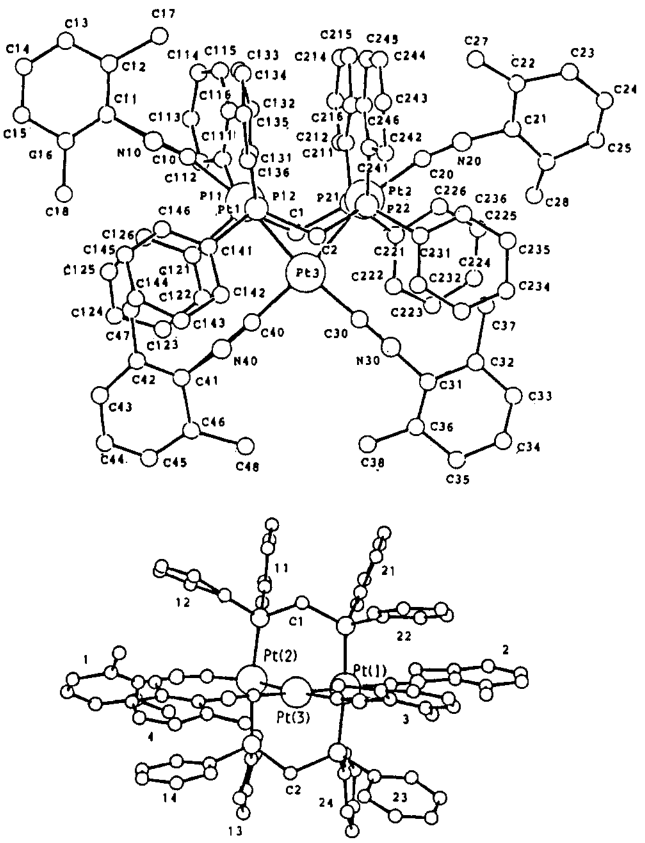


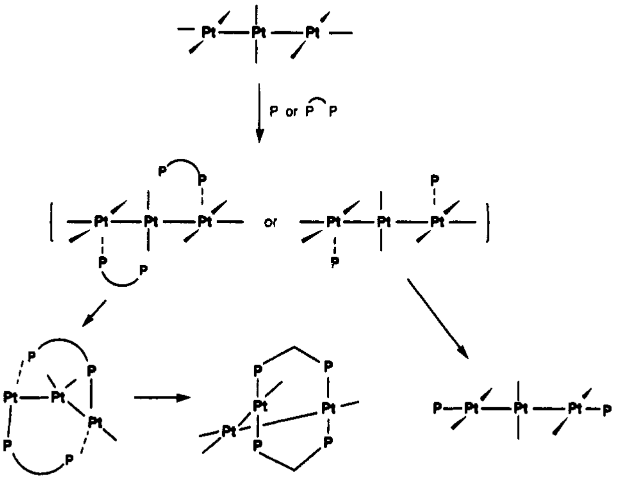
Figure 2. Molecular structure of the cation in $[Pt_3(XylNC)_4(dppm)_2][PF_6]_2$ (**5f**).

dertaken by Mingos et al.[9] Since the structure is essentially the same and has been reported briefly in the previous paper,[6] we do not describe it here.

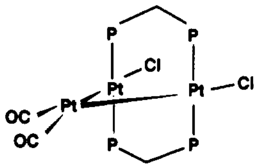
Addition of bis(diphenylphosphino)methane (dppm) to **3a** gave yellow crystls formulated as $[Pt_3(XylNC)_4(dppm)_2][PF_6]_2CH_2Cl_2$ (**5f**), after recrystallization from CH_2Cl_2 and ether. The infrared spectrum showed three peaks at 2174, 2118, and 2104 cm^{-1}, assignable to terminal isocyanide ligands. The ^1H NMR spectrum showed two singlets at δ 1.66 and 2.03 in a 1:1 ratio, due to 2- and 6-methyl groups, and a complicated resonance at δ ca. 4.5, due to the methylene protons. It was determined by an X-ray analysis (Figure 2) that the molecular geometry is a discrete A-frame structure. This complex was also obtained by electrochemical reduction of **2f** by passing 1.5 F/mol of the complex at −1.3 V. A similar palladium complex, $[Pd_3(XylNC)_4(dppm)_2][X]_2CH_2Cl_2$ (**5d**, X = ClO_4; **5g**, X = PF_6) was readily obtained from the reaction of **3d** or **3g** with dppm and is isostructural with the platinum complex **5f**.

In the transformation from 3 to 5, we suggest that an initial attack of the phosphorus ligand to a vacant axial position occurs and forms a five-coordinated intermediate. In the case of triphenylphosphine, complex 4 is formed by elimination of the isocyanide ligand. However, in the reaction with dppm, the Pt–Pt–Pt bond is bent, and the A-frame structure would be completed by approach of another free phosphorus site to the vacant position of another platinum and subsequently by elimination of the isocyanide ligands. In this transformation, the geometry of the inner Pt atom probably changes as trans → tetrahedral → cis form to assist a 1,3-addition of bidentate ligands (Scheme III).

Scheme III. Transformation from a Linear Complex to an A-Frame Complex (Isocyanide Ligands Omitted for Clarity)



In the publication dealing with the electronic structure of A-frame molecules, Hoffman and Hoffmann employed the isolobal analogy between CH_2, d^{10} ML_2, and d^8 ML_4 metal fragments to predict the existence of trimetallic clusters, so-called "A-frames" with a bridging ML_2 moiety as follows:[5]



Complex **5f** can be regarded as the adduct generated by insertion of the 14-electron fragment $Pt(RNC)_2$, being isolobal with CH_2, into the Pt–Pt bond of **2f**. This reaction is considered to be a reasonable candidate to confirm the prediction mentioned by Hoffman and Hoffmann. The reaction of **2f** with $[HgPt_6(XylNC)_{12}]$, being a precursor of the 14-electron fragment, was carried out in toluene at reflux and, as expected, gave **5f** in a moderate yield. This reaction is the first example of the A-frame structure formed by insertion of the 14-electron metal fragment into a metal–metal bond.

