Journal of Organometallic Chemistry, 440 (1992) 1–5
Elsevier Sequoia S.A., Lausanne
JOM 22909

Uptake of a Hg or Hg_2 unit into the center of cage-type platinum clusters supported by diphosphines having long methylene carbon chains: X-ray structure of $[Hg_2Pt_6(dpphex)_3(RNC)_6] \cdot 2C_6H_6$ (dpphex = 1,6-bis(diphenylphosphino)hexane, R = 2,6-dimethylphenyl)

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(Received February 21, 1992)

Abstract

When $Pt(COD)Cl_2$ was treated with sodium amalgam in the presence of aromatic isocyanide (RNC, R = $2,6\text{-}Me_2C_6H_3$ (Xyl) or $2,4,6\text{-}Me_3C_6H_2$ (Mes)) and diphosphine with long methylene chain (diphos = $Ph_2P(CH_2)_nPPh_2$, $n = 5$ (dpppn) or 6 (dpphex)), two kinds of Hg–Pt mixed metal clusters, $[Hg_2Pt_6(diphos)_2(RNC)_8]$ (**2**) and $[Hg_2Pt_6(diphos)_3(RNC)_6]$ (**3**), were obtained. The structure of **3b** (R = Xyl, diphos = dpphex) was determined by an X-ray analysis to be a cage-type cluster where a Hg_2 unit was incorporated into a trigonal-anti-prismatic platinum core, two Pt_3 triangles being supported by three dpphex ligands (close-type). The cluster **2** was assumed to have an incomplete cage-type structure (open-type), and was converted to close-type **3** by treatment with an equivalent diphosphine ligand. When dppb ($n = 4$) was used, an open-type mixed metal cluster in which one mercury atom was captured, $[HgPt_6(dppb)_2(RNC)_8]$ (**4**), was obtained as the sole product.

Metal clusters are of interest as a potential bridge between homogeneous and heterogeneous catalytic reactions [1]. We reported that treatment of dichlorobis(2,6-xylyl isocyanide)platinum(II) with sodium amalgum gave the high nuclearity cluster, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ [2]. A similar reduction in the presence of isocyanide (RNC) produced the trigonal prismatic Hg–Pt mixed cluster, $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**1**) [3]. Electrochemical reduction of $PtCl_2(RNC)_2$ and $[Pt(RNC)_4]^{2+}$ gave di- and trinuclear complexes, $Pt_2Cl_2(RNC)_4$, $[Pt_2(RNC)_6]^{2+}$, and $Pt_3(RNC)_8]^{2+}$, whose selectivities varied depending on the charge controlled conditions [4,5]. Recently, di- and trinuclear platinum complexes

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containing isocyanides and chelating diphosphines (diphos = $Ph_2P(CH_2)_nPPh_2$ $2 \le n \le 4$) have been prepared by the electrochemical techniques, in which the length of the methylene carbon chain of diphos influenced their stereochemistry [6]. In particular, when the charge of 1.5 F/mol of $[Pt(RNC)_2(dppp)]^{2+}$ ($n = 3$) was passed, novel linear triplatinum complexes involving a coordinatively "naked" platinum center were obtained. Here, we introduce diphosphines with long methylene chains ($4 \le n \le 6$) to the platinum-isocyanide system, and report on the synthesis and characterization of novel cage-type mixed-metal clusters supported by diphosphines.

