

## Five-coordination in Platinum(II) Species: When and Why

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The ground state geometry of the platinum(II) complexes [Pt(N–N)(L)X<sub>2</sub>] (N–N = bidentate N-donor ligand; L, X = monodentate ligands) becomes five-coordinate trigonal-bipyramidal whenever a strong  $\pi$ -accepting ligand (L) is present in the coordination sphere, in absence of it even a rigid phenanthroline acts as monodentate ligand and the complex is four-coordinate.

A five-coordinate platinum(II) complex containing two anionic ligands in axial positions, an alkene and a bidentate N-donor ligand in the equatorial plane was reported in this journal in 1973.<sup>1</sup> Several complexes of platinum and palladium, having the same basic structure, have been synthesized ever since.<sup>2–5</sup> The role of the alkene and the possibility that other ligands could stabilize the five-coordination have not been fully established.

We have prepared a series of platinum(II) complexes having the same formula, [Pt(dmphen)(L)X<sub>2</sub>], where L is either an alkene or a ligand with C, N, or P donor atom (dmphen = 2,9-dimethyl-1,10-phenanthroline; X = Cl, L = C<sub>2</sub>H<sub>4</sub>, **1**;<sup>6</sup> X = I, L = CO **2**, PPh<sub>3</sub> **3**, ONPh **4**).<sup>†</sup> In all cases <sup>1</sup>H NMR spectra down to –90 °C were in accord with a symmetrically bound phenanthroline molecule (at least in the experiment time response).

The X-ray structures, however, have shown that this is not the case in the solid but, depending upon the nature of L, the phenanthroline shifts from a symmetric doubly bonded to a

non-symmetric singly bonded situation (Fig. 1 and Table 1).<sup>‡</sup> A measure of the degree of asymmetry in the coordination mode of dmphen is given by the difference between the N(1)–Pt–L and N(2)–Pt–L angles (for L = ethylene we take

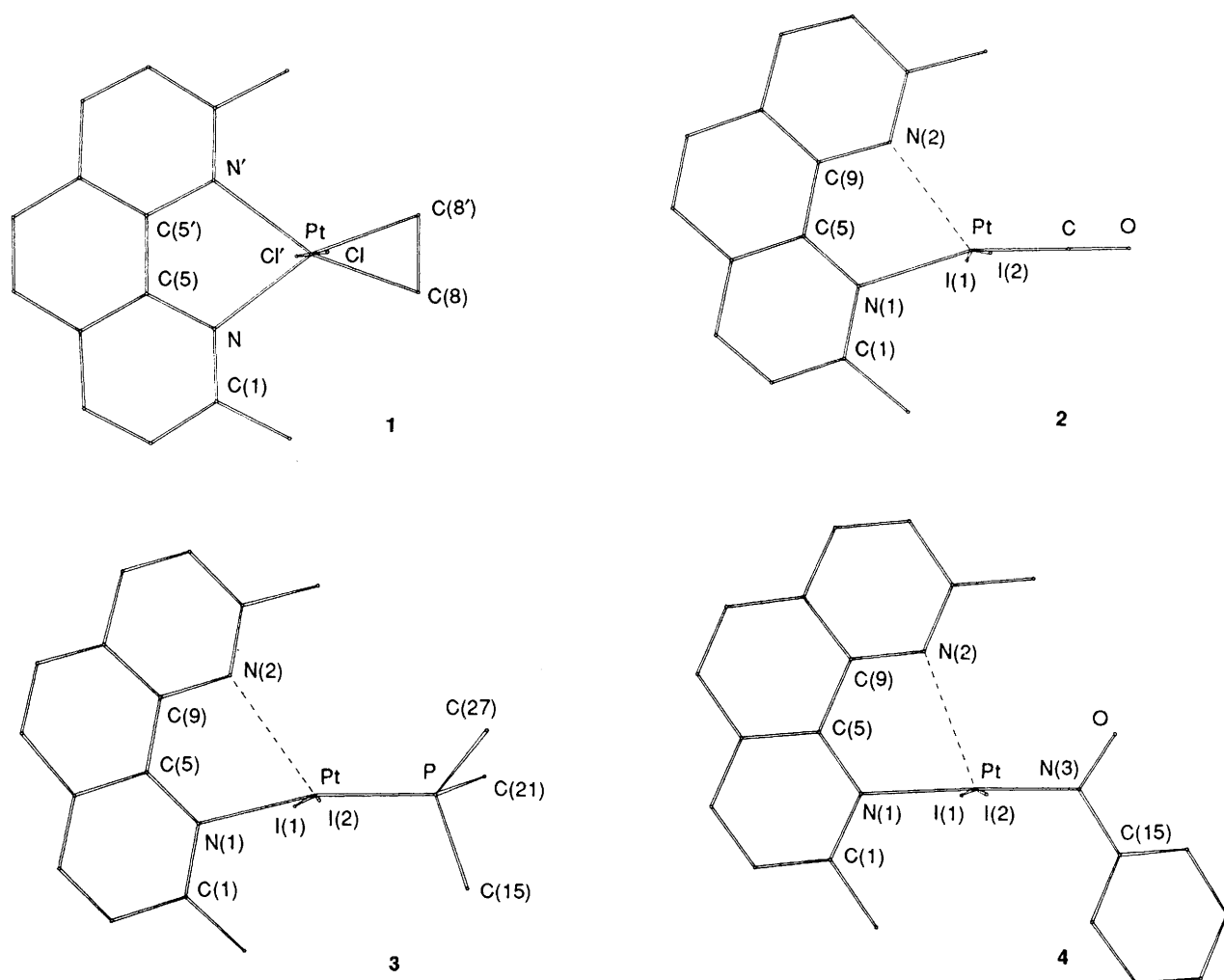
<sup>‡</sup> Crystal data for [Pt(dmphen)(CO)I<sub>2</sub>] **2**, C<sub>15</sub>H<sub>12</sub>I<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt, *M* = 685.17, monoclinic, space group *P*2<sub>1</sub>/*a*, *a* = 14.307(5), *b* = 11.696(4), *c* = 10.122(2) Å,  $\beta$  = 105.44(2)°, *U* = 1632.6(9) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 2.788 g cm<sup>–3</sup>, *F*(000) = 1232, niobium-filtered Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 124.27 cm<sup>–1</sup>.