An initial step of this reaction consists of an interaction of platinum vacant p_y orbitals of the square $Pt_2P_4C_2$ plane with the filled p_y orbital of PtL_2, and the reaction completes by bending Pt–CNR groups from the original planes and by cleavage of the metal–metal bond.

Figure 3 shows the molecular orbitals of $[Pt_3(H_2PCH_2PH_2)_2(HNC)_4]^{2+}$. For the PtL_2 fragment, the dominant bonding interaction will be between the filled Pt_2 $3a_1$ orbital and the empty $2a_2$ of PtL_2. Another interaction occurs between the empty Pt_2 $3b_2$ orbital and the b_2 orbital of the filled PtL_2 fragment. This bonding mode is apparent by the observation that the charge distribution in the inner and outer platinum atom is relatively small.

An attempt to examine the reactions of dinuclear complex **2f** or **2h** with 2,6-xylyl isocyanide was made in toluene at 80 °C for 20 h, and then the reaction recovered the starting material. The reactions with 4-nitrophenyl isocyanide in a 1:1 molar ratio at room temperature led to an insertion of an adding isocyanide into a metal–metal bond to give $[M_2(\mu\text{-}CNC_6H_4\text{-}4\text{-}NO_2)(XylNC)_2(XylNC)_2][PF_6]_2$ (**6f**, M = Pt; **6h**, M = Pd). The infrared spectra showed the signals due to terminal and bridging isocyanide

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[9] Briant, C.; Gilmour, D. I.; Mingos, D. M. P. *J. Organomet. Chem.* 1986, *308*, 381.

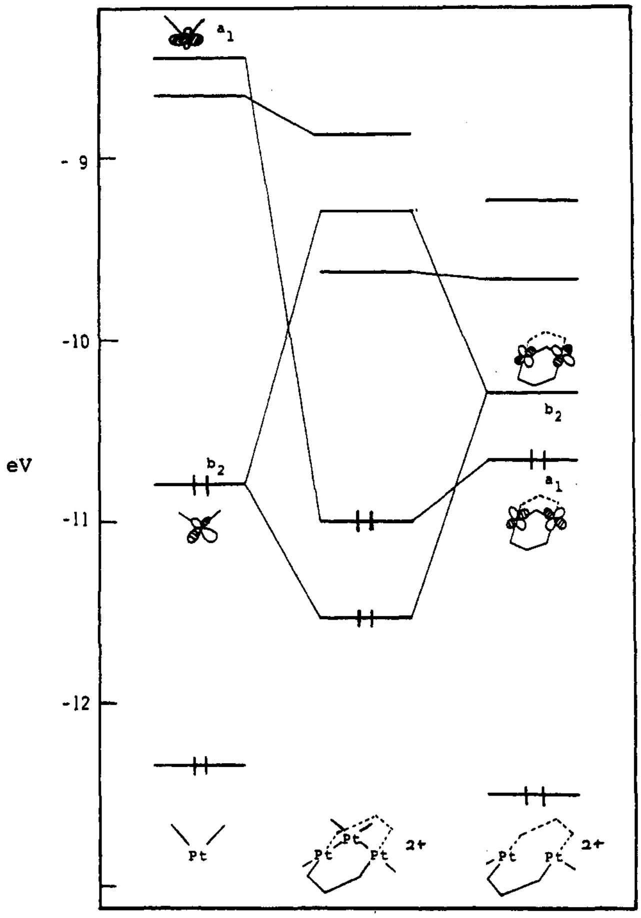
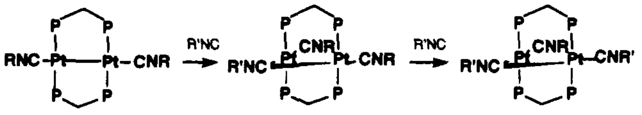


Figure 3. Molecular orbital diagram of $[Pt_3(HNC)_4(H_2PCH_2PH_2)_2]^{2+}$.

ligands (2150 and 1560 cm^{-1} for **6f** and 2162, 1629, and 1568 cm^{-1} for **6 h**). The ^{1}H NMR spectra showed a singlet due to 2- and 6-methyl protons of 2,6-xylyl isocyanide (δ 2.81 for **6f** and 2.86 for **6 h**). The analogous reactions with 4-nitrophenyl isocyanide in a 1:2 ratio underwent replacement of terminal isocyanide with added isocyanide to give $[M_2(\mu\text{-}CNC_6H_4\text{-}4\text{-}NO_2)(4\text{-}NO_2C_6H_4NC)(XylNC)(dppm)_2][PF_6]_2$ (**7f**, M = Pt; **7h**, M = Pd). The infrared spectra showed the presence of terminal and bridging isocyanide groups. The ^{1}H NMR spectrum of **7h** showed a singlet at δ 2.94 due to 2- and 6-methyl protons. The ^{31}P NMR spectrum showed two doublets at δ 29.96 and 28.54 (J_{PP} = 63.0 Hz). These spectroscopic data are in agreement with a proposed structure. A similar reaction of **2h** with an excess of cyclohexyl isocyanide also gave $[Pd_2(\mu\text{-}CNC_6H_{11})(C_6H_{11}NC)(XylNC)(dppm)_2][PF_6]_2$ (**7i**). These results suggest that the steric effect of adding isocyanide molecules is responsible for insertion of isocyanide into a metal–metal bond. Similar insertion reactions of isocyanide into a metal–metal bond in cationic dinuclear dppm complexes of platinum and palladium have been reported.[10–13]



In an attempt to obtain further information for the reaction path, the ^{1}H NMR spectrum of a mixture of **2f** and 2,6-xylyl isocyanide was measured and showed the absence of ligand exchange. This may suggest an initial interaction of the vacant p_y orbitals of Pt atoms with lone pair electrons of isocyanide as well as in the reaction with PtL_2.

Electronic Spectra. The electronic spectra of dinuclear and linear trinuclear complexes of platinum are depicted in Figure 4. On the whole, the absorption patterns of **3** shifted to a wavelength longer than those of dinuclear complexes **2a–d**, and the latter complexes also red-shifted to those of mononuclear complexes.

