

# Elongation of the Quadruple Cr<sup>II</sup>–Cr<sup>II</sup> Bond Induced by Two PtMe<sub>2</sub> Moieties in the Linearly Aligned Tetrametal System, PtMe<sub>2</sub>···Cr–Cr···PtMe<sub>2</sub>

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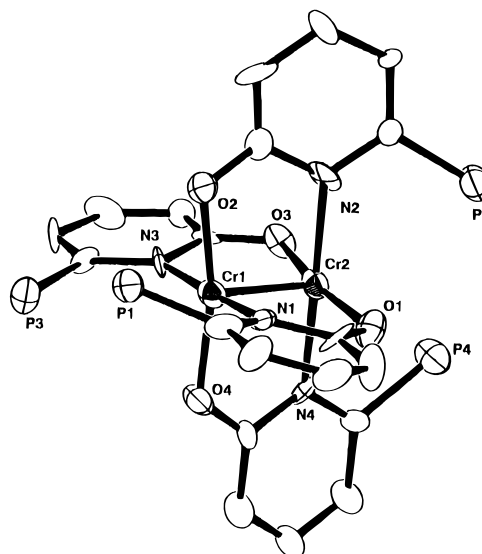
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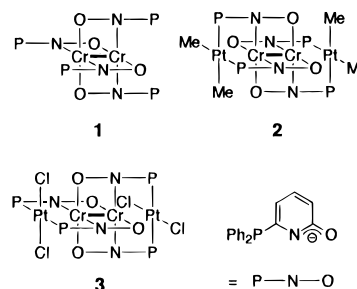
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Dinuclear compounds bearing the multiple metal–metal bond, to date, have been prepared and characterized crystallographically, and the nature of their multiple bond has been theoretically and spectroscopically investigated.<sup>1,2</sup> We have recently reported the new reaction of the dinuclear dimolybdenum(II) complex with two palladium(I) species at both of the axial positions of the Mo<sub>2</sub> core to form metal–metal-bonded tetranuclear complexes such as Mo<sub>2</sub>Pd<sub>2</sub>Cl<sub>2</sub>(pyphos)<sub>4</sub> (pyphos = 6-(diphenylphosphino)-2-pyridonate).<sup>3,4</sup> This reaction involves the coordination of two Pd(II) metals at the axial positions of Mo<sub>2</sub> and is followed by the reduction of Pd(II) to Pd(I) to result in the formation of the Mo–Pd  $\sigma$ -bonds. For the extension of our continuous interest in this area, we have focused on the axial interaction of group 10 metal in +2 oxidation state with the quadruple metal–metal bond of a different metal. Here, we report the axial interaction of the quadruple Cr–Cr bond with two platinum(II) atoms surrounded by pyphos ligands, i.e., d–d dative bond, whereas the quadruple bonded Cr–Cr core is significantly elongated by the axial interaction with organic  $\pi$ -systems, (i.e., d–p dative bond).<sup>5</sup> The strength of this interaction delicately depends on the nature of the ligands on the Pt(II) atoms.

The starting dinuclear complex Cr<sub>2</sub>(pyphos)<sub>4</sub> (**1**) was prepared in 67% yield by the reaction of sodium salt of pyphos with Cr<sub>2</sub>(OAc)<sub>4</sub> in ethanol.<sup>6</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** exhibited a broad singlet at  $\delta$  –4.3 (fwhm = 660 Hz), indicating that all four phosphorus atoms are magnetically equivalent and are free from the coordination of transition metals. Figure 1<sup>7</sup> shows that **1** is a dinuclear complex comprised of a quadruple Cr–Cr bond (2.015(5) Å), a value which is longer than those



