4978 *Organometallics* **2002,** *21,* 4978−4983

Diplatinum-Center-Mediated Transformation of a Substituted Benzene to a Cyclohexadienyl Dianion and the Breaking of C−Cl Bonds: Syntheses and Structures of Pt_2R_4(ttab) and $Pt_2(CH_3)_4$(ttab)Cl_2

Datong Song, Katherine Sliwowski, Jun Pang, and Suning Wang*

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6 Canada

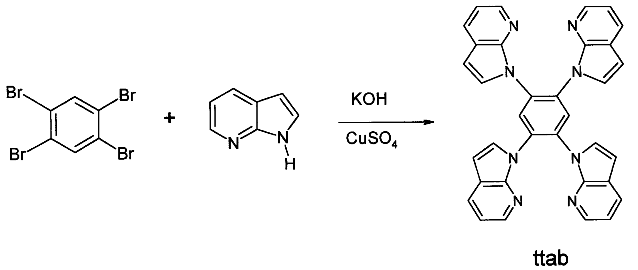
Received August 8, 2002

Two novel dinuclear platinum(II) complexes, $Pt_2(CH_3)_4$(ttab), **1**, and Pt_2Ph_4(ttab), **2**, have been synthesized from the reaction of 1,2,4,5-tetrakis(1-*N*-7-azaindolyl)benzene (ttab) with $Pt_2(CH_3)_4(SMe_2)_2$ and $[PtPh_2(SMe_2)]_n$ (n = 2, 3), respectively. The Pt(II) centers in both complexes are within van der Waals contact distances with the central benzene ring of the ttab ligand. Compound **1** was found to react readily with saturated chlorinated molecules such as $CFCl_3$, CCl_4, $CHCl_3$, and CH_2Cl_2 at ambient temperature to yield a dinuclear platinum(IV) complex, $Pt_2(CH_3)_4$(ttab)Cl_2, **3**, quantitatively. The central benzene ring of the ttab ligand in **1** was transformed to a 1,4-cyclohexadiene dianion in **3**, accompanied by the formation of two internal Pt−C bonds. The structures of **1**, **2**, and **3** are determined by X-ray diffraction analyses.

Introduction

Organoplatinum complexes are an important class of molecules because of their well-established roles in catalysis and photochemistry.[1,2,18] Recently luminescent organoplatinum compounds have attracted much attention due to their potential applications in organic light emitting devices (OLEDs).[3] Our group has shown recently that chelate ligands containing the 7-azaindolyl or indolyl functional groups can coordinate to a Pt(II) or Pd(II) center to produce luminescent Pt(II) or Pd(II) complexes.[4] Some of our Pt(II) complexes have been demonstrated to be promising emitters in OLEDs.[4c] In search of new luminescent Pt(II) complexes and to explore their chemistry, we synthesized a new ligand, 1,2,4,5-tetrakis(1-*N*-7-azaindolyl)benzene (ttab, Scheme 1), and investigated its coordination chemistry with Pt(II) ions. The ttab molecule is a very bright blue emitter with a quantum yield of 43%. However, upon coordination to the Pt(II) center, the ligand's luminescence is completely quenched by the metal center. The resulting complexes do not show significant luminescence in the visible region in solution or the solid state. Although the lack of luminescence is disappointing, the Pt(II) complexes of ttab display unusual reactivity toward C−X bonds (X = halogen) and interesting structural features. We reported herein three new dinuclear Pt complexes, $Pt_2(CH_3)_4$(ttab) (**1**), Pt_2Ph_4(ttab) (**2**), and $Pt_2(CH_3)_4$(ttab)Cl_2 (**3**), the unusual reactivity of compound **1** toward C−Cl bonds in saturated chlorinated molecules, and the transformation of the coordinated ttab ligand to its dianion in **3**.

Scheme 1



Experimental Section

7-Azaindole, dimethyl sulfide, and 1,2,4,5-tetrabromobenzene were obtained from Aldrich Chemical Co. All solvents used in syntheses and spectroscopic measurements were purified according to the literature methods. $Pt_2(CH_3)_4(S(CH_3)_2)_2$ and $[PtPh_2(S(CH_3)_2)]_n$ (n = 2 or 3) were synthesized according to previously reported methods.[5,6] The syntheses of the Pt complexes were carried out under a nitrogen atmosphere. Elemental analyses of C, H, and N were performed by Canadian Microanalytical Service, Ltd, Delta, British Colum-

---

(1) (a) Houlding, V. H.; Miskowski, V. M. *Coord. Chem. Rev.* **1991**, *111*, 145. (b) Pettijohn, C. N.; Jochnowitz, E. B.; Chuong, B.; Nagle, J. K.; Vogler, A. *Coord. Chem. Rev.* **1998**, *171*, 85. (c) Yersin, H.; Humbs, W.; Strasser, J. *Coord. Chem. Rev.* **1997**, *159*, 325. (d) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Gieger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125. (e) McGarrah, J. E.; Kim, Y. J.; Hissler, M.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 4510.