In the EHMO calculations of $[Pt_n(HNC)_{2n+2}]^{2+}$ (n = 1–3), the energies of HOMOs increase with the number of metals, but those of LUMOs mostly remain unchanged. It is likely related to the rise of the HOMO energy that the lowest energy band shifts to a longer wavelength with the number of metals. The electronic spectra of dinuclear isocyanide complexes **2a–d** in CH_2Cl_2 showed an absorption at ca. 315 nm, assignable to a σ–σ^* transition.

In the electronic spectra of the dinuclear dppm complexes, the σ–σ^* transition appears at 290 nm for the platinum complex and at 370 nm for the palladium one, suggesting a bond strength greater in the platinum complex than in the palladium one (Figure 5). A similar trend was observed in the electronic spectra of linear trimetal complexes: the difference of the λ_{max} value between platinum and palladium complexes is ca. 20 nm and smaller than that in the dinuclear complexes. The lowest energy band of the linear trinuclear complex containing triphenylphosphine red-shifts by ca. 70 nm in comparison with that of the parent trinuclear complex, because the energy of the HOMO increases by introduction of donor phosphorus ligands (Figure 6). In the electronic spectra of A-frame complexes of platinum and palladium, absorption bands shift to shorter wavelengths than those of the parent trinuclear complexes, contrasted with the case of the linear phosphine complexes, probably due to the difference in geometries between linear and A-frame structures (Figure 7).

The electronic spectra of the isocyanide insertion complexes showed patterns similar to those of triplatinum A-frame complexes, suggesting similarity of the structures.

Structure of $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_4(dppm)_2][PF_6]_2$ (5f). The structure of **5f** is depicted in Figure 2. The molecular geometry is a discrete A-frame structure. The geometries around the Pt atoms are planar. The P ligands are bent away from the isocyanide ligands, giving rise to the mean value of 95.1(10)° for the PPtC angles. The eight-membered ring consists of two Pt atoms and two dppm ligands and adopts a boat form in which two carbon atoms are bent toward the Pt(3) atom. The Pt–Pt bond lengths are 2.589(2) and 2.596(2) Å, slightly shorter than those of $Pt_3(t\text{-}BuNC)_6$,[14] $[HgPt_6(XylNC)_{12}]$,[7] and $[Pt_3(XylNC)_6(PPh_3)_2][PF_6]_2$. The nonbonded Pt(1)Pt(2) distance is 3.303(2) Å, longer than those found in $[Pt_2Cl_2(\mu\text{-}CH_2)(dppm)_2]$ (3.16 Å)[1] and $[Pd_2(\mu\text{-}CNMe)(MeNC)_2(dppm)_2]^{2+}$ 3.215(2) Å).[11] The Pt(1)–Pt(3)–Pt(2) bond angle is 79.14(6)°, narrower by ca. 20° than the MCM angles.[1,12,13] This arises from the differences in the bond radii of the Pt and C atoms and also from the difference in hybridization about the central Pt and C atoms.

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(10) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

(11) Olmstead, M. M.; Hope, H.; Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502.

(12) Khan, M. A.; McAlees, M. J. *Inorg. Chim. Acta* **1985**, *104*, 109.

(13) Uson, R.; Fornies, J.; Espinet, P.; Fortuno, C. *J. Chem. Soc., Dalton Trans.* **1986**, 1849.

(14) Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509.

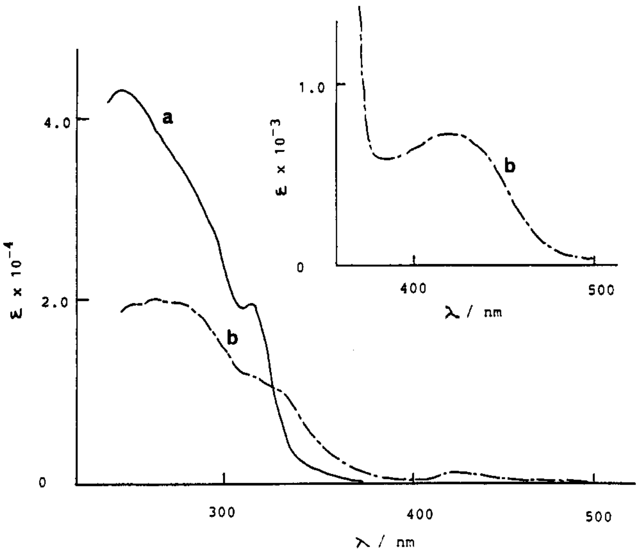

Figure 4. Electronic spectra of $[Pt_2(XylNC)_6][PF_6]_2$ (a) and $[Pt_3(XylNC)_8][PF_6]_2$ (b) in CH_2Cl_2.

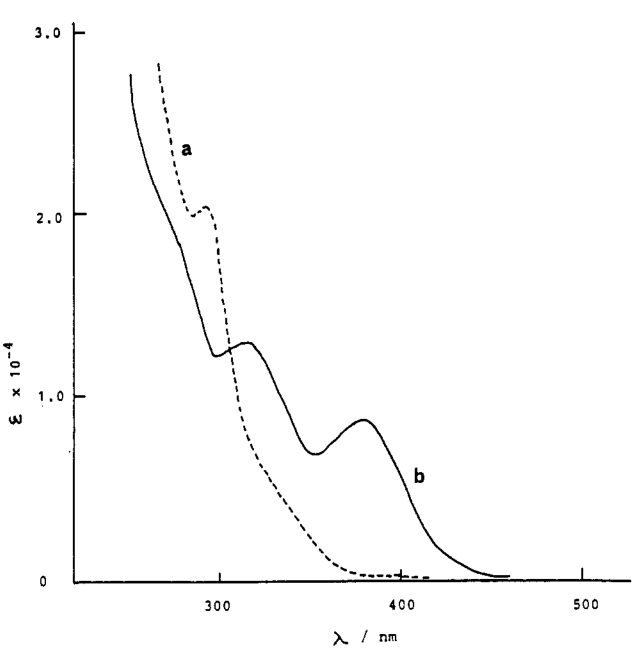

Figure 5. Electronic spectra of $[M_2(XylNC)_2(dppm)_2][PF_6]_2$ (a, M = Pt; b, M = Pd) in CH_2Cl_2.

