

## Communications to the Editor

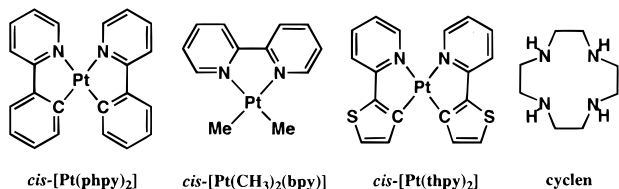
## The First Examples of Platinum(II)–Cadmium(II) Bonds: The Role of Strong Field Ligands in Making Dative Pt→M Bonds

Tadashi Yamaguchi,\* Fumie Yamazaki, and Tasuku Ito\*

Department of Chemistry, Graduate School of Science  
Tohoku University, Sendai 980-8578, Japan

Received April 2, 1999

It has been shown that the occupied  $d_{z^2}$  orbital of a  $d^8$  transition metal ion with square-planar coordination geometry can act as a potential donor to another metal ion (M) resulting in a dative  $M(d^8) \rightarrow M$  bond. Many examples of  $Pt(II) \rightarrow M$  dative bonds have been reported.<sup>1–3</sup> However, this type of bond is generally supported by a bridging ligand<sup>1</sup> or a weakly bridging interaction.<sup>2</sup> The molecular orbital scheme for  $Pt(II) \rightarrow M$  dative bonds<sup>1c,4</sup> suggests that stronger dative  $Pt(II) \rightarrow M$  bonds will be formed as the  $d_{z^2}$  level moves higher in energy. This will occur when platinum is placed in a strong ligand field. The present study has been undertaken to explore the formation of short unsupported  $Pt(II) \rightarrow M$  dative bonds by using platinum(II) complexes with carbon  $\sigma$ -donor ligands which exert a strong ligand field. We report here dative  $Pt^{II} \rightarrow Cd^{II}$  bonds which are found to exist in  $\{[Pt(phpy)_2]\{Cd(cyclen)\}\}(ClO_4)_2$  (**1**),  $\{[Pt(CH_3)_2(bpy)]\{Cd(cyclen)\}\}(ClO_4)_2$  (**2**), and  $\{[Pt(thpy)_2]\{Cd(cyclen)\}\}(ClO_4)_2$  (**3**) (Hphpy = 2-phenylpyridine, cyclen = 1,4,7,10-tetraazacyclododecane, bpy = 2,2'-bipyridine, Hthpy = 2-(2-thienyl)pyridine). To our knowledge, this is the first report of Pt–Cd interelement bonds.



(1) (a) Brown, P. M.; Cooper, J. S.; Frew, A. A.; Manojlovic-Muir, L.; Muir, W. K.; Puddephatt, J. R.; Seddon, R. K.; Thomson, A. M. *Inorg. Chem.* **1981**, *20*, 1500. (b) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 700. (c) Mealli, C.; Pichiari, F.; Randaccio, L.; Zangrando, E.; Krumm, M.; Holtentrich, D.; Lippert, B. *Inorg. Chem.* **1995**, *34*, 3418. (d) Kitano, K.; Tanaka, K.; Nishioka, T.; Ichimura, A.; Kinoshita, I.; Isobe, K.; Ooi, S. *J. Chem. Soc., Dalton Trans.* **1998**, 3177 and references therein.

(2) (a) Cotton, A. F.; Falvello, R. L.; Uson, R.; Fornies, J.; Tomas, M.; Casas, M. J. Ara, I. *Inorg. Chem.* **1987**, *26*, 1366. (b) Uson, R.; Fornies, J.; Tomas, M.; Ara, I.; Casas, M. J.; Martin, A. *J. Chem. Soc., Dalton Trans.* **1991**, 2253. (c) Fornies, J.; Navarro, R.; Tomas, M.; Urriolabeitia, P. E. *Organometallics* **1993**, *12*, 940 and references therein.

(3) (a) Falvello, R. L.; Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Inorg. Chem.* **1997**, *36*, 6166. (b) Rocnon, D. F.; Melanson, R. *Acta Crystallogr., Sect. C* **1988**, *C44*, 474. (c) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Chem. Soc., Dalton Trans.* **1999**, 273.

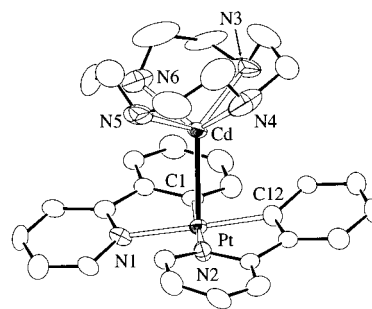
(4) Aullon, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137.

(5) Chassot, L.; Muller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249.

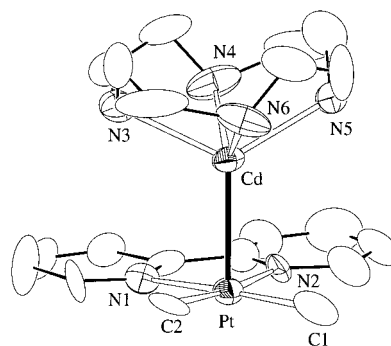
(6)  $[Cd(cyclen)(MeOH)_2](ClO_4)_2$  was synthesized by the method similar to that of  $[Zn(cyclen)(EtOH)](ClO_4)_2$  (Schrodt, A.; Neubrand, A.; van Eldik, R. *Inorg. Chem.* **1997**, *36*, 4579).