(2) (a) Chassot, L.; Müller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249. (b) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 3107. (c) Vogler, A.; Kunkely, H. *Coord. Chem. Rev.* **1998**, *177*, 81. (d) Wan, K. T.; Che, C. M.; Cho, K. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1077.

(3) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S. T.; Che, C. M. *Chem. Commun.* **2002**, 206.

(4) (a) Wu, Q.; Hook, A.; Wang, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3933. (b) Song, D.; Wu, Q.; Hook, A.; Kozin, I.; Wang, S. *Organometallics* **2001**, *20*, 4683. (c) Liu, Q.; Thorne, L.; Kozin, I.; Song, D.; Seward, C.; D'Iorio, M.; Tao, Y.; Wang, S. *J. Chem. Soc., Dalton Trans.* **2002**, 3234.

(5) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

(6) Song, D.; Wang, S. *J. Organomet. Chem.* **2002**, *648*, 302.

10.1021/om020641y CCC: $22.00

Table 1. Crystallographic Data

	1	**2**	**3**
formula	$C_{38}H_{34}N_8Pt_2{\cdot}2CH_2Cl_2$	$C_{58}H_{42}N_8Pt_2{\cdot}2THF$	$C_{38}H_{34}N_8Pt_2Cl_2{\cdot}2CHCl_3$
fw	1162.76	1385.38	1302.55
wavelength, Å	0.71073	0.71073	0.71073
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.642(3)	11.3873(15)	8.9191(11)
b, Å	11.000(4)	12.4534(17)	10.3123(12)
c, Å	12.097(4)	12.4824(17)	12.3782(16)
α, deg	113.939(6)	62.288(2)	78.821(2)
β, deg	112.469(6)	83.909(2)	82.760(2)
γ, deg	93.465(7)	63.030(2)	84.995(2)
V, Å^3	1047.8(6)	1384.3(3)	1105.7(2)
Z	1	1	1
$D_{\mathrm{calc,}}$ g·cm^{-3}	1.843	1.662	1.956
T, K	296	296	296
μ, cm^{-1}	69.63	51.01	68.43
2θ, max, deg	56.6	56.6	46.6
no. of reflns measd	7281	10 021	5573
no. of reflns used	4657	6346	3145
no. of params	245	335	271
final R [$I > 2\sigma(I)$]	$R_1 = 0.0496$	$R_1 = 0.0251$	$R_1 = 0.0356$
	$wR_2 = 0.1224$	$wR_2 = 0.0570$	$wR_2 = 0.0854$
R (all data)	$R_1 = 0.0627$	$R_1 = 0.0313$	$R_1 = 0.0467$
	$wR_2 = 0.1271$	$wR_2 = 0.0563$	$wR_2 = 0.0886$
goodness-of-fit on F^2	1.006	0.968	0.929

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

bia. ^{1}H NMR spectra were measured on a Bruker Advance 500 MHz spectrometer.

Synthesis of 1,2,4,5-Tetrakis(1-*N*-7-azaindolyl)benzene (ttab). 1,2,4,5-Tetrabromobenzene (2.5 g, 6.3 mmol), 4.88 g of 7-azaindole (41 mmol), 2.296 g of KOH (41 mmol), and 0.5 g of $CuSO_4$ were mixed together and heated at 260 °C for 1.5 h. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 and washed until pH = 7−8 with water. The CH_2Cl_2 solution was then decolorized with activated carbon and dried over $MgSO_4$. After filtration, CH_2Cl_2 was removed under vacuum, and the remaining solid was separated through a silica gel column with ethyl acetate/hexanes as eluent and recrystallized from CH_2Cl_2/hexanes to afford yellow crystals of TTAB (yield 30%, mp 265 °C). ^{1}H NMR (CD_2Cl_2, 25 °C, ppm): δ 8.25 (s, 2H; benzene), 8.16 (dd, $^3J = 5.0$ Hz, $^4J = 1.5$ Hz, 4H; 7-azain), 7.85 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 4H; 7-azain), 7.05 (dd, $^3J_1 = 7.5$ Hz, $^3J_2 = 5.0$ Hz, 4H; 7-azain), 6.98 (d, $^3J = 3.5$ Hz, 4H; 7-azain); 6.37 (d, $^3J = 3.5$ Hz, 4H; 7-azain). ^{13}C NMR (CD_2Cl_2, 25 °C, ppm): δ 148.5, 144.0, 128.6, 128.4, 120.9, 117.1, 102.3 (7-aza); 134.0, 129.1 (benzene). Anal. Calcd for $C_{34}H_{22}N_8{\cdot}0.25CH_2Cl_2$: C 72.84, H 4.16, N 19.85. Found: C 72.90, H 4.04, N 19.87.

