

## First Transition Metal Complex of 1,8-Bis(dimethylamino)naphthalene (*proton sponge*)

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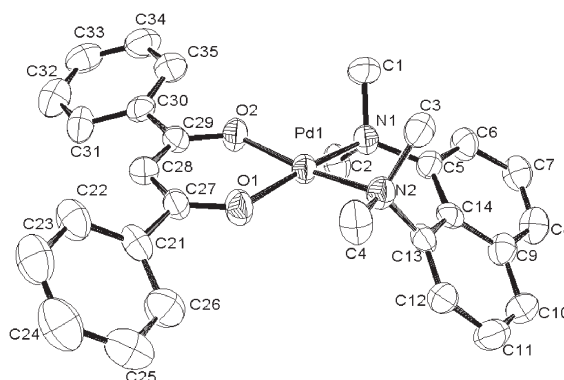
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(Received April 2, 2004; CL-040360)

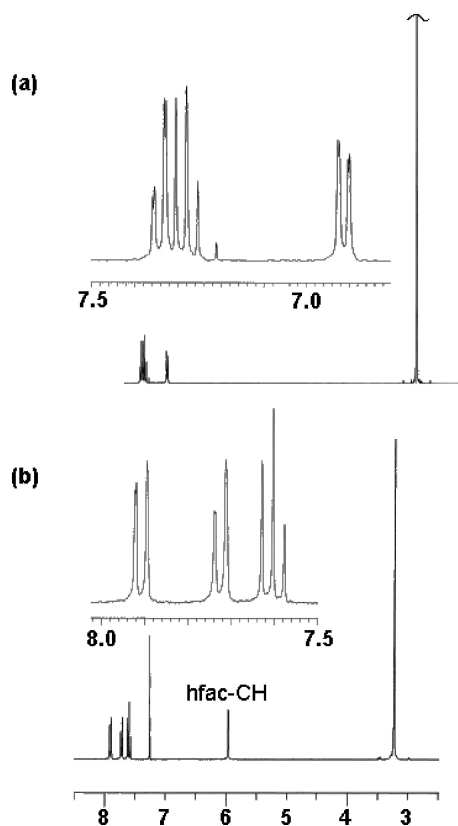
First transition metal complexes of 1,8-bis(dimethylamino)naphthalene (*proton sponge*), *N,N'*-chelated Pd(II) complexes, were prepared and the strong coordination ability of the proton sponge was demonstrated. The high transition energy for the coordination could be lowered by the existence of the intermediate charge-transfer complex which was isolated.

If a large steric interference around the N-donor atom exists in the base, the coordination ability decreases greatly. 1,8-Bis(dimethylamino)naphthalene (N::N) is one of the strongest N-bases ( $pK_a$  12.34)<sup>1</sup> but a very weak nucleophile, so it is called a "proton sponge." Nearly two hundred papers about the chemistry of this proton sponge, with particular interest shown in an isolated strong hydrogen bond in (N:H:N)<sup>+</sup>, have been written. But to the best of our knowledge no paper has yet reported a transition metal complex with N::N, while 1,8-bis(alkylamino)naphthalene usually coordinates as a diamido(2-) type chelating or bridging ligand. N::N reacted with bis(hexafluoroacetylacetonato)palladium(II), [Pd(hfac)<sub>2</sub>]<sub>2</sub> in *n*-hexane immediately depositing dark violet crystals of the charge-transfer (CT) complex [Pd(hfac)<sub>2</sub>](N::N) **1** in an 80% yield. When the reaction mixture was allowed to stand at room temperature for 1 week without separating **1**, the crystals of **1** disappeared and red crystals of [Pd(hfac)(N::N-*N,N'*)](hfac) **2a** gradually grew (63%). **2a** reacted with  $\beta$ -diketones in Et<sub>2</sub>O to give the yellow crystals of [Pd( $\beta$ -dik-*O,O'*)(N::N-*N,N'*)](hfac) ( $\beta$ -dik; acac: **2b**, dbm: **2c**) in 50–80% yields.<sup>3</sup> Figure 1 shows the X-ray structure of **2c**.<sup>4</sup> The coordination plane of Pd is slightly distorted from a square plane. The dihedral angle between a least squares plane of the naphthalene ring and the PdN<sub>2</sub>O<sub>2</sub> plane is 43.2(2)°. The ipso carbons, C(5) and C(13), deviate slightly from the naphthalene plane in the opposite direction from each other, 0.15(6) and –0.13(6) Å, respectively. The torsion angle between C(5)–N(1) and C(13)–N(2) is 34.7(6)°. The N1–N2 distance (2.94(6) Å) is larger than an idealized value, 2.51 Å. This distortion of N::N could come from the stress caused by the required width of the bite angle in coordination with Pd(II). Some transition metal complexes of 4,9-dichloroquinoline[7,8-*h*]quinoline (*another proton sponge*) have been reported and the structure of the Pt(II) complex is similar to **2c**.<sup>5</sup> The high energy barrier for coordination is also due to the strong electrostatic repulsion between two nonbonding electron pairs which need to be the same direction (*syn*) as each other along the naphthalene's plane for coordination to proceed. However these electron pairs are arranged in the opposite direction (*anti*) in the free ligand.<sup>6</sup> This high transition energy for the rearrangement could be lowered by the existence of the intermediate CT complex **1** which would decrease the electron density of the lone pair electrons of N::N in **1**. The trial to obtain the NMR