A mixture of $Pt(COD)Cl_2$, RNC, diphos, and NH_4PF_6 (R = 2,6-$Me_2C_6H_3$ (Xyl) or 2,4,6-$Me_3C_6H_2$ (Mes), diphos = dpppn ($n = 5$) or dpphex ($n = 6$)) was treated with Na–Hg at room temperature for several hours. The dark green solution was chromatographed on deactivated alumina. After work-up of the eluate, the residue was recrystallized from benzene/hexane to give two kinds of dark green crystals (**2** and **3**), formulated as $[Hg_2Pt_6(diphos)_2(RNC)_8] \cdot C_6H_6$ (**2a**, diphos = dpppn, R = 2,4,6-$Me_3C_6H_2$ 7%; 2b, diphos = dpphex, R = 2,6-$Me_2C_6H_3$ 5%) and $[Hg_2Pt_6(diphos)_3(RNC)_6] \cdot C_6H_6$ (**3a**, diphos = dpppn, R = 2,4,6-$Me_3C_6H_2$ 10%; **3b**, diphos = dpphex, R = 2,6-$Me_2C_6H_3$ 38%) [7*,8*]. The IR spectrum of **3** indicated the presence of only bridging isocyanide groups (ν(C=N) *ca.* 1840m, 1710 cm^{-1}). The electronic absorption spectrum showed a characteristic absorption around 650 nm, similar to that of **1**. To clarify the structure, an X-ray analysis of **3b** was undertaken (Fig. 1) [9*]. The molecule consists of two triangular Pt_3 units which are connected by three diphosphines (dpphex). The six isocyanide molecules act as bridging ligands in each triangular unit. Two mercury atoms are captured in an anti-trigonal-prismatic cage (called "close-type"). A similar cluster $[Hg_2Pt_6(\mu\text{-}CO)_6(PPh\text{-}^iPr_2)_6]$ (**5**), in which two Hg atoms were sandwiched between two Pt_3 units, has been reported by Albinati [10]. The Hg–Hg distance of 2.872(7) Å is significantly shorter than that of the carbonyl cluster **5** (3.225 Å) and slightly shorter than is found in the crystalline α form of metallic Hg (2.99 Å), but longer than those of Hg_2X_2 salts for X = halide (2.49–2.69 Å) [11]. The average Pt–Hg and Pt–Pt distances are 2.950 Å and 2.664 Å, respectively, compared with those found in the clusters **1** and **5**. Preliminary extended Hückel MO calculations were carried out on a model compound $[Hg_2Pt_6(\mu\text{-}CNH)_6(PH_3)_6]$ (D_{3h} symmetry) [12]. On the basis of the long Hg–Hg distance comparable to that of metallic mercury, the molecular orbital analysis was simplified to an interaction of $[Pt_3(\mu\text{-}CNH)_3(PH_3)_3]_2^0$ with Hg_2^0 ($d_{Hg-Hg} = 2.87$ Å). The HOMO is derived from a repulsive interaction between the filled Pt d orbitals in the triangular plane (depicted as **I** for the single Pt_3 triangle in Fig. 2) and the filled σ^* orbital (Hg 6s), and is stabilized by a bonding interaction with the empty orbital composed of (μ-CNH) π^* and Pt p_z (depicted as **II** in Fig. 2). From these, the Hg–Hg interaction is presumed to be weak, although the repulsive character between Hg atoms is somewhat relaxed through the empty (μ-CNH) π^* and Pt p_z orbitals.

Heating of cluster **3** in refluxing toluene led to a recovery of the starting material, whereas a similar treatment of **1** extracted mercury from the prismatic

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* Reference with asterisk indicates a note in the list of references.