Synthesis of $Pt_2(CH_3)_4$(ttab), 1. ttab (0.108 g, 0.02 mmol) and 0.115 g of $Pt_2(CH_3)_4(SMe_2)_2$ (0.02 mmol) were dissolved in 20 mL of THF and stirred at room temperature for 3 h. The solution was decanted, and the yellow solid was washed in diethyl ether and then dried under vacuum to afford **1** as a yellow powder (yield 74%). ^{1}H NMR (CD_2Cl_2, 25 °C, ppm): δ 8.61 (dd, $^3J = 5.5$ Hz, $^4J = 1.3$ Hz, 4H; 7-azain), 7.89 (dd, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz, 4H; 7-azain), 7.52 (d, $^3J = 3.5$ Hz, 4H; 7-azain), 7.22 (s, 2H; benzene), 7.02 (dd, $^3J_1 = 8.0$ Hz, $^3J_2 = 5.5$ Hz, 4H; 7-azain); 6.60 (d, $^3J = 3.5$ Hz, 4H; 7-azain); 0.40 (s, satellite, $^2J_{\mathrm{Pt-H}} = 88.0$ Hz, 12H; Pt−CH_3). ^{13}C NMR (CD_2Cl_2, 25 °C, ppm): δ 149.2, 145.4, 131.5, 129.3, 123.3, 117.9, 103.2 (7-aza); 138.8, 131.6 (benzene); −22.1 (satellite, $^1J_{\mathrm{Pt-C}} = 895.4$ Hz; methyl). Anal. Calcd for $C_{38}H_{34}N_8Pt_2{\cdot}0.5THF$: C 46.69, H 3.70, N 10.89. Found: C 46.75, H 3.91, N 10.85.

Synthesis of Pt_2Ph_4(ttab), 2. ttab (0.108 g, 0.02 mmol) and 0.166 g of $[PtPh_2(SMe_2)]_n$ ($n = 2$, 0.02 mmol) were mixed in 20 mL of THF. The solution was allowed to stand overnight at room temperature to afford light yellow crystals of **2** in a 56% yield. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 8.67 (dd, $^3J = 5.4$ Hz, $^4J = 1.2$ Hz, 4H; 7-azain), 7.91 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 4H; 7-azain), 7.71 (s, 2H; benzene ring of TTAB), 7.21 (d, $^3J = 3.6$ Hz, 4H; 7-azain), 7.08 (m, 12H; 7-azain and Ph); 6.81 (m, 12H; Ph), 6.55 (d, $^3J = 3.6$ Hz, 4H; 7-azain). ^{13}C (CD_2Cl_2, 25 °C, δ, ppm): 103.3 (7-azain), 117.7 (7-azain), 121.6 (phenyl), 123.8 (7-azain), 126.3 (phenyl), 130.7 (7-azain), 131.1 (benzene ring of ttab), 131.8 (7-azain), 137.5 (benzene ring of ttab), 138.7 (phenyl), 141.4 (phenyl), 145.4 (7-azain), 148.3 (7-azain). Anal. Calcd for $C_{58}H_{42}N_8Pt_2{\cdot}2THF$: C 57.23, H 4.19, N 8.09. Found: C 57.51, H 4.27, N 8.16.