**Figure 1.** ORTEP drawing of the complex cation in **2c**. Ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–N1 2.086(6), Pd1–N2 2.056(6), Pd1–O1 1.990(5), Pd1–O2 2.012(5), N1–C5 1.485(9), N2–C13 1.472(10), N1–Pd1–N2 90.7(2), O1–Pd1–O2 90.4(2).

spectra of **1** resulted in a mixture of [Pd(hfac)<sub>2</sub>] and N::N. Unfortunately a suitable crystal of **1** for X-ray analysis has not yet been obtained. IR absorption bands of complex **1** in the C=O and C=C stretching region exist between 1620 and 1520 cm<sup>-1</sup> being different from those of [Pd(hfac)<sub>2</sub>] (1590–1530 cm<sup>-1</sup>).<sup>2</sup> The Pd–O(hfac) bonds in **2a** appear to weaken because of the ligand-to-metal charge transfer. Figure 2 shows the <sup>1</sup>H NMR spectra of the free N::N and **2a**. All signals showed down field shift in the coordination state relative to the free ligand state. The <sup>1</sup>H chemical shifts and multiplicity of N::N in **2a**, **2b**, and **2c** are similar to those of [N:H:N]<sup>+</sup> except the NMe signal (see the data of (N:H:N)<sup>+</sup> in **3**), the former is a singlet and the latter is a doublet coupled with H<sup>+</sup>. In solution the N::N plane in **2** flips up and down quickly along the coordination plane because only one kind of N–Me signal (<sup>1</sup>H and <sup>13</sup>C) was observed for **2a**, **2b**, and **2c** at room temperature but the signal in **2c** broadened at –100 °C. The hfac-CH signal (<sup>1</sup>H and <sup>13</sup>C) and –CF<sub>3</sub> signal (<sup>19</sup>F) in **2a** were a singlet at room temperature, but these signals split into two at low temperatures through their coalescences. The high field one is assigned to the hfac<sup>-</sup> as a counter anion and the other to the *O,O'*-chelate.<sup>7</sup> Thus the chelating hfac ligand and counter hfac anion in **2a** exchange with each other on NMR time scale, but the other chelating  $\beta$ -diketonate ligand in **2b** and **2c** does not exchange with the counter hfac anion. Complex **2a** gradually reacts with a small quantity of water in solution to afford (N:H:N)<sup>+</sup>[(Pd(hfac)<sub>2</sub>)( $\mu$ -CF<sub>3</sub>CO<sub>2</sub>)( $\mu$ -CHCO-CF<sub>3</sub>)]<sup>-</sup> **3** as the results of the nucleophilic attack of OH<sup>-</sup> on one carbonyl carbon in hfac, following the CF<sub>3</sub>C(O)–CHC(O)CF<sub>3</sub> bond rupture.<sup>8</sup> But the N::N chelate in



**Figure 2.**  $^1\text{H}$  NMR spectra of (a) free N::N and (b) **2a** in  $\text{CDCl}_3$  (RT).

**2a** is generally not reactive with other weak Brønsted acids as shown in the reaction with  $\beta$ -diketones. The thermodynamic stability of **2** could be brought about by the overcoming advantages of the strong Pd–N bond energy and the removal of the electrostatic repulsion between the two electron pairs.