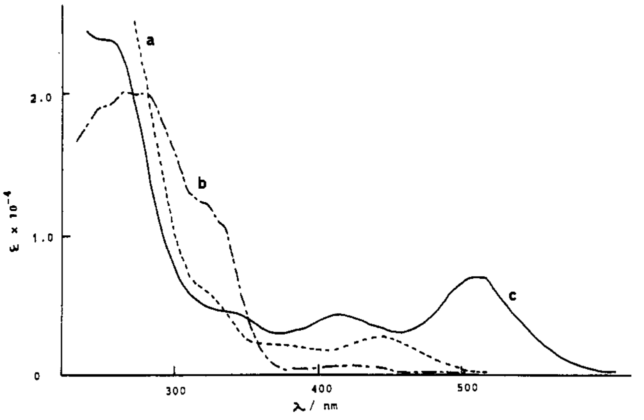

Figure 6. Electronic spectra of $[M_3(XylNC)_8][PF_6]_2$ (a, M = Pd; b, M = Pt) and $[Pd_3(XylNC)_6(PPh_3)_2][PF_6]_2$ (c) in CH_2Cl_2.

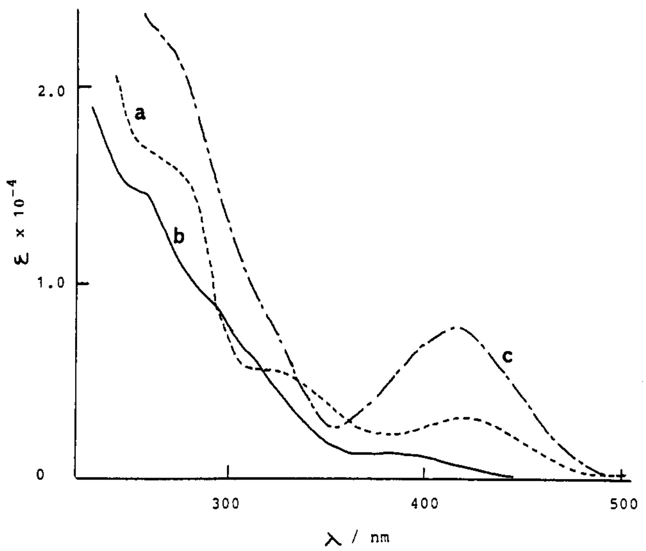

Figure 7. Electronic spectra of A-frame complexes in CH_2Cl_2: (a) $[Pd_3(XylNC)_4(dppm)_2][PF_6]_2$; (b) $[Pt_3(XylNC)_4(dppm)_2][PF_6]_2$; (c) $[Pd_2(XylNC)_4(\mu\text{-}CNC_6H_4\text{-}4\text{-}NO_2)][PF_6]_2$.

The average Pt–Pt–C and Pt–C–N bond angles of the outer isocyanide ligands are 166(1) and 167(3)°, respectively, bent toward the outer position from the ideal A-frame to minimize the steric repulsion between the phenyl rings. The average Pt–C–N angle associated with the inner isocyanide ligands is ca. 178(3)°. The C–N–C bond angles have the normal values of ca. 174°. The C(30)–Pt(3)–C(40) bond angle is 96.7(12)°, minimizing steric repulsion between two isocyanide ligands.

Experimental Section

All reactions were carried out under nitrogen atmosphere. Acetonitrile was purified by distillation from calcium hydride. Tetra-*n*-butylammonium perchlorate and sodium perchlorate as supporting electrolytes were used as purchased. Isocyanides,[15,16] $[M(RNC)_4][PF_6]_2$, $[Pt(RNC)_2(PPh_3)_2][PF_6]_2$, and $[M(RNC)_2(dppm)][PF_6]_2$ (M = Pd, Pt), were prepared according to literature methods, some with modification.[2,3,9] Electronic and IR spectra were recorded on Shimadzu UV-240 and JASCO 442 spectrometers, respectively. Proton NMR spectra were recorded on a JEOL FX100, using TMS as a reference. Potentiostatic electrolyses with coulometry and polarographic measurements were carried out using a HUSO 956B potentiostat and a HUSO 321 potential scanning unit. The electrochemical procedures were carried out according to literature methods.[2] A reference electrode ($Ag/AgNO_3$–$[n\text{-}Bu_4N][ClO_4]$/MeCN) potential was 310 ± 3 mV versus a saturated calomel electrode (sce). All potentials are versus an aqueous sce.

Electrochemical Reactions. Complexes of platinum and palladium (ca. 0.3 mmol) were dissolved or suspended in a 0.1 mol dm^{-3} $NaClO_4$–MeCN solution (30 cm^3). The solution was deaerated by bubbling with nitrogen. The mercury pool electrode was used for preparation of platinum complexes, and a Pt plate (3 × 3 cm^2) electrode, for palladium complexes. After passage of an appropriate amount of charge at a constant potential, the solution was separated by decantation and the solvent was removed to dryness under reduced pressure. The residue was extracted with CH_2Cl_2, and then the solvent was removed to ca. 3 cm^3. Ether was added to the solution, and a pale yellow or yellow complex was obtained as crystals. Reaction conditions and yields are shown in Table I.

$[Pt_2(XylNC)_4(PPh_3)_2][PF_6]_2$ (2e) (Pale Yellow). IR (Nujol): 2158 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.92 (s, Me), ca. 7.3 (complex = c, aromatic protons = ap). Electronic spectrum (=AB) (CH_2Cl_2): λ_{max} 303 (ε 22 500), 263 (23 700), 215 (sh, 21 700) nm. Anal.

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(15) Walborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187.

(16) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.