Synthesis of $Pt_2(CH_3)_4$(ttab)Cl_2, 3. $Pt_2(CH_3)_4$(TTAB) (0.075 g, 0.076 mmol) was dissolved in 8 mL of $CHCl_3$ (0.099mol) and stirred at ambient temperature under nitrogen for 2 h. The yellow solution was dried under vacuum to afford **3** as a brown-green powder (yield 95%). ^{1}H NMR ($CDCl_3$, 25 °C, ppm): δ 9.38 (dd, $^4J = 1.8$ Hz, $^3J = 6$ Hz, 2H; 7-azain), 8.72 (dd, $^4J = 1.2$ Hz, $^3J = 5.4$ Hz, 2H; 7-azain), 7.88 (m, 4H; 7-azain), 7.70 (d, $^3J = 3.6$ Hz, 4H; 7-azain), 7.18 (dd, $^4J = 2.1$ Hz, $^3J = 7.8$ Hz, 2H; 7-azain), 7.02 (dd, $^3J_1 = 5.7$ Hz, $^3J_2 = 7.8$ Hz, 2H; 7-azain), 6.58 (dd, $^3J_1 = 3.9$ Hz, $^3J_2 = 11.7$ Hz, 2H; 7-azain), 6.23 (s, satellite, $^4J_{\mathrm{Pt-H}} = 7.5$ Hz, $^3J_{\mathrm{Pt-H}} = 22.2$ Hz, 2H; cyclohexadiene), 1.85 (s, satellite, $^2J_{\mathrm{Pt-H}} = 73.2$ Hz, 6H; Pt−CH_3), 1.45 (s, satellite, $^2J_{\mathrm{Pt-H}} = 70.2$ Hz, 6H; Pt−CH_3). ^{13}C NMR ($CDCl_3$, 25 °C, ppm): δ 143.6, 142.5, 131.1, 129.5, 123.2, 117.4, 102.8 (7-azain); 151.2, 138.4, 130.5, 125.8, 118.5, 117.1, 104.7 (7-azain); 129.6, 123.5, 45.2 (C_6 ring); 0.8 (satellite, $^1J_{\mathrm{Pt-C}} = 644.9$ Hz; methyl), −3.9 (satellite, $^1J_{\mathrm{Pt-C}} = 668.0$ Hz; methyl). Anal. Calcd for $C_{38}H_{34}N_8Pt_2Cl_2{\cdot}0.25\ CHCl_3$: C 41.99, H 3.13, N 10.25. Found: C 41.76, H 3.16, N 9.85.

The reaction of compound **1** with CCl_4 proceeded rapidly in the same manner as described above and produced compound **3** as the exclusive product. The reactions of $CFCl_3$ and CH_2Cl_2 with **1** took about 24 h to achieve the complete conversion of **1** to **3** under the same conditions as described for $CHCl_3$.

X-ray Crystal Structure Determination. The diffraction experiments were carried out on a Siemens P4 diffractometer with a Bruker CCD 1000 detector and graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 mA at 23 °C. The software used were SMART[7] for collecting frames of data, indexing reflections, and determination of lattice parameters; SAINT[8] for integration of intensities of reflections and scaling; SADABS[8] for empirical absorption corrections;

---

(7) *SMART for Window NT* v5.050; Bruker AXS Inc: Madison, WI, 1998.

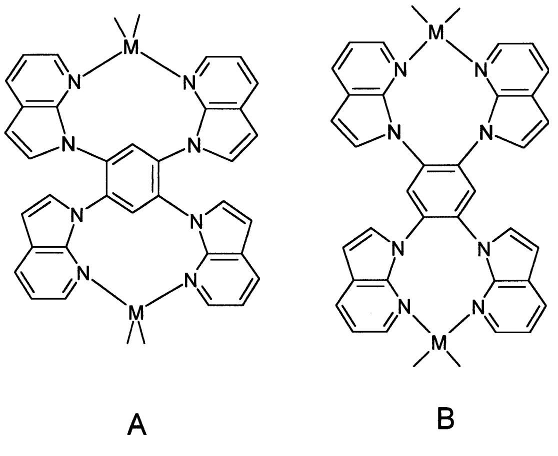
(8) *SAINT+ for NT* v5.00; Bruker AXS Inc: Madison, WI, 1998.

and SHELXTL[9] for space group determination and structure solution and least-squares refinements on $|F|^2$. The crystals were mounted at the end of glass fibers. All three compounds belong to the triclinic space group $P\bar{1}$. All structures were solved by direct methods.

The crystals of **1** were obtained from a CH_2Cl_2/hexane solution, the crystals of **2** were obtained from a THF solution, and the crystals of **3** were grown from a $CHCl_3$ solution. Each molecule of **1** cocrystallizes with 2 CH_2Cl_2 solvent molecules, each molecule of **2** with 2 THF solvent molecules, and each molecule of **3** with 2 $CHCl_3$ molecules. All solvent molecules show some degree of disordering. The positions of all hydrogen atoms in all compounds except those of the disordered solvent molecules were calculated and refined using the riding model (the coordinates of the hydrogen atoms ride on the coordinates of the carbon atoms they are attached to). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times those of the carbon atoms they are attached to. Details of the data collections and refinements are listed in Table 1.