For [Pt(dmphen)(PPh<sub>3</sub>)I<sub>2</sub>] **3**, C<sub>32</sub>H<sub>27</sub>I<sub>2</sub>N<sub>2</sub>PPt·CH<sub>2</sub>Cl<sub>2</sub>, *M* = 1004.38, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 20.424(7), *b* = 9.612(4), *c* = 17.322(7) Å,  $\beta$  = 102.07(2)°, *U* = 3325(2) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 2.006 g cm<sup>–3</sup>, *F*(000) = 1896, niobium-filtered Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 63.36 cm<sup>–1</sup>.

For [Pt(dmphen)(ONPh)I<sub>2</sub>] **4**, C<sub>20</sub>H<sub>17</sub>I<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Pt, *M* = 764.27, triclinic, space group *P* $\bar{1}$ , *a* = 15.046(4), *b* = 9.180(2), *c* = 7.994(2) Å,  $\alpha$  = 104.33(2)°,  $\beta$  = 100.17(2)°,  $\gamma$  = 91.80(2)°, *U* = 1049.7(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 2.418 g cm<sup>–3</sup>, *F*(000) = 700, niobium-filtered Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 96.78 cm<sup>–1</sup>.

The intensity data for the compounds were collected on a Siemens diffractometer, using the  $\theta$ – $2\theta$  scan technique at room temperature. 3578 **2**, 7297 **3** and 5077 **4** unique reflections were measured [with  $\theta$  in the range 3–27° (**2** and **3**) and 3–28° (**4**)], 1913 **2**, 3193 **3** and 3211 **4**, having *I* > 2 $\sigma$ (*I*), were used in the refinement. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms, excepting for those of the solvent in **3**. The hydrogen atoms were introduced in calculated positions and refined 'riding' on the carbon atoms. The *R* and *R*<sub>w</sub> values were 0.0382 and 0.0576 for **2**, 0.0665 and 0.0852 for **3**, 0.0408 and 0.0532 for **4**. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>†</sup> Complexes **2–4** were prepared by reaction of [Pt(dmphen)I<sub>2</sub>] with L [L = CO (gas, 1 atm), PPh<sub>3</sub> (stoichiometric amount), ONPh (slight excess)] in dichloromethane at 20 °C. After few minutes stirring, diethyl ether was added to the reaction solution and the addition complexes [Pt(dmphen)(L)I<sub>2</sub>] precipitated as yellow **2**, orange **3** and dark-red **4** solids. All compounds gave satisfactory elemental analyses. <sup>1</sup>H NMR [ $\delta$ , downfield from SiMe<sub>4</sub>; CDCl<sub>3</sub> solution; *J*/Hz *J*(H–H) (in parentheses) and *J*(Pt–H) (in square brackets) are given when assignable; integral values in braces]: **2**, 3.36 s [7] {6}, 7.69 d (8) [4] {2}, 7.82 s {2}, 8.26 d (8) {2}. **3**, 3.38 s [7] {6}, 7.59 d (8), 7.74 s {2}, 8.15 d (8) {2}, multiplets at 7.41 {6} and 7.86 {9} of PPh<sub>3</sub> protons. **4**, 3.78 s [7] {6}, 7.67 d (8) {2}, 7.75 s {2}, 8.16 d (8) {2}, multiplets at 7.54 {2}, 7.80 {1} and 8.51 {2} of ONPh protons.