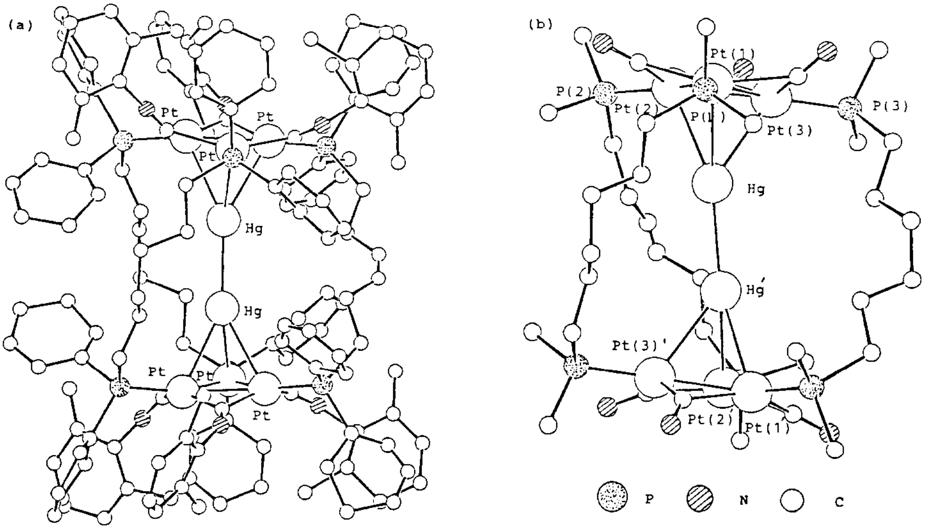


Fig. 1. (a) A perspective drawing of $[Hg_2Pt_6(dpphex)_3(XylNC)_6]$ (**3b**). (b) Cluster core of **3b**. Some selected bond distances and angles: Hg–Hg' 2.872(7), Hg–Pt(1) 2.980(6), Hg–Pt(2) 2.993(6), Hg–Pt(3) 2.878(6), Pt(1)–Pt(2) 2.664(3), Pt(1)–Pt(3) 2.672(4), Pt(2)–Pt(3) 2.656(5) Å, Pt(1)–Hg–Pt(2) 53.0(1), Pt(1)–Hg–Pt(3) 54.2(1), Pt(2)–Hg–Pt(3) 53.8(1), Hg–Pt(1)–Pt(2) 63.8(1), Hg–Pt(1)–Pt(3) 61.0(1), Hg–Pt(2)–Pt(1) 63.3(1), Hg–Pt(2)–Pt(3) 60.9(1), Hg–Pt(3)–Pt(1) 64.8(2), Hg–Pt(3)–Pt(2) 65.3(2), Pt(2)–Pt(1)-Pt(3) 59.7(1), Pt(1)–Pt(2)–Pt(3) 60.3(1), Pt(1)–Pt(3)–Pt(2) 60.0(1)°.

core to give $Pt_3(2,6\text{-}Me_2C_6H_3NC)_6$ [3]. The unusual stability of cluster **3** is probably responsible for a cage effect.

The IR spectrum of cluster **2** indicated the presence of both bridging and terminal isocyanide groups (ν(N≡C) *ca.* 2100, 1920, ν(C=N) *ca.* 1700, 1660 cm^{-1}). The electronic absorption spectrum (λ_{max} *ca.* 670 nm) was similar to that of **3**. Further, cluster **2** reacted smoothly with diphosphines to yield the close-type cluster **3**. From these, cluster **2** was assumed to have an incomplete cage structure (called "open-type") in which a Hg_2 unit was incorporated (Scheme 1).

When dppb ($n = 4$) was used, the green complex formulated as $[HgPt_6(dppb)_2(RNC)_8]\cdot C_6H_6$ (**4a**, $R = 2,6\text{-}Me_2C_6H_3$ 62%; **4b**, $R = 2,4,6\text{-}Me_3C_6H_2$ 30%) was obtained as the only product [13*]. The analytical and spectral data suggested that the cluster **4** had an open-type cage structure where a single mercury atom was sandwiched between the two Pt_3 triangles (Scheme 1). Unlike cluster **2**, the single