(7) Elemental analysis data. **1**· $C_3H_6O$ : Calcd: C, 37.28; H, 4.17; N, 7.90. Found: C, 37.39; H, 3.91; N, 7.84. **2**· $C_3H_6O$ : Calcd: C, 29.36; H, 4.50; N, 8.93. Found: C, 29.02; H, 4.10; N, 9.22. **3**· $C_3H_6O$ : Calcd: C, 32.95; H, 3.62; N, 7.95. Found: C, 32.93; H, 3.31; N, 7.79.

(8) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171.



**Figure 1.** ORTEP drawing of **1** in  $1 \cdot C_3H_6O$ . Relevant bond lengths (Å) and angles (deg): Pt–Cd = 2.6389(8), Pt–N(1) = 2.139(8), Pt–N(2) = 2.128(8), Pt–C(1) = 2.00(1), Pt–C(12) = 2.05(1), Cd–N(3) = 2.321(9), Cd–N(4) = 2.30(1), Cd–N(5) = 2.36(1), Cd–N(6) = 2.34(1); N(1)–Pt–C(1) = 78.5(3), N(2)–Pt–C(12) = 78.9(3), Pt–Cd–N(3) = 126.7(3), Pt–Cd–N(4) = 117.9(3), Pt–Cd–N(5) = 109.5(2), Pt–Cd–N(6) = 117.0(3).



**Figure 2.** ORTEP drawing of **2** in  $2 \cdot C_3H_6O$ . Relevant bond lengths (Å) and angles (deg): Pt–Cd = 2.6101(8), Pt–N(1) = 2.12(2), Pt–N(2) = 2.13(2), Pt–C(1) = 2.06(2), Pt–C(2) = 2.04(2), Cd–N(3) = 2.38(3), Cd–N(4) = 2.350(7), Cd–N(5) = 2.28(1), Cd–N(6) = 2.295(7); N(1)–Pt–C(1) = 174(1), N(2)–Pt–C(2) = 98.8(9), Pt–Cd–N(3) = 117(1), Pt–Cd–N(4) = 110.7(3), Pt–Cd–N(5) = 117.8(7), Pt–Cd–N(6) = 125.9(2).

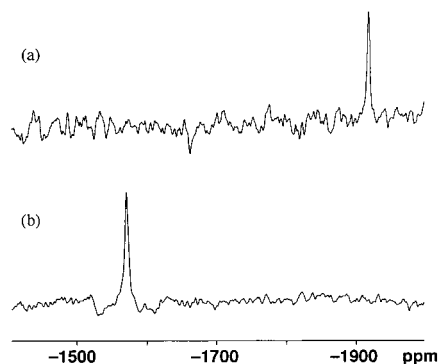
Compound **1** was prepared in acetone solution by combining  $[Pt(phpy)_2]^5$  and  $[Cd(cyclen)(MeOH)_2](ClO_4)_2^6$  in a 1:1 molar ratio at room temperature for 3–4 days. Yellow crystals of  $\{[Pt(phpy)_2]\{Cd(cyclen)\}\}(ClO_4)_2 \cdot C_3H_6O$  (**1**· $C_3H_6O$ )<sup>7</sup> were isolated from this reaction mixture. Yellow crystals of  $\{[Pt(CH_3)_2(bpy)]\{Cd(cyclen)\}\}(ClO_4)_2 \cdot C_3H_6O$  (**2**· $C_3H_6O$ )<sup>7</sup> and yellow powder of  $\{[Pt(thpy)_2]\{Cd(cyclen)\}\}(ClO_4)_2 \cdot C_3H_6O$  (**3**· $C_3H_6O$ )<sup>7</sup> were obtained in the same way using  $[Pt(CH_3)_2(bpy)]^8$  or  $[Pt(thpy)_2]^9$  in place of  $[Pt(phpy)_2]$ .

ORTEP drawings of  $\{[Pt(phpy)_2]\{Cd(cyclen)\}\}^{2+}$  in **1**<sup>10</sup> and  $\{[Pt(CH_3)_2(bpy)]\{Cd(cyclen)\}\}^{2+}$  in **2**<sup>11</sup> show clearly that a platinum-to-cadmium dative bond is formed in both compounds (Figures 1 and 2). The Pt–Cd bond distances in **1** and **2** are 2.639(1) and 2.610(1) Å, respectively. These are far shorter (ca. 0.25 Å) than the sum of the metallic bond radii of platinum and

(9) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.

(10) Crystal data for **1**· $C_3H_6O$ : yellow prismatic, monoclinic space group  $P2_1/n$  (No. 14),  $a = 13.352(1)$  Å,  $b = 14.035(1)$  Å,  $c = 20.269(2)$  Å,  $\beta = 106.599(2)^\circ$ ,  $V = 3640.0(6)$  Å<sup>3</sup>,  $Z = 4$ ;  $R1 = 0.051$ ,  $wR2 = 0.145$ ,  $GOF = 0.78$ .