**Figure 1.** A drawing of **1** with the labeling scheme. Phenyl groups bound to the phosphorus atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cr1–Cr2, 2.015(5); Cr1–O1, 1.93(2); Cr1–O3, 1.94(1); Cr2–O2, 2.00(2); Cr2–O4, 1.94(2); Cr1–N2, 2.12(2); Cr1–N4, 2.09(2); Cr2–N1, 2.04(2); Cr2–N3, 2.07(2); O1–Cr1–O3, 167.8(7); N2–Cr1–N4, 179.0(8); O2–Cr2–O4, 167.4(7); N1–Cr2–N3, 177.1(8).



of Cr<sub>2</sub>(chp)<sub>4</sub> (chp = 6-chloro-2-pyridonate) (1.955(2) Å)<sup>8</sup> and Cr<sub>2</sub>(mhp)<sub>4</sub> (mhp = 6-methyl-2-pyridonate) (1.889(1) Å),<sup>9</sup> while it is shorter than that (2.288(2) Å) of Cr<sub>2</sub>(OAc)<sub>4</sub>.<sup>10</sup> At both sides of the Cr<sub>2</sub> core, **1** has two *trans*-arranged phosphine atoms capable of coordinating to transition metals.

Treatment of **1** with 2 equiv of PtMe<sub>2</sub>(cod) in THF afforded **2** in quantitative yield.<sup>11</sup> During the reaction course, the geometry of the four pyphos ligands changed from *trans*-fashion to *cis*-one, which is attributed to the *trans*-effect of the methyl group on the platinum. Complex **2** is also prepared by the treatment of PtMe<sub>2</sub>(pyphos-H)<sub>2</sub> (pyphos-H = 6-(diphenylphosphino)-2-pyridone) with Cr<sub>2</sub>(OAc)<sub>4</sub> in the presence of NaOMe in THF. In sharp contrast to **1**, compound **2** exhibited no signal in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum due to the formation of the paramagnetic species, which was produced by the partial disruption of the quadruple Cr–Cr bond by the interaction with the two PtMe<sub>2</sub> cores. The similar partial contribution of the open-shell ( $\sigma$ )<sup>2</sup>( $\pi$ )<sup>4</sup>( $\delta$ )<sup>1</sup>( $\delta^*$ )<sup>1</sup> configuration on the Cr–Cr bond was reported for the Cr<sub>2</sub> species coordinated by organic ligands at both of the axial positions.<sup>5</sup> The temperature-dependence of the paramagnetism has been used to estimate the separation

(8) Cotton, F. A.; Ilesley, W. H.; Kaim, W. *Inorg. Chem.* **1980**, *19*, 1453.

(9) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(10) Cotton, F. A.; Rice, C. E.; Rice, G. W. *J. Am. Chem. Soc.* **1977**, *99*, 4704.

(11) For **2**: mp > 300 °C; UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$  = 303 (ε, 1.7 × 10<sup>4</sup>), 386 nm (ε, 8.9 × 10<sup>3</sup>); ESI MS  $m/z$  = 1668.1 (MH<sup>+</sup>). Anal. Calcd. for C<sub>72</sub>H<sub>64</sub>Cr<sub>2</sub>N<sub>4</sub>O<sub>4</sub>Pt<sub>2</sub>·2(C<sub>4</sub>H<sub>10</sub>O): C, 52.92; H, 4.66; N, 3.09. Found: C, 53.17; H, 4.72; N, 3.05.

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988.

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

(3) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 11632.

(4) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1996**, *118*, 9083.

(5) Cotton, F. A.; Chen, H.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 8980.