Results and Discussion

Syntheses of the Ligand ttab and Complexes 1 and 2. The novel 1,2,4,5-tetra(1--*N*-7-azaindolyl)benzene (ttab) molecule was synthesized using Ullmann-condensation methods[10] by the reaction of excess 7-azaindole with 1,2,4,5-tetrabromobenzene in the presence of KOH and $CuSO_4$ as the HBr scavenger and the catalyst, respectively (Scheme 1). Despite the use of a large excessive amount of 7-azaindole in the reaction, a number of di- and trisubstituted products were observed, which were separated from the ttab compound by running column chromatograph several times. The ttab ligand was obtained and isolated in ~30% yield. The ttab ligand reacts readily with a variety of transition metal ions to produce usually dinuclear complexes. We have observed two typical bonding modes, **A** and **B**, of the ttab ligand in the dinuclear compounds, as shown, depending on the metal ions. If the metal ion has a tetrahedral geometry such as Ag(I), the bonding mode **A** was observed.[11] In contrast, if the metal ion has a square-planar geometry such as Pd(II) and Pt(II), the bonding mode **B** was observed. Based on crystallographic data, the factor that determines which of these two bonding modes is adopted by the complex is steric interactions (see structure discussion below).



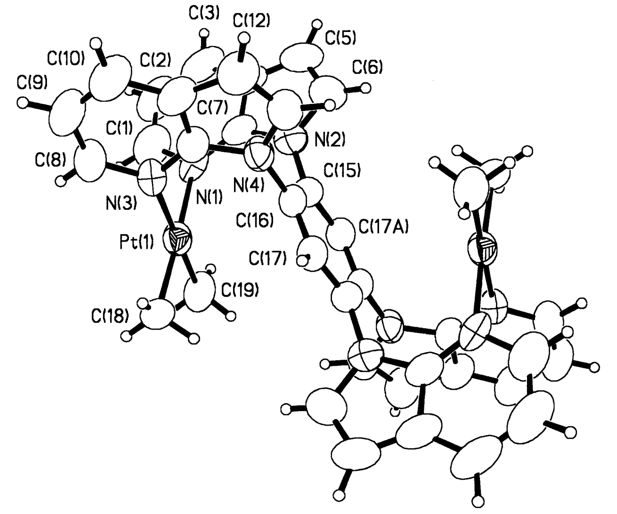


Figure 1. Molecular structure of **1** with 50% thermal ellipsoids and labeling schemes.

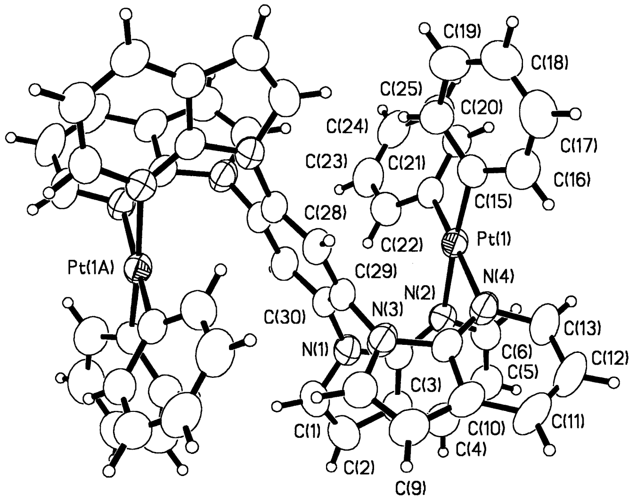


Figure 2. Molecular structure of **2** with 50% thermal ellipsoids and labeling schemes.

Compounds $Pt_2(CH_3)_4$(ttab), **1**, and Pt_2Ph_4(ttab), **2**, were synthesized readily in good yields by the reaction of ttab with $Pt_2(CH_3)_4(SMe_2)_2$ and $[PtPh_2(SMe_2)]_n$ ($n = 2, 3$), respectively, in a Pt:ttab ratio of 2:1. The starting material $[PtPh_2(SMe_2)]_n$ ($n = 2, 3$) is known to exist as a dinuclear compound and a cyclic trinuclear compound in the solid state.[6] Both compounds **1** and **2** are stable in nonhalogenated solvents under air in solution and the solid state.

Structures of Complexes 1 and 2. The structures of **1** and **2** are shown in Figures 1 and 2, respectively. Important bond lengths and angles are listed in Table 2. Both structures have a crystallographically imposed inversion center symmetry. Each of the Pt(II) centers in **1** and **2** has a typical square-planar geometry and is coordinated by two *ortho* 7-azaindolyl groups of the ttab ligand and two methyl groups in a *cis*-fashion. The Pt−C and Pt−N bond lengths in these two compounds are typical.[3−6] The central benzene ring displaying bond lengths and angles typical for benzene is situated midway between the two Pt(II) square planes with the distance between the center of the benzene ring and the

---

[9] *SHELXTL NT* v. 5.1; Bruker AXS Inc: Madison, WI, 1998.

[10] (a) Goodbrand, H. B.; Hu, N. X. *J. Org. Chem.* **1999**, *64*, 670. (b) Lindley, J. *Tetrahedron* **1984**, *40*, 1433. (c) Fanta, P. E. *Synthesis* **1974**, 1.