Table I. Electrochemical Reduction of Isocyanide Complexes of Platinum(II) and Palladium(II)[a]

complex	*E*(sce) (V)	*n* (F)	yield (%)	product[c]
$[Pt(XylNC)_4]^{2+}$ (**1a**)	−1.5	1	63	**2a**
	−1.4	1.5	47	**3a**
			9	**2a**
$[Pt(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_4]^{2+}$ (**1b**)	−1.5	1	65	**2b**
	−1.6	1.5	74	**3b**
			3	**2b**
$[Pt(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_4]^{2+}$ (**1c**)	−1.6	1	59	**2c**
$[PtCl_2(XylNC)_2]$[b]	−1.5	1	69	**2d**
	−1.6	1.5	68	**3d**
			3	**2d**
$[Pt(XylNC)_2(PPh_3)_2]^{2+}$ (**1e**)	−1.3	1	74	**2e**
$[Pt(XylNC)_2(dppm)]^{2+}$ (**1f**)	−1.3	1	73	**2f**
	−1.3	1.5	43	**5f**
$[Pd(XylNC)_4]^{2+}$ (**1g**)	−1.0	1	63	**2g**
	−1.1	1.5	43	**3g**
			4	**2g**
$[Pd(XylNC)_2(dppm)]^{2+}$ (**1h**)	−1.1	1	62	**2h**
	−1.1	1.5	53	**5g**
			8	**2h**

[a] Complex concentration: ca. 0.3 mM/$NaClO_4$–MeCN (30 mL). [b] In the presence of 2,6-xylyl isocyanide. [c] **2a–c**: $[Pt_2(RNC)_6][PF_6]_2$ [R = (**a**) Xyl, (**b**) 2,4-*t*-Bu_2-6-MeC_6H_2, (**c**) 2,4,6-*t*-$Bu_3C_6H_2$]. **2d**: $[Pt_2(XylNC)_6][ClO_4]_2$. **2e**: $[Pt_2(XylNC)_2(PPh_3)_2][PF_6]_2$. **2f**, **2h**: $[M_2(XylNC)_2(dppm)_2][PF_6]_2$ [M = (**f**), Pt, (**h**) Pd]. **3a**, **3b**, **3g**: $[M_3(RNC)_8][PF_6]_2$ [(**a**) M = Pt, R = Xyl; (**b**) M = Pt, R = 2,4-*t*-Bu_2-6-MeC_6H_2; (**g**) M = Pd, R = Xyl). **3d**: $[Pt_3(XylNC)_8][ClO_4]_2$. **5f**, **5g**: $[M_3(XylNC)_4(dppm)_2][PF_6]_2$ [M = (**f**) Pt, (**g**) Pd].

Table II. Selective Bond Distances and Angles of A-Frame Complex $[Pt_3(XylNC)_4(dppm)_2][PF_6]_2$ (5f)

Bond Distances (Å)			
Pt(1)–Pt(3)	2.589(2)	Pt(2)–Pt(3)	2.596(2)
Pt(1)–P(11)	2.293(10)	Pt(1)–P(12)	2.300(11)
Pt(1)–C(10)	2.022(28)	Pt(2)–P(21)	2.292(11)
Pt(2)–P(22)	2.298(11)	Pt(2)–C(20)	1.966(39)
Pt(3)–C(30)	1.967(31)	Pt(3)–C(40)	2.017(30)
C(10)–N(10)	1.055(39)	C(20)–N(20)	1.199(55)
C(30)–N(30)	1.165(46)	C(40)–N(40)	1.097(47)
Pt(1)–Pt(2)	3.303(2)		
Bond Angles (deg)			
Pt(1)–Pt(3)–Pt(2)	79.14(6)	Pt(3)–Pt(1)–P(11)	82.9(3)
Pt(3)–Pt(1)–P(12)	85.7(3)	Pt(3)–Pt(1)–C(10)	169.2(8)
P(11)–Pt(1)–P(12)	168.4(4)	P(11)–Pt(1)–C(10)	94.5(8)
P(12)–Pt(1)–C(10)	96.3(9)	Pt(3)–Pt(2)–C(20)	163.2(11)
Pt(3)–Pt(2)–P(22)	84.7(3)	P(21)–Pt(2)–C(20)	98.8(12)
P(22)–Pt(2)–C(20)	91.0(12)	Pt(1)–Pt(3)–C(30)	171.6(9)
Pt(1)–Pt(3)–C(40)	92.7(8)	Pt(2)–Pt(3)–C(30)	92.6(9)
Pt(2)–Pt(3)–C(40)	171.3(9)	C(30)–Pt(3)–C(40)	95.7(12)
Pt(1)–C(10)–N(10)	165.6(27)	C(10)–N(10)–C(11)	174.6(34)
Pt(2)–C(20)–N(20)	167.8(35)	C(20)–N(20)–C(21)	170.6(42)
Pt(3)–C(30)–N(30)	178.6(33)	C(30)–N(30)–C(31)	178.7(40)
Pt(3)–C(40)–N(40)	178.1(31)	C(40)–N(40)–C(41)	170.3(45)

Calcd for $C_{72}H_{66}N_4P_4F_{12}Pt_2$: C, 50.01; H, 3.85; N, 3.24. Found: C, 49.58; H, 3.79; N, 3.09.

$[Pt_2(XylNC)_2(dppm)_2][PF_6]_2$ (2f) (Pale Yellow). IR (Nujol): 2149 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.58 (s, Me), 5.21 (t, t, $^3J_{PtH}$ = 29 Hz, J_{PH} = 4.5 Hz), ca. 7 (c, ap). AB (CH_2Cl_2): λ_{max} 292 (ϵ 20 900), 235 (51 900) nm. Anal. Calcd for $C_{67}H_{62}N_2P_6F_{12}Pt_2$: C, 47.73; H, 3.65; N, 1.64. Found: C, 47.48; H, 3.65; N, 1.58.

$[Pd_2(XylNC)_2][PF_6]_2CH_2Cl_2$ (2h) (Yellow). IR (Nujol): 2157 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, Me), 4.80 (t, CH_2), 5.30 (s, CH_2Cl_2), ca. 7.0 (c, ap). ^{31}P NMR (CD_3COCD_3, reference H_3PO_4): δ 9.49 (s). AB (CH_2Cl_2): λ_{max} 317 (ϵ 13 100), 378 (8900) nm. Anal. Calcd for $C_{68}H_{64}N_2P_4F_{12}Cl_2Pt_2$: C, 51.20; H, 3.98; N, 1.73. Found: C, 50.94; H, 3.91; N, 1.78.