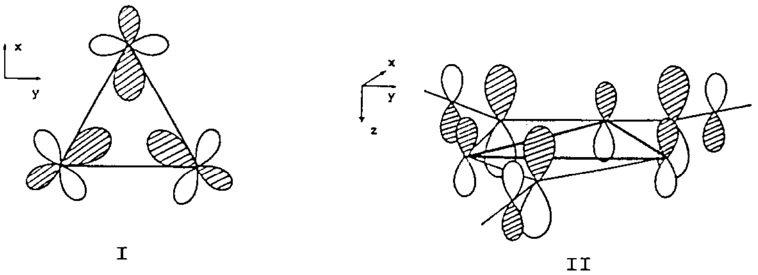
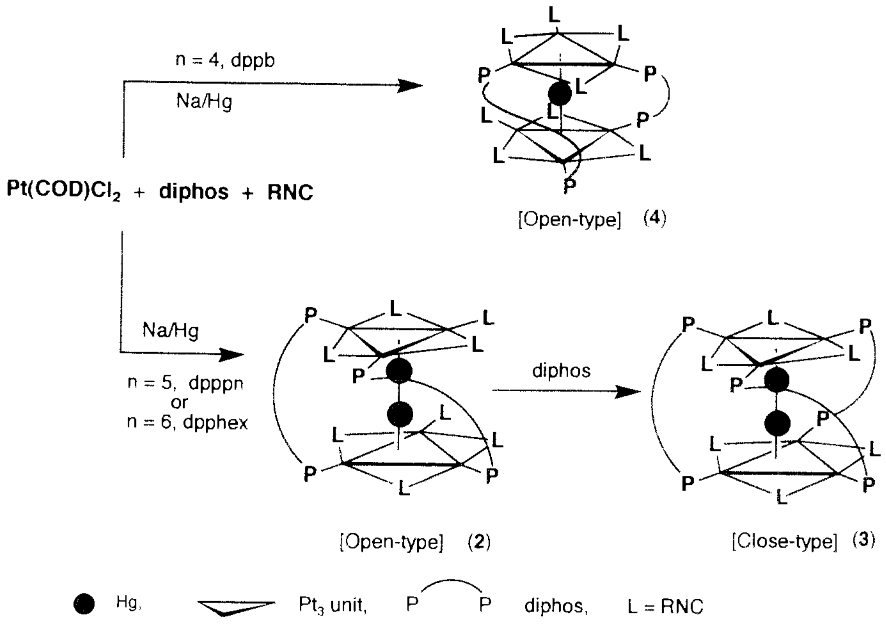


Fig. 2. Molecular orbitals of the Pt_3 triangular unit.



Scheme 1.

mercury cluster **4** could not be converted to a close-type one when treated with dppb, presumably because the steric repulsions of phenyl rings between the two Pt_3 triangles increased with dppb which has a relatively short methylene chain ($n = 4$). Employing dppe ($n = 2$) and dppp ($n = 3$), no Hg–Pt mixed metal cluster was obtained. Thus, the number of methylene groups of the diphosphines plays an important factor in the formation of the mixed-metal clusters.

Acknowledgement

This work was partially support by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (02640484).

References and notes

1 (a) R. Ugo, Catal. Rev., 11 (1975) 225; (b) E.L. Muetterties, Bull. Soc. Chim. Belg., 84 (1975) 959; (c) B.F.G. Johnson, Transition Metal Clusters, Wiley, Chichester, 1980.

2 (a) Y. Yamamoto, K. Aoki and H. Yamazaki, Organometallics, 2 (1983) 1377; (b) Y. Yamamoto, K. Aoki and H. Yamazaki, Chem. Lett., (1979) 391.

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

4 Y. Yamamoto, K. Takahashi and H. Yamazaki, Chem. Lett., (1985) 201.

5 Y. Yamamoto, K. Takahashi and H. Yamazaki, J. Chem. Soc.. Dalton Trans., (1987) 1833.

6 T. Tanase, Y. Kudo, M. Ohno, K. Kobayashi and Y. Yamamoto, Nature, 344 (1990) 526.

7 Analytical and spectral data for **2a**: Anal. Found: C, 46.98; H, 4.17; N, 2.95. $C_{144}H_{154}N_8Hg_2Pt_6P_4$ calc.: C, 46.84; H, 4.20; N, 3.03%. IR (nujol): 2110, 1933 (N≡C), 1700, 1662 (C=N) cm^{-1}. UV-vis (in benzene): λ_{max} ($\log \epsilon$) 676 (3.85), 466 (3.77), 346 (3.97) nm (mol^{-1} cm^{-1} dm^3). For **2b**: Anal. Found: C, 46.46; H, 4.10; N, 3.10. $C_{138}H_{142}N_8Hg_2Pt_6P_4$ calc.: C, 45.94; H, 4.00; N, 3.11%. IR (nujol): 2104, 1901 (N≡C), 1690, 1661 (C=N) cm^{-1}. UV-vis (in benzene): λ_{max} ($\log \epsilon$) 670 (3.55), 463 (3.47), 327 (3.67) nm (mol^{-1} cm^{-1} dm^3).