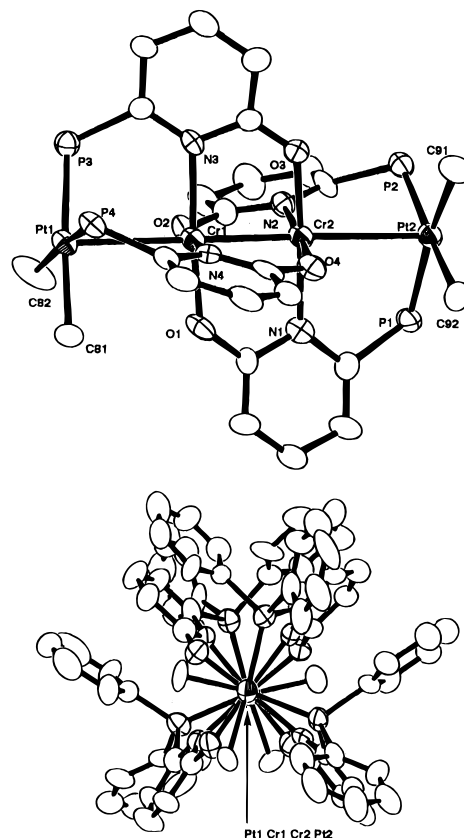
(6) For **1**: mp 159–160 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  5.94 (1H, d,  $J$  = 8 Hz), 6.23 (1H, d,  $J$  = 7 Hz), 7.03 (1H, t,  $J$  = 7 Hz), 7.24–7.33 (10H, m); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  –4.3 (bs, fwhm = 660 Hz); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}$  = 275 (ε, 3.7 × 10<sup>4</sup>), 330 (ε, 2.1 × 10<sup>4</sup>), 455 (ε, 4.7 × 10<sup>2</sup>); FAB MS  $m/z$  = 1217 (MH<sup>+</sup>). Anal. Calcd. for C<sub>60</sub>H<sub>52</sub>Cr<sub>2</sub>N<sub>4</sub>O<sub>4</sub>P<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 63.65; H, 4.18; N, 4.30. Found: C, 63.87; H, 4.12; N, 4.36.

(7) Crystal data for **1**: fw = 1302.00, monoclinic space group P2<sub>1</sub>/a,  $a$  = 18.645(5) Å,  $b$  = 17.896(3) Å,  $c$  = 19.338(3) Å,  $\beta$  = 104.12(2)°,  $V$  = 6257(2) Å<sup>3</sup>,  $Z$  = 4,  $d_{\text{calcd}}$  = 1.382,  $\mu$  = 5.88 cm<sup>–1</sup>, no. of unique data = 9983, no. of observations with  $I > 3\sigma(I)$  = 2251, goodness of fit = 1.85,  $R$  = 0.072,  $R_w$  = 0.082.

between the singlet ground state and the lowest triplet state (the open-shell  $(\sigma)^2(\pi)^4(\delta)^1(\delta^*)^1$  configuration on the Cr–Cr bond).<sup>5,12,13</sup> We measured the solid state  $^{31}\text{P}\{^1\text{H}\}$ -MAS (magic angle spinning) NMR spectra for **1** and **2** between 138 and 350 K at the resonance frequency of 121.5 MHz to obtain the  $J$  values for **1** ( $-340\text{ cm}^{-1}$ ) and **2** ( $\sim -10\text{ cm}^{-1}$ ).<sup>14</sup> By measuring the temperature-dependence of the magnetic susceptibilities of **1** and **2** by the SQUID magnetometer, we obtain similar  $J$  values of  $-340$  and  $-29\text{ cm}^{-1}$ , respectively.<sup>14</sup> The singlet–triplet separation of **1** is thus comparable to those found for  $\text{Cr}_2(\text{O}_2\text{-CR})_4\text{L}_2$ ,<sup>5</sup> while that of **2** is small and is consistent with the highly paramagnetic character of **2** observed on its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Consequently, the  $\text{PtMe}_2$  core interacted significantly with the  $\text{Cr}_2$  core to induce the elongation of the Cr–Cr bond, which was revealed by the crystal structure of **2** (vide infra).