#### References and Notes

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- 3 *Abbr.* hfac: 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, acac: 2,4-pentanedionate, dbm: 1,3-diphenyl-1,3-propanedionate. Selected data for **1**, Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{OPd}$ : C 39.23, H 2.74, N 3.81. Found: C 39.22, H 2.76, N 3.95%; IR (Nujol/ $\nu(\text{CO})$  and  $\nu(\text{C}=\text{C})$  region): 1620vs, 1570vs, 1552s, 1520m. **2a**, ESIMS (MeCN):  $m/z$  527 ( $\text{M}^+$ ); IR (KBr): 1668vs, 1633s, 1616s, 1550vs, 1531s;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-80^\circ\text{C}$ ): 3.19 (12H, s, NMe), 5.58 (1H, s, hfac-CH), 6.50 (1H, s, hfac-CH), 7.70 (2H, t,  $J = 7$  Hz, naph-3,3'), 7.83 (2H, d, naph-2,2'), 8.04 (2H, d, naph-4,4');  $^{13}\text{C}$  NMR ( $-80^\circ\text{C}$ ): 46.5 (NMe), 84.1 (hfac-CH), 94.1 (hfac-CH), 116.0 (q,  $J(\text{F}-\text{C}) = 283$  Hz, hfac- $\text{CF}_3$ ), 118.5 (q,  $J(\text{F}-\text{C}) = 293$  Hz, hfac- $\text{CF}_3$ ), 119.4, 121.1, 127.2, 130.1, 136.6, 142.2 (naph-ring), 173.0 (q,  $J(\text{F}-\text{C}) = 30$  Hz, hfac-CO), 175.2 (q,  $J(\text{F}-\text{C}) = 37$  Hz, hfac-CO);  $^{19}\text{F}$  NMR (Ext. Ref.,  $\text{C}_6\text{F}_6$ ,  $-90^\circ\text{C}$ ): 90.0 (6F, s, hfac- $\text{CF}_3$ ), 92.1 (6F, s, hfac- $\text{CF}_3$ ). **2b**, IR (KBr): 1671vs, 1561vs, 1524vs;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.01 (6H, s, acac-Me), 3.13 (12H, s, NMe), 5.56 (1H, s, acac-CH), 5.59 (1H, s, hfac-CH), 7.59 (2H, t,  $J = 7$  Hz, naph-3,3'), 7.75 (2H, dd,  $J = 1, 7$  Hz, naph-2,2'), 7.84 (2H, dd, naph-4,4');  $^{13}\text{C}$  NMR: 25.9 (acac-Me), 53.8 (NMe), 84.2 (hfac-CH), 102.0 (acac-CH), 118.8, 121.2, 126.8, 129.1, 136.4, 143.6 (naph-ring), 173.2 (q,  $J(\text{F}-\text{C}) = 29$  Hz, hfac-CO), 187.0 (acac-CO). **2c**, IR (KBr): 1672s, 1600w, 1589w, 1561s, 1533vs, 1520vs;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ): 3.28 (12H, s, NMe), 5.46 (1H, s, hfac-CH), 6.91 (1H, s, dbm-CH), 7.54 (4H,  $\approx t$ ,  $J = 7$  Hz, m), 7.64 (2H,  $\approx t$ ,  $J = 7$  Hz, p), 7.68 (2H, t,  $J = 8$  Hz, naph-3,3'), 7.82 (2H, dd,  $J = 1, 8$  Hz, naph-2,2'), 7.90 (4H,  $\approx d$ ,  $J = 7$  Hz, o), 7.97 (2H, dd,  $J = 1, 8$  Hz, naph-4,4'); ( $-100^\circ\text{C}$ ) 3.30 (br, 12H, NMe), 5.60 (1H, s, hfac-CH), 6.99 (1H, s, dbm-CH), 7.61 (4H, t,  $J = 7$  Hz, m), 7.71 (2H, t,  $J = 7$  Hz, p), 7.74 (2H, t,  $J = 8$  Hz, naph-3,3'), 7.86 (2H, d,  $J = 8$  Hz, naph-2,2'), 7.99 (4H, d,  $J = 7$  Hz, o), 8.04 (2H, d,  $J = 8$  Hz, naph-4,4').
- 4 Crystallographic Data for **2c**,  $\text{C}_{34}\text{H}_{30}\text{F}_6\text{N}_2\text{O}_4\text{Pd}$ ,  $M_r = 751.03$ , orthorhombic,  $P2_12_12_1$  (No. 19),  $a = 12.068(2)$ ,  $b = 22.067(2)$ ,  $c = 11.888(2)$  Å,  $V = 3165.8(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.576$  Mg m<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0.663$ , 5132 reflections measured and 5103 independent reflections were used for all calculations. The final  $R = 0.0559$  ( $F_o > 4.0\sigma(F_o)$ ), 3366 reflections and 424 parameters),  $wR(F^2) = 0.1762$  (all data) and goodness of fit = 1.015 (all data).
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- 8 Selected data for **3**, ESIMS (MeCN):  $m/z$  850 ( $\text{M}^-$ ); IR (KBr): 1673s, 1627m, 1612w, 1552m, 1530s;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 3.20 (12H, d,  $J = 3$  Hz, NMe), 4.56 (1H, q,  $J(\text{F}-\text{H}) = 2$  Hz,  $\mu\text{-CHCOCF}_3$ ), 5.98 (2H, s, hfac-CH), 7.70 (1H, t,  $J = 8$  Hz, naph-3,3'), 7.80 (1H, dd,  $J = 1, 8$  Hz, naph-2,2'), 7.99 (1H, dd,  $J = 1, 8$  Hz, naph-4,4'), 19.1 (1H, m,  $J = 3$  Hz, N:H:N);  $^{19}\text{F}$  NMR: 91.3 (3F, d,  $J(\text{H}-\text{F}) = 1$  Hz,  $\mu\text{-CHCOCF}_3$ ), 91.6, 92.1 (3F each, s, hfac- $\text{CF}_3$ ), 94.7 (3F, s,  $\mu\text{-CF}_3\text{CO}_2$ ).