8 Analytical and spectral data for **3a**: Anal. Found: C, 47.65; H, 4.10; N, 2.18. $C_{153}H_{162}N_6Hg_2Pt_6P_6$ calc.: C, 47.82; H, 4.25; N, 2.19%. IR (nujol): 1857m, 1714 (C=N) cm^{-1}. UV-vis (in benzene); λ_{max} (log ϵ) 662 (3.97), 430 (3.67), 325 (3.86) nm (mol^{-1} cm^{-1} dm^3). For **3b**: Anal. Found: C, 47.34; H, 4.16; N, 2.14. $C_{150}H_{156}N_6Hg_2Pt_6P_6$ calc.: C, 47.41; H, 4.13; N, 2.21%. IR (nujol): 1834m, 1711 (C=N) cm^{-1}. UV-vis (in benzene): λ_{max} (log ϵ): 642 (3.91), 437 (3.75), 332 (3.93) nm (mol^{-1} cm^{-1} dm^3).

9 The crystals of **3b** were extremely unstable in air, so a crystal sealed into a glass tube capillary with a small droplet of the mother liquid was used to collect diffraction data. Even under such condition, intensities of the standard reflections exhibited a time-dependent decrease, and two crystals were used to obtain diffraction data of $2\theta < 45°$ on a Rigaku AFC4 four-circle automated diffractometer. The unit cell dimensions were determined with 20 reflections in the range of $20 < 2\theta < 30°$ for each crystal, and the arithmetic mean was used as the unit cell dimensions in the subsequent structure solution. Crystal data: $C_{142}H_{145}N_6Hg_2Pt_6P_6 \cdot 2C_6H_6$, $M = 3878.6$, monoclinic, space group $C2/c$, $a = 56.86(8)$, $b = 15.120(8)$, $c = 31.01(3)$ Å, $\beta = 141.29(6)°$, $V = 16673$ Å^3, $Z = 4$, $D_c = 1.546$ g cm^{-3}, Mo-K_α radiation. The structure was solved by direct methods (MULTAN 78) and refined by block-diagonal least squares techniques to $R = 0.104$, $R_w = 0.085$ using 4990 unique reflections with $F_o > 3\sigma(F_o)$ (Hg, Pt and P atoms were refined with anisotropic thermal parameters and the others with isotropic parameters). All calculations were carried out on a FACOM M-780 computer with the program system UNICS III (T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55 (1979) 69). Tables of supplementary material are available from the authors.

10 A. Albinati, A. Moor, P.S. Pregosin and L.M. Venazi, J. Am. Chem. Soc., 104 (1982) 7672.

11 A.F. Wells, Structural Inorganic Chemistry, 3rd edition, Oxford University Press, London, 1962.

12 D.J. Underwood, R. Hoffmann, K. Tatsumi, A. Nakamura and Y. Yamamoto, J. Am. Chem. Soc., 107 (1985) 5968.

13 Analytical and spectral data for **4a**; Anal. Found: C, 47.70; H, 4.32; N, 2.87. $C_{134}H_{134}N_8HgPt_6P_4$ calc.: C, 48.02; H, 4.03; N, 3.34%. IR (nujol): 2088, 1897 (N≡C), 1741, 1660 (C=N) cm^{-1}. UV-vis (in benzene): λ_{max} (log ϵ) 651 (3.57), 445 (3.40), 356 (3.65) nm (mol^{-1} cm^{-1} dm^3). For **4b**: Anal. Found: C, 48.87; H, 4.39; N, 3.37. $C_{142}H_{150}N_8HgPt_6P_4$ calc.: C, 49.24; H, 4.37; N, 3.24%. IR (nujol): 2067, 1860 (N≡C), 1800, 1664 (C=N) cm^{-1}. UV-vis (in benzene): λ_{max} (log ϵ): 643 (3.74), 460 (3.40), 340 (3.92) nm (mol^{-1} cm^{-1} dm^3).