On the other hand, we observed the complete opposite effect of the chloro ligand on the platinum atom. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the chloro derivative **3**,<sup>15</sup> which was synthesized by the reaction of **1** with 2 equiv of  $\text{PtCl}_2(\text{cod})$  ( $\text{cod} = 1,5$ -cyclooctadiene), displayed a sharp singlet at  $\delta$  12.6 ( $J_{\text{Pt}} = 3590\text{ Hz}$ ), indicating that **3** is the typical diamagnetic complex. The quadruple Cr–Cr bond is highly sensitive to the electron-donating property of ligand on the Pt(II) atom.

The bonding nature of **2** was verified by the X-ray crystallographic study.<sup>16</sup> Figure 2 shows the ORTEP diagram of **2**, in which the Cr–Cr distance (2.389(9) Å) is longer by 0.374 Å than that of **1** and is comparable to those (2.329(2)–2.396(2) Å) of  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2$  where  $\text{L} = \text{H}_2\text{O}$ ,<sup>17</sup> Py,<sup>18</sup> MeOH,<sup>5</sup> and MeCN.<sup>5</sup> This is the first example where transition metals act as axial donors to the quadruple Cr–Cr bond resulting in elongation of the bond. The donor properties of the metal atoms in square planar complexes have been recognized.<sup>19–24</sup> The interatomic distances (2.806(9) and 2.811(3) Å) between the platinum atom and the chromium atom indicate that they are the dative Pt→Cr bonds, though they are longer than the sum of Cr and Pt atomic radii (2.6 Å).<sup>25</sup> Similar dative bonding between platinum and palladium (Pt→Pd bond) has been reported so far.<sup>22–24</sup> It is noteworthy that the two square planes comprised of the two methyl groups and the two phosphorus atoms in a *cis*-arrangement are parallel to each other and perpendicular to the vector of the Cr–Cr bond. The platinum atom shifted close to the chromium atom by 0.03 Å from the normal position in the square planar geometry. The angles of Cr–Pt–P [83.2(3), 86.5(2), 85.38(6), and 83.3(1)°] and Cr–Pt–Me [92(1), 97(2), 97(2), and 96.08(8)°] are acutely and obtusely deviated from 90°, respectively.



**Figure 2.** Drawings of **2** with the labeling scheme: a perspective perpendicular to the Cr–Cr vector (top) and a view down the metal–metal bond (bottom). Phenyl groups bound to the phosphorus atoms are omitted for clarity (top). Selected bond distances (Å) and angles (deg): Cr1–Cr2, 2.389(9); Cr1–Pt1, 2.806(9); Cr2–Pt2, 2.811(3); Pt1–C81, 2.12(5); Pt2–C82, 2.088(9); Pt1–P3, 2.282(7); Pt1–P4, 2.304(4); Pt2–P1, 2.313(3); Pt2–P2, 2.261(5) Cr1–O1, 1.96(2); Cr1–O2, 1.95(3); Cr2–O3, 1.99(3); Cr2–O4, 1.98(3); Cr1–N3, 2.14(5); Cr1–N4, 2.145(2); Cr2–N1, 2.16(3); Cr2–N2, 2.12(2); Pt1–Cr1–Cr2, 178.87(3); Cr1–Cr2–Pt2, 178.1(2); Cr1–Pt1–C81, 92(1); Cr1–Pt1–C82, 97(2); Cr1–Pt1–P3, 83.2(3); Cr1–Pt1–P4, 86.5(2); Cr2–Pt2–C91, 97(1); Cr2–Pt2–C92, 96.08(8); Cr2–Pt2–P1, 85.38(6); Cr2–Pt2–P2, 83.3(1); O1–Cr1–N3, 176(1); O2–Cr1–N4, 176.1(9); O3–Cr2–N1, 175(15); O4–Cr2–N2, 176(1).