(11) Crystal data for **2**· $C_3H_6O$ : pale yellow prismatic, monoclinic space group  $C2$  (No. 5),  $a = 20.966(2)$  Å,  $b = 11.314(1)$  Å,  $c = 16.582(2)$  Å,  $\beta = 120.944(2)^\circ$ ,  $V = 3373.7(5)$  Å<sup>3</sup>,  $Z = 4$ ;  $R1 = 0.037$ ,  $wR2 = 0.0883$ ,  $GOF = 0.94$ .



**Figure 3.**  $^{195}\text{Pt}$  NMR spectra of (a)  $\text{CD}_3\text{NO}_2$  solution containing only  $[\text{Pt}(\text{phpy})_2]$  and (b)  $\text{CD}_3\text{NO}_2$  solution containing  $[\text{Pt}(\text{phpy})_2]$  and  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$  in a 1:3 molar ratio. Chemical shift is referenced to  $\text{K}_2\text{PtCl}_4$  in  $\text{D}_2\text{O}$ .

cadmium (2.88 Å), thus indicating the formation of strong Pt→Cd dative bonds. Furthermore, these bonds are not supported by any other interaction. The coordination geometry around  $\text{Cd}^{2+}$  is of a square pyramidal type with an  $\text{N}_4$  basal plane in each compound. In **1**, the Pt–Cd bond is tilted by  $13.0^\circ$  from the normal to the mean square plane around platinum, whereas the corresponding tilt in **2** is  $6.8^\circ$ . This indicates that the  $d_{z^2}$  electrons are involved in the formation of the Pt→Cd dative bond.

In each of the synthetic reactions leading to **1–3**, an immediate color change from deep yellow (**1**), or orange (**2** and **3**) to yellow, was observed when the platinum complexes were mixed with  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$ . However, no distinct absorption peak appeared in UV–vis spectra. Experiments varying the Pt:Cd molar ratio and following the UV–vis absorption intensity in solution showed the exclusive formation of the 1:1 complex and gave no evidence for the formation of a 1:2 complex ( $\text{PtCd}_2$ ).

Figure 3, parts a and b, compares  $^{195}\text{Pt}$  NMR spectra of a  $\text{CD}_3\text{-}$

$\text{NO}_2$  solution containing  $[\text{Pt}(\text{phpy})_2]$  and  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$  in a 1:3 molar ratio and a  $\text{CD}_3\text{NO}_2$  solution containing only  $[\text{Pt}(\text{phpy})_2]$ , respectively. The  $^{195}\text{Pt}$  NMR chemical shifts are  $-1571$  and  $-1918$  ppm, respectively. The shift to lower field upon complexation to  $\text{Cd}^{2+}$  suggests a decrease in electron density on Pt caused by the formation of the Pt→Cd dative bond. Similarly, in the presence of a 3-fold excess of  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$ ,  $[\text{Pt}(\text{CH}_3)_2(\text{bpy})]$  and  $[\text{Pt}(\text{thpy})_2]$  showed their  $^{195}\text{Pt}$  NMR signals at  $-1562$  and  $-1748$  ppm in  $\text{CD}_3\text{NO}_2$ , whereas in the absence of  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$ , their signals appeared at  $-1749$  and  $-2194$  ppm, respectively. However, compounds **1–3** did not show well-defined  $^{195}\text{Pt}$  NMR signals in  $\text{CD}_3\text{NO}_2$ . It appears that the Pt→Cd dative bond in these compounds is dissociated partly in solution to give an equilibrium mixture of Pt and Cd complexes. In fact, a  $\text{CD}_3\text{NO}_2$  solution of **1** showed exactly the same spectrum as mentioned above, when an excess of  $[\text{Cd}(\text{cyclen})(\text{MeOH})_2](\text{ClO}_4)_2$  was added to it. These observations indicate that the Pt→Cd dative bond can be maintained in solution under appropriate conditions.

In this study, we demonstrated that square-planar Pt(II) in a strong ligand field gives rise to strong Pt→Cd dative bonds. It has been found that  $[\text{Pt}(\text{phpy})_2]$  and  $[\text{Pt}(\text{thpy})_2]$  react also with  $\text{Ag}^+$  to give compounds with Pt→Ag dative bonds.<sup>12</sup>

**Acknowledgment.** This work was supported by Grant-in-Aid for Scientific Research (No. 10740299 and Priority Areas No. 10149102 “Metal-assembled Complexes”) from the Ministry of Education, Science, and Culture, Japan. We thank Prof. C. P. Kubiak for valuable discussion.

**Supporting Information Available:** Tables of crystallographic data, experimental conditions, atomic positional and thermal parameters, and interatomic distances and bond angles for **1** and **2** (PDF). An X-ray crystallographic file (CIF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

JA991053N

(12) Yamazaki, F. MS dissertation, Tohoku University, Sendai, 1998 (in Japanese). Details will be reported elsewhere.