$[Pt_3(XylNC)_8][PF_6]_2$ (3a) (Yellow). IR (Nujol): 2146, 2176 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.30 (s, 24 H, Me), 2.48 (s, 12 H, Me), 2.59 (s, 12 H, Me), ca. 7.0 (c, ap). AB (CH_2Cl_2): λ_{max} 423 (ϵ 700), 318 (sh, 12 400), 280 (19 900), 263 (20 200), 247 (19 000) nm. Anal. Calcd for $C_{72}H_{72}N_8P_2F_{12}Pt_3$: C, 44.93; H, 3.77; N, 5.82; Pt, 30.41. Found: C, 45.59; H, 3.83; N, 5.90; Pt, 30.03.

$[Pt_3(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_8][PF_6]_2$ (3) (Yellow). IR (Nujol): 2174, 2147 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.19 (s, 36 H, 4-*t*-Bu), 1.21 (s, 36 H, 2-*t*-Bu), 1.32 (s, inner 18 H, *o*-*t*-Bu), 1.36 (s, axial, 18 H, 4-*t*-Bu), 1.49 (s, inner, 18 H, 2-*t*-Bu), 1.59 (s, axial 18 H, 2-*t*-Bu), ca. 7.0 (c, ap). AB (CH_2Cl_2): λ_{max} 428 (ϵ 1580), 334 (30 900), 293 (37 300) nm. Anal. Calcd for $C_{128}H_{184}N_8P_2F_{12}Pt_3$: C, 56.73; H, 6.84; N, 4.13. Found: C, 56.86; H, 6.79; N, 4.16.

$[Pt_3(XylNC)_8][ClO_4]_2$ (3d) (Yellow). IR (Nujol): 2149, 2163 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.26 (s, 24 H, *o*-Me), 2.46 (s, inner, 12 H, *o*-Me), 2.56 (s, axial, 12 H, *p*-Me), 6.89 (d, 7.7 Hz, outer 8 H, *m*-H), 7.11 (t, 7.7 Hz, outer 4 H, *p*-H), 7.23 (d, 7.7 Hz, inner, 4 H, *m*-H), 7.27 (d, 7.7 Hz, azial, 4 H, *m*-H), 7.38 (t, 7.7 Hz, axial, 2 H, *p*-H), 7.40 (t, 7.7 Hz, inner, 2 H, *p*-H). Anal. Calcd for $C_{72}H_{72}N_8Cl_2O_8Pt_3$: C, 47.16; H, 3.96; N, 6.11. Found: C, 46.89; H, 3.92; N, 6.22.

$[Pd_3(XylNC)_8][PF_6]_2$ (**3g**) was prepared by the chemical or electrochemical reaction.

Chemical Preparation of $[Pd_3(XylNC)_8][PF_6]_2$ (3g). A mixture of $PdCl_2(cod)$ (0.07 g, 0.25 mmol), $Pd_2(dba)_3CHCl_3$ (0.4 g, 0.25 mmol), XylNC (0.355 g, 2.71 mmol), and $[NH_4][PF_6]$ (0.12 g, 0.66 mmol) in acetone (20 mL) was stirred at room temperature. After 2 h, the solvent was removed under reduced pressure and the residue was extracted with benzene. Benzene was removed to dryness, and the residue was crystallized from CH_2Cl_2–ether to give yellow crystals of **3g** (0.38 g, 93.5%). IR (Nujol): 2147, 2129 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.29 (bs, outer 24 H, *o*-Me), 2.49 and 2.55 (s, inner and axial 12 H, *o*-Me). AB (CH_2Cl_2): λ_{max} 442 (ϵ 2700), 260 (30 100) nm. Anal. Calcd for $C_{72}H_{72}N_8P_2F_{12}Pd_3$: C, 52.14; H, 4.38; N, 6.76. Found: C, 52.66; H, 4.36; N, 6.76.

Reaction of 3a with Triphenylphosphine. Triphenylphosphine (0.032 g, 0.122 mmol) was added to a solution of **3a** (0.10 g, 0.052 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. The solution color changed from pale orange to orange. After 1 h, the solvent was removed to 3 cm^3 and ether was added to give orange crystals of **4e**, $[Pt_3(XylNC)_6(Pph_3)_2][PF_6]_2CH_2Cl_2$ (0.103 g, 91%). IR (Nujol): 2144, 2126 cm^{-1}. AB (CH_2Cl_2): λ_{max} 278 (ϵ 15 500), 328 (12 100), 381 (12 900), 473 (1300) nm. ^{1}H NMR (CD_2Cl_2): δ 1.78 (s, 24 H, *o*-Me), 2.42 (s, 12 H, *o*-Me), ca. 7.0 (c, ap). Anal. Calcd for $C_{91}H_{86}N_6P_4F_{12}Cl_2Pt_3$: C, 48.11; H, 3.82; N, 3.70. Found: C, 48.10; H, 3.75; N, 3.57.

Palladium complexes were prepared from the reaction of **3g** with PPh_3.

$[Pd_3(XylNC)_6(PPh_3)_2][ClO_4]_2$ (4h) (78.7%, Orange Yellow). IR (Nujol): 2146, 2125 cm^{-1}. AB (CH_2Cl_2): λ_{max} 250 (ϵ 20 400), 288 (17 200), 381 (12 000), 470 (1260) nm. Anal. Calcd for $C_{90}H_{84}N_6P_2Cl_2O_8Pd_3$: C, 51.58; H, 4.04; N, 4.01. Found: C, 52.01; H, 4.06; N, 3.75.

$[Pd_3(XylNC)_6(PPh_3)_2][PF_6]_2CH_2Cl_2$ (4g) (57%, Wine Red). IR (Nujol): 2118 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.81 (s, outer, 24 H, *o*-Me), 2.46 (s, inner, 12 H, *o*-Me), ca. 7.0 (c, ap). AB (CH_2Cl_2): λ_{max} 508 (ϵ 7100), 412 (4500), 330 (sh, 4990), 250 (26 800) nm. Anal. Calcd for $C_{91}H_{86}N_6P_4F_{12}Cl_2Pd_3$: C, 54.49; H, 4.32; N, 4.19. Found: C, 54.34; H, 4.25; N, 4.12.