Complex **3** has two  $\text{PtCl}_2$  moieties, and thereby the orbital interaction between the filled  $d_z^2$ -orbital on  $\text{PtCl}_2$  and  $\sigma$ -orbital of  $\text{Cr}_2$  core induces the closed-shell repulsion, although the vacant  $p_z$ -orbital interacts attractively with the filled  $\sigma$  orbital on  $\text{Cr}_2$  to stabilize the bonding.<sup>26,27</sup> In partial support of this repulsive effect, the X-ray analysis of the molybdenum analogue of **3**,  $\text{Mo}_2\text{Pt}_2\text{Cl}_4(\text{pyphos})_4$  (**4**),<sup>3,4</sup> showed that the two platinum atoms at both of the axial positions of the  $\text{Mo}_2$  core slightly deviated outside from the normal position in the square planar geometry. Such 2-fold ligand effect of the axial metal center is the first case observed for influencing the metal–metal bond.

In summary, we demonstrated that the two Pt atoms can interact with the  $\text{Cr}_2$  moiety attractively or repulsively, depending upon the nature of the ligands on the platinum atom, i.e., methyl or chloro.

**Supporting Information Available:** Experimental details for the preparation of **1–3**, crystallographic data, final positional parameters and final thermal parameters for **1** and **2**, and figures giving additional atom labeling for **1** and **2** (25 pages). See any current masthead page for ordering and Internet access instructions.

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(26) Aullón, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137. Aullón, G.; Alemany, P.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 5061.

(27) Smith, D. C.; Miskowski, V. M.; Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* **1990**, *112*, 3759. Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 6261.

(12) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915.

(13) Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *Inorg. Chem.* **1993**, *32*, 2104.

(14) Experimental details are given in the Supporting Information.

(15) For **3**: mp > 300 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.50 (1H, br), 6.80 (1H, br), 7.27–7.57 (11H, m);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  12.6 ( $J_{\text{Pt}} = 3590\text{ Hz}$ ); UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}} = 275$  ( $\epsilon$ ,  $2.5 \times 10^4$ ), 310 ( $\epsilon$ ,  $2.3 \times 10^4$ ); FAB MS  $m/z = 1607$  ( $\text{M}^+ - 4\text{Cl}$ ). Anal. Calcd. for  $\text{C}_{68}\text{H}_{52}\text{Cl}_4\text{Cr}_2\text{N}_4\text{O}_4\text{P}_4\text{Pt}_2 \cdot 2(\text{CH}_2\text{Cl}_2)$ : C, 43.82; H, 2.94; N, 2.92. Found: C, 43.62; H, 3.80; N, 2.86.

(16) Crystal data for **2**: fw = 1571.30, monoclinic space group  $P2_1/n$ ,  $a = 15.58(1)\text{ Å}$ ,  $b = 17.534(4)\text{ Å}$ ,  $c = 28.455(7)\text{ Å}$ ,  $\beta = 99.74(3)^\circ$ ,  $V = 7663(4)\text{ Å}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.362$ ,  $\mu = 40.25\text{ cm}^{-1}$ , no. of unique data = 8499, no. of observations with  $I > 3\sigma(I) = 8097$ , goodness of fit = 2.75,  $R = 0.064$ ,  $R_w = 0.064$ .

(17) Kranz, M.; Witkowska, A. *Inorg. Synth.* **1960**, *6*, 144.

(18) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 328.

(19) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4123.

(20) Balch, A. L.; Olmstead, M. M.; Oram, D. E.; Reedy, P. E., Jr.; Reimer, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 4021.

(21) Balch, A. L.; Catalano, V. J.; Chatfield, M. A.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1252.

(22) Krumm, M.; Lippert, B.; Randaccio, L.; Zangrando, E. *J. Am. Chem. Soc.* **1991**, *113*, 5129.

(23) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 700.

(24) Mealli, C.; Pichierri, F.; Randaccio, L.; Zangrando, E.; Krumm, M.; Holtenrich, D.; Lippert, B. *Inorg. Chem.* **1995**, *34*, 3418.

(25) Emsley, J. *The Elements*; Oxford University Press: New York, 1989.