[11] The Ag(I) and Pd(II) complexes of ttab will be published in due course.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1−3

compound **1**		compound **2**		compound **3**	
Pt(1)−C(18)	2.031(10)	Pt(1)−C(15)	2.005(4)	Pt(1)−C(15)	2.059(9)
Pt(1)−C(19)	2.037 (10)	Pt(1)−C(21)	2.006(3)	Pt(1)−C(16)	2.072(8)
Pt(1)−N(3)	2.132(7)	Pt(1)−N(2)	2.122(3)	Pt(1)−C(18)	2.133(8)
Pt(1)−N(1)	2.133(7)	Pt(1)−N(4)	2.144(3)	Pt(1)−N(2)	2.172(7)
				Pt(1)−N(4)	2.181(6)
C(18)−Pt(1)−C(19)	87.9(5)	C(15)−Pt(1)−C(21)	92.74(15)	Pt(1)−Cl(1)	2.413(2)
C(18)−Pt(1)−N(3)	92.7(4)	C(15)−Pt(1)−N(2)	175.60(12)	C(17)−C(19A)	1.342(11)
C(19)−Pt(1)−N(3)	179.3(3)	C(21)−Pt(1)−N(2)	91.00(13)	C(17)−C(18)	1.462(11)
C(18)−Pt(1)−N(1)	177.7(3)	C(15)−Pt(1)−N(4)	92.77(13)	C(18)−C(19)	1.501(11)
C(19)−Pt(1)−N(1)	91.8(4)	C(21)−Pt(1)−N(4)	174.22(12)		
N(3)−Pt(1)−N(1)	87.6(3)	N(2)−Pt(1)−N(4)	83.43(11)	C(15)−Pt(1)−C(16)	87.7(4)
				C(15)−Pt(1)−C(18)	94.9(4)
				C(16)−Pt(1)−C(18)	93.8(3)
				C(15)−Pt(1)−N(2)	177.4(3)
				C(16)−Pt(1)−N(2)	93.6(3)
				C(18)−Pt(1)−N(2)	82.8(3)
				C(15)−Pt(1)−N(4)	89.8(3)
				C(16)−Pt(1)−N(4)	177.1(3)
				C(18)−Pt(1)−N(4)	87.9(3)
				N(2)−Pt(1)−N(4)	89.0(2)
				C(15)−Pt(1)−Cl(1)	90.7(3)
				C(16)−Pt(1)−Cl(1)	87.3(3)
				C(18)−Pt(1)−Cl(1)	174.3(2)
				N(2)−Pt(1)−Cl(1)	91.61(19)
				N(4)−Pt(1)−Cl(1)	91.26(18)

Pt(II) atom being 3.449(2) Å for **1** and 3.616(1) Å for **2**. The distances between the carbon atoms of the benzene ring and the Pt(II) centers in both compounds are close to the sum of van der Waals radii (3.47 Å).[12] The dihedral angle between the central benzene plane and the Pt(II) plane is 28.4° for **1** and 34.4° for **2**, respectively. The relatively large separation distance and the dihedral angle between the central benzene ring and the Pt center in **2** are clearly caused by the relatively crowded phenyl groups on the Pt(II) center, compared to the methyl groups in **1**. Clearly, the structures of **1** and **2** are dictated by the geometry of the ttab ligand. The structures of **1** and **2** indicate that if the square-planar Pt(II) center were replaced by a tetrahedral metal ion such as Ag(I), the resulting complex would not show the same bonding mode as **1** and **2** because it could bring the ligands on the metal center into close contact with the central benzene ring of the ttab ligand. Indeed, our preliminary study showed that the Ag(I) complex[11] of the ttab ligand adopts the bonding mode **A**, instead of **B**, where the central benzene ring is much farther away from the metal center than it is in compounds **1** and **2**.

Reactivity of Compounds 1 and 2 toward C−Cl Bonds and the Structure of Compound 3. Compounds **1** and **2** are not stable in halogenated solvents. Compound **1** reacts with halogenated solvents rapidly, while compound **2** reacts with halogenated solvents slowly, compared to compound **1**. For example, upon dissolution in $CHCl_3$, compound **1** reacts with the solvent molecule and the reaction is complete instantaneously at ambient temperature. Under the same conditions compound **2** remains unchanged for hours as monitored by NMR spectra. Because the methyl groups on the Pt(II) centers in **1** can be monitored readily by ^1H NMR spectroscopy, we conducted a detailed study on the reactivity of compound **1** toward C−Cl bonds. In addition to $CHCl_3$, we have observed that **1** also reacts readily with C−Cl bonds in CCl_4, $CFCl_3$, and CH_2Cl_2. Remarkably, these reactions of **1** all lead to the formation of one product exclusively and quantitatively, as shown by ^1H NMR spectra, which was identified and characterized as $Pt_2(CH_3)_4(ttab)Cl_2$ (**3**). The structure of **3** was determined by single-crystal X-ray diffraction analysis. Attempts to obtain single crystals from the reaction mixture of **2** with $CHCl_3$ or CCl_4 were unsuccessful. The exact nature of the reaction mixture between **2** and halogenated solvent molecules has not been established conclusively.