Reaction of 3d with dppm. Dppm (0.02 g, 0.052 mmol) was added to a solution of **3d** (0.04 g, 0.022 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. The solution color changed from yellow to orange. After 1 h, the solution color changed back yellow. The removal of the solvent and crystallization of the residue from CH_2Cl_2 and hexane gave yellow crystals (**5d**) containing CH_2Cl_2 as a solvated molecule (0.015 g, 63%). IR (Nujol): 2120, 2094 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.66 (s, 12 H, *o*-Me), 2.03 (s, 12 H, *o*-Me), ca. 4.5 (c, CH_2), ca. 7.3 (c, ap). AB (CH_2Cl_2): λ_{max} 383 (ϵ 2070), 254 (21 600) nm. Anal. Calcd for $C_{87}H_{82}N_4P_4Cl_4O_8Pt_3$: C, 48.32; H, 3.82; N, 2.59. Found: C, 48.18; H, 3.74; N, 2.52.

The PF_6 compounds of platinum (**5f**, yellow, 72%) and palladium (**5g**, orange, 48%) containing CH_2Cl_2 as a solvated molecule were obtained from the reaction of **3a** and/or **3g** with dppm according to similar procedures described above.

$[Pt_3(XylNC)_4(dppm)_2][PF_6]_2CH_2Cl_2$ (5f). IR (Nujol): 2147, 2118, 2104 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.66 (s, 12 H, *o*-Me), 2.03 (s, 12 H, *o*-Me), ca. 4.5 (c, 2 H, CH_2), ca. 7.0 (c, ap). AB (CH_2Cl_2): λ_{max} 375 (ϵ 1450), 258 (14 700) nm. Anal. Calcd for

$\mathrm{C_{87}H_{82}N_4P_6F_{12}Cl_2Pt_3}$: C, 46.37; H, 3.67; N, 2.49. Found: C, 46.01; H, 3.60; N, 2.42.

$\mathbf{[Pd_3(XylNC)_4(dppm)_2][PF_6]_2CH_2Cl_2}$ (5g). IR (Nujol): 2146, 2128, 2115 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 1.67 (s, 12 H, *o*-Me), 1.95 (s, 12 H, *o*-Me), ca. 4.4 (c, 2 H, $\mathrm{CH_2}$), ca. 7.0 (c, ap). AB ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ 421 (ϵ 3170), 318 (5600), 258 (sh, 16 400) nm. Anal. Calcd for $\mathrm{C_{87}H_{82}N_4P_6F_{12}Pd_3}$: C, 52.57; H, 4.16; N, 2.82. Found: C, 52.44; H, 4.11; N, 2.68.

Reaction of 2f with 4-Nitrophenyl Isocyanide in a 1:1 or 1:2 Ratio. (a) 4-Nitrophenyl isocyanide (0.01 g, 0.068 mmol) was added to a yellow solution of **2f** (0.10 g, 0.058 mmol) in $\mathrm{CH_2Cl_2}$(10 cm^3) at room temperature. After the mixture was stirred for 0.5 h, the solvent was removed under reduced pressure, and the residue was crystallized from $\mathrm{CH_2Cl_2}$ and ether to give orange crystals of $\mathrm{[Pt_2(XylNC)_2(\mu\text{-}4\text{-}NO_2C_6H_4NC)(dppm)_2][PF_6]_2}$ (**6f**) (0.073 g, 68%). IR (Nujol): 2150, 1570, 1504 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 2.81 (s, 12 H, *o*-Me), ca. 3.4 (c, $\mathrm{CH_2}$), ca. 7.5 (c, ap). AB ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ 424 (ϵ 3720), 310 (14 260) nm. Anal. Calcd for $\mathrm{C_{75}H_{66}N_4O_2P_6F_{12}Pt_2}$: C, 48.45; H, 3.58; N, 3.01. Found: C, 48.76; H, 3.70; N, 2.83.

(b) Reaction of **2f** (0.1 g, 0.58 mmol) with 4-nitrophenyl isocyanide (0.02 g, 0.135 mmol) was carried out according to procedures similar to those described above. $\mathrm{[Pt_2(XylNC)(\mu\text{-}4\text{-}NO_2C_6H_4NC)(4\text{-}NO_2C_6H_4NC)(dppm)_2][PF_6]_2}$ (**7f**) (0.098 g, 90%) was obtained as orange crystals. IR (Nujol): 2165, 1610, 1592 cm^{-1}. ^{1}H NMR ($\mathrm{CD_3COCD_3}$): δ 2.89 (s, 6 H, *o*-Me), ca. 3.5 (c, $\mathrm{CH_2}$), ca. 7.5 (c, ap). AB ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ 443 (ϵ 2330), 300 (12 400) nm. Anal. Calcd for $\mathrm{C_{73}H_{61}N_5O_4P_6F_{12}Pt_2}$: C, 46.73; H, 3.28; N, 3.73. Found: C, 46.55; H, 3.39; N, 3.66.

Reaction of 2h with 4-Nitrophenyl Isocyanide. A mixture of **2h** (0.046 g, 0.029 mmol) and 4-nitrophenyl isocyanide (0.005 g, 0.03 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was stirred at room temperature. After 2 h, the solvent was removed under reduced pressure. The residue was crystallized from $\mathrm{CH_2Cl_2}$–ether to give orange yellow crystals of $\mathrm{[Pd_2(XylNC)_2(\mu\text{-}4\text{-}NO_2C_6H_4NC)(dppm)_2][PF_6]_2CH_2Cl_2}$ (**6 h**) (0.042 g, 89%). IR (Nujol): 2162, 1629, 1568 cm^{-1}. AB ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ 418 (ϵ 8070) nm. Anal. Calcd for $\mathrm{C_{76}H_{68}N_4O_2P_6F_{12}Cl_2Pd_2}$: C, 51.66; H, 3.88; N, 3.17. Found: C, 51.67; H, 3.81; N, 3.23.

$\mathrm{[Pd_2(XylNC)(\mu\text{-}4\text{-}NO_2C_6H_4NC)(4\text{-}NO_2C_6H_4NC)(dppm)_2][PF_6]_2\cdot CH_2Cl_2}$ (**7h**) (96%, orange) was obtained from **2h** (0.046 g, 0.029 mmol) and 4-nitrophenyl isocyanide (0.010 g, 0.06 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) according to procedures similar to those described above. IR (Nujol): 2163, 1625 cm^{-1}. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 2.94 (s, 6 H, *o*-Me), ca. 4.0 (c, $\mathrm{CH_2}$), ca. 7.5 (c, ap). ^{31}P NMR ($\mathrm{CD_3COCD_3}$): δ 29.96 ($J_{\mathrm{PP}} = 63.0$ Hz), 28.54 ($J_{\mathrm{PP}} = 63.0$ Hz). Anal. Calcd for $\mathrm{C_{74}H_{63}N_5O_4P_6F_{12}Cl_2Pd_2}$: C, 49.83; H, 3.56; N, 3.93. Found: C, 50.21; H, 3.57; N, 3.95.

$\mathrm{[Pd_2(XylNC)(\mu\text{-}C_6H_{11}NC)(C_6H_{11}NC)][PF_6]_2\cdot 2CH_2Cl_2}$ (**7i**) (62%, orange) was obtained from the reaction of **2h** with cyclohexyl isocyanide in a 1:2.5 ratio in $\mathrm{CH_2Cl_2}$ (10 mL). IR (Nujol): 2181, 2162, 1656 cm^{-1}. Anal. Calcd for $\mathrm{C_{75}H_{79}N_3P_6F_{12}Cl_4Pd_2}$: C, 50.30; H, 4.45; N, 2.35. Found: C, 50.54; H, 4.39; N, 2.29.

Reaction of $\mathbf{[Pt_2(XylNC)_2(dppm)_2][PF_6]_2}$ (2h) with $\mathbf{[HgPt_6(XylNC)_{12}]}$. A mixture of **2h** (0.1 g, 0.058 mmol) and $\mathrm{[HgPt_6(XylNC)_{12}]}$ (0.047 g, 0.016 mmol) in a solution of benzene (5 mL) and MeCN (5 mL) was heated at 90 °C. After 2 h the solution was filtered through a glass filter (3G4) and the solvent was removed to dryness. The residue was crystallized from a $\mathrm{CH_2Cl_2}$–ether solution at room temperature to give $\mathrm{[Pt_3(XylNC)_4(dppm)_2][PF_6]_2}$ (0.085 g, 63.5%), in comparison with spectroscopic data of the authentic compound.

Table III. Crystal and Experimental Data for 5f

formula	$\mathrm{C_{87}H_{82}N_4P_6Cl_2F_{12}Pt_3}$
mol wt	2253.6
a, Å	21.861(7)
b, Å	21.822(8)
c, Å	18.146(8)
α, deg	90.0
β, deg	90.0
γ, deg	90.0
V, Å^3	8656.3(59)
Z	4
space group	$P2_12_12_1$
density, g cm^{-3}	1.73 (calcd), 1.74 (found)
radiation (λ, Å)	Mo Kα (0.710 73) from graphite monochromator
μ, cm^{-1}	52.3
transm factor	0.47–0.52
scan speed, deg/min	4
2θ limits, deg	30.0–50.0
scan mode	ω scan ($2\theta < 30°$), ω–2θ scan ($2\theta \geq 30°$)
no. of unique data measd/used ($F_o > 3\sigma(F_o)$)	5040/4899
final no. of variables	503
R	0.084
R_w	0.095

Structure Determination. Compound **5f** was recrystallized from $\mathrm{CH_2Cl_2}$–ether. Preliminary measurement showed the crystals to be orthorhombic with the space group $P2_12_12_1$. Cell constants were determined from 14 reflections ($15° < 2\theta < 18°$) on a Rigaku automated diffractometer. The crystal parameters along with data collection are summarized in Table III. Throughout the data collection the intensities of the three standard reflections were measured every 100 reflections as a check of the stability of the crystals; a maximum variation in intensity of 2% was noted, and no decay correction was applied to the data. The diffraction pattern was in general weak and did not extend beyond $2\theta = 40°$, mostly due to the small crystal size (0.18 {001}, 0.07 {0,0,-1}, and 0.078 {111} mm). Of a total 5040 independent intensities measured in the range $2\theta \leq 40°$, 4899 reflections for which $F_o \geq 3\sigma(F_o)$ were used in the solution and refinement of the structure. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient for Mo Kα radiation is 52.3 cm^{-1}, and the absorption correction was made. The calculated transmission factors varied from 0.47 to 0.52. The platinum atoms were solved by a direct method using the program MULTAN78[17] and refined by the block-diagonal least-squares method. Subsequent Fourier maps gave the positions of the remaining non-hydrogen atoms. The function $\sum w(F_o) - |F_c|)^2$ was minimized with the weighing factor *w* equal to unity. A total of 9 atoms out of the 114 non-hydrogen atoms was refined anisotropically. Hydrogen atoms were not determined. The final difference Fourier map showed no other features with a value greater than 0.8 e A^{-3} except near the platinum positions (2.1 e A^{-3}). Atomic scattering factors were used with Pt, P, N, C, F, and Cl corrected for anomalous dispersion.[18] Computation was carried out with UNICS III system.[19]

Appendix

The parameters used in the extended Huckel molecular orbital calculations were taken from ref 20. The Pt–Pt, Pt–C(axial) and Pt–C(equatorial) distances were set to 2.56, 1.92, and 2.00 Å, respectively. All C–N and N–H distances were set to 1.17 and 1.01 Å, respectively. The Pt–Pt–C and C–Pt–C bond angles were idealized to be linear.

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Supplementary Material Available: Listings of bond distances and angles and positional and thermal parameters (13 pages). Ordering information is given on any current masthead page.

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(17) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Delercq, J.-P.; Woolfson, M. M. MULTAN78, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. Universities of York and Louvain, England and Belgium, 1978.

(18) *International Tables for X-ray Crystallography*; Kynock Press: Birmingham, England, 1974; Vol. IV.

(19) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyuusho Houkoku* **1979**, *55*, 69.

(20) Dedieu, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2074.