As shown in Figure 3, compound **3** also possesses a crystallographically imposed inversion center symmetry. Each Pt center is again chelated by two *ortho* 7-azaindolyl groups. However, in comparison to **1**, each of the Pt centers in **3** has two new bonds, Pt(1)−Cl(1) (2.413(2) Å) and Pt(1)−C(18) (2.133(8) Å), that are *trans* to each other with normal bond lengths.[13,14] The chloride ligand is from the chlorinated organic molecule. The central C_6 ring retains its planarity as observed in **1**

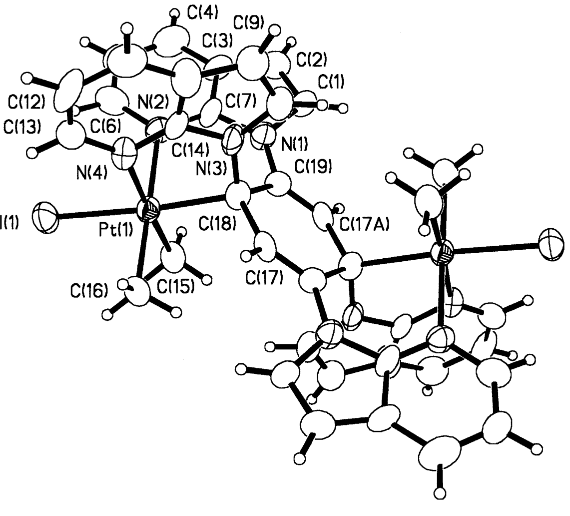
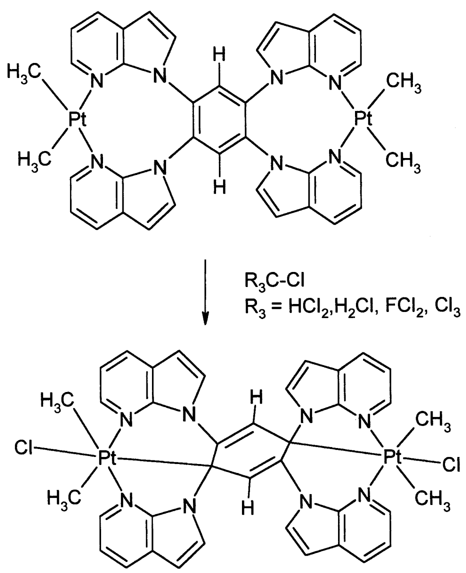


Figure 3. Molecular structure of **3** with 50% thermal ellipsoids and labeling schemes.

---

[12] Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1991.

Scheme 2



and **2**. However, the C−C bond lengths within the six-membered ring are no longer consistent with benzene: two of the C−C bonds (C(17)−C(19A), C(17A)−C(19)) have a bond length of 1.342(11) Å, typical of C−C double bonds, but the remaining four C−C bonds have bond lengths of 1.462(11)−1.501(11) Å, comparable to C−C single bonds.[12] The C(17)−C(18)−C(19) bond angle is 111.0(7)°, close to that of a typical tetrahedral carbon. The octahedral geometry displayed by the Pt center in **3** is typical of Pt(IV). The $^{2}J_{\mathrm{Pt-H(methyl)}}$ coupling constant change from 88.0 Hz in **1** to 73.2 and 70.2 Hz in **3** (the two methyl groups on the Pt center in **3** are distinct) observed in the ^{1}H NMR spectrum is also consistent with the Pt oxidation state change[15] from +2 to +4. Compound **3** is a neutral complex. Therefore, the +4 formal oxidation state of the two platinum centers requires the ttab ligand in **3** to be formally −2 charged. On the basis of the bond lengths and angles and the oxidation state of the Pt centers, the central C_6 ring is therefore rationalized as 1,4-cyclohexadiene dianion. The transformation of **1** to **3** is illustrated in Scheme 2.

Compound **3** is remarkably stable under air in solution and the solid state. The well-resolved $^{3}J_{\mathrm{Pt-H}}$ (22.2 Hz) and $^{4}J_{\mathrm{Pt-H}}$ (7.5 Hz) coupling pattern of the protons on the central C_6 ring with the two Pt(IV) centers in the ^{1}H NMR spectrum of **3** confirms that the Pt(1)−C(18) bond is retained in solution. Formally the change from **1** to **3** involves the change of two Pt(II) centers to two Pt(IV) centers (4e^- oxidation) and the change of the substituted benzene to the dianion (2e^- reduction). Therefore, the overall conversion of **1** to **3** is a *two-electron oxidation* process where the chlorinated molecule acts as the oxidant. To convert benzene or substituted benzene to the cyclohexadiene dianion (or sometimes referred to as benzene dianions), the conventional method is to use strong reducing agents such as alkaline metals to reduce the benzene ring.[16] The most plausible explanation for the unconventional formation of the ttab^{2-} ion in **3** under oxidizing conditions is that the two Pt(II) centers in **1** are initially oxidized to Pt(III) ions by the chlorinated molecule, which in turn, due to its instability, reduce the central benzene ring by giving up one electron from each Pt(III) center, thus becoming Pt(IV) and converting the benzene ring to the dianion. The fact that the Pt(II) centers and the benzene ring are in close proximity in **1** clearly facilitates the conversion of **1** to **3**. The formation of two Pt−C bonds in **3** clearly stabilizes the dianion by effectively reducing its negative charge. Pt(III) species have been proposed previously as intermediates in oxidative addition reactions of Pt(II) complexes with C−X bonds via radical mechanisms.[18] It has also been well-documented previously that when two Pt(II) centers in a dinuclear Pt(II) complex are in close proximity, C−X oxidative additions can lead to the formation of a dinuclear Pt(III) complex or a mixed-valence Pt(III)−Pt(II) complex where the Pt(III) ion is stabilized by the formation of a Pt−Pt bond (or a partial bond).[17] In compound **3**, instead of the formation of a $\mathrm{Pt^{III}}-\mathrm{Pt^{III}}$ bond, because of the proximity of the central benzene ring, the electrons are transferred to the benzene ring, resulting in the formation of two Pt−C bonds. The facile formation of the ttab^{2-} ligand in **3** can be therefore attributed to the capability of the Pt(II) center to transform to Pt(III) and then Pt(IV) and the availability and the joint action of two Pt(II) centers in **1**. Cyclohexadiene dianions or benzene dianions are rarely observed as ligands due to their poor stability. Well-characterized examples and crystal structures involving such dianions are scarce.[16]

The reaction of compound **1** with chlorinated molecules appears to proceed via radical mechanisms initiated by light because it does not occur in the dark but proceeds rapidly when exposed to ambient light. Compound **1** has a pale yellow color with two broad absorption bands at $\lambda_{\mathrm{max}} = 254$ and 286 nm, respectively, which are characteristic of the ttab ligand. The 286 nm band tails off at ~400 nm. The precise photoexcitation energy responsible for initiating the radical reaction is yet to be determined. Oxidative additions of C−X bonds to Pt(II) centers via radical mechanisms have been reported previously.[18] There are abundant examples of oxidative additions of C−Br and C−I bonds to Pt(II) centers. A few examples involving C−Cl oxidative additions to Pt(II) centers have also been reported previously.[13,14,18] Nonetheless, the facile and quantitative cleavage of C−Cl bonds in relatively inert molecules by compound **1** is quite remarkable for Pt(II) compounds. The transformation of a noncoordinate benzene ring to a 1,4-cyclohexadienyl dianion is unprecedented in organoplatinum chemistry.

---

(13) (a) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (b) Fraser, C. S. A.; Jenkins, H. A.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 1635. (c) Baar, C. R.; Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 32.

(14) (a) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233. (b) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 77.

(15) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1291. (b) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1786. (c) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 2749. (d) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2622.

(16) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1996**, 1987.

(17) (a) Che, C. M.; W. Mak, T. C.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 4386. (b) Che, C. M.; Lee, W. M.; Cho, K. C.; Harvey, P. D.; Gray, H. B. *J. Phys. Chem.* **1989**, *93*, 3095. (c) Roundhill, D. M.; Gray, H. B.; Che, C. M. *Acc. Chem. Res.* **1989**, *22*, 55, and references therein.

(18) (a) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1689. (b) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218. (c) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720.

In summary, two new dinuclear Pt(II) complexes containing the novel ttab ligand have been synthesized and fully characterized. The unprecedented transformation of the ttab ligand in **1** to its dianion, accompanied by C−Cl bond cleavages and two Pt−C bond formations and facilitated by the two Pt(II) centers in complex **1**, has been established. The details of the reaction mechanism involved in the transformation of the ligand and the complex and the potential of using compound **1** as a catalyst for catalytic C−Cl bond cleavages are being investigated by our laboratory.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Details of crystal structural data, tables of atomic coordinates, complete lists of bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020641Y