**Fig. 1** Schematic projections of complexes **1-4** {[Pt(dmphen)(L)X<sub>2</sub>]; X = Cl, L = C<sub>2</sub>H<sub>4</sub>, **1**; X = I, L = CO, **2**, PPh<sub>3</sub>, **3**, ONPh, **4**} on the plane defined by the N(1), N(2) and Pt atoms. In complex **3** only the P-attached carbon atoms of the phenyl groups have been represented for clarity.

the midpoint of the C=C bond) and the difference between the Pt-N(1) and Pt-N(2) distances. These differences are both 0 in compound **1** in which dmphen is symmetrically bound to the metal, but in compound **4** which can be considered a canonical four-coordinate complex with singly bonded dmphen, the corresponding values are 65.7° and 0.581 Å.<sup>§</sup>

The degree of bonding interaction between the second end of dmphen [N(2)] and platinum can also be evaluated from the difference between the Pt-N(1)-C(5) and Pt-N(1)-C(1) angles;<sup>7</sup> this difference is -10.9° in **1** and 4.6° in **4**.

The carbonyl complex **2** represents an intermediate situation between **1** and **4** with values of 36.2°, 0.312 Å and 0.7° for the variations in N-Pt-L, Pt-N and Pt-N(1)-C parameters, respectively.

To account for the different structures, *ab initio* Hartree-Fock SCF molecular orbital calculations were performed on **1**, **2**, **3** and **4**.<sup>¶</sup> To reduce the computational complexity, dmphen, Cl and I, PPh<sub>3</sub> and ONPh were replaced by bipyridyl (bipy), F,

**Table 1** Selected structural data (distances Å, angles °) of complexes **1-4**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Pt-N(1)	2.236(5)	2.164(9)	2.182(17)	2.081(7)
Pt-N(2)	2.236(5)	2.476(10)	2.661(18)	2.662(7)
N(1)-Pt-L	142.7(2)	162.7(5)	165.8(5)	176.6(3)
N(2)-Pt-L	142.7(2)	126.5(5)	124.8(4)	110.9(3)
Pt-N(1)-C(5)	115.0(4)	120.4(8)	121.5(15)	122.2(6)
Pt-N(1)-C(1)	125.9(5)	119.7(8)	113.2(15)	117.6(6)
[N(1)-Pt-L]- [N(2)-Pt-L]	0	36.2	41.0	65.7
[Pt-N(2)]-[Pt-N(1)]	0	0.312	0.479	0.581
[Pt-N(1)-C(5)]- [Pt-N(1)-C(1)]	-10.9	0.7	8.3 <sup>a</sup>	4.6

<sup>a</sup> Value less accurate than the others.

PH<sub>3</sub> and ONMe, respectively. All the atoms were treated at all electron levels with the exception of the Pt atom for which a relativistic core potential was used.<sup>8</sup> A MINI-1 basis set was used for the bipy and F ligands<sup>9</sup> and a split valence or double-zeta basis set, for Pt,<sup>8</sup> C<sub>2</sub>H<sub>4</sub>, CO, PH<sub>3</sub> and ONMe.

A series of calculations was performed on the [Pt(bipy)(L)F<sub>2</sub>] complexes assuming a fixed five-coordinate geometry of the type found in **1**. The distances are from crystallographic data. The Pt-L distance was optimized and

<sup>§</sup> Compound **1** contains Cl ligands, the other structures contain I ligands, however, several reported structural studies on trigonal bipyramidal complexes analogous to **1** (refs. 3-5) have shown that the nature of the axial ligands has little or no effect on the structural parameters of the ligand lying in the equatorial plane.

<sup>¶</sup> The MOLECULE-ALCHEMY program package was used to obtain the electronic wave functions.

**Table 2.** Results of the CSOV analysis of change in interaction energy and dipole moment in [Pt(bipy)(L)F<sub>2</sub>] complexes (L = C<sub>2</sub>H<sub>4</sub>, CO, PH<sub>3</sub>, ONMe).

L	$r_c(\text{Pt-L})/\text{\AA}$	$\sigma$ -Donation		$\pi$ -Back donation	
		$\Delta E_{\text{int}}/\text{kJ mol}^{-1}$	$\Delta\mu/\text{au}$	$\Delta E_{\text{int}}/\text{kJ mol}^{-1}$	$\Delta\mu/\text{au}$
C <sub>2</sub> H <sub>4</sub>	2.10	180	+0.49	179	-0.94
CO	2.13	104	+0.33	83	-0.41
PH <sub>3</sub>	2.53	200	+1.22	37	-0.18
ONMe	2.08 <sup>a</sup>	99	+0.29	59	-0.18

<sup>a</sup> Distance not optimized.

the interaction energy between Pt(bipy)F<sub>2</sub> and L decomposed according to the constrained space orbital variation procedure (CSOV).<sup>10</sup> Values of the energy contribution and of the change in the molecular dipole moment,  $\Delta\mu$ , associated to the  $\sigma$  and  $\pi$  component of the Pt-L bond are given in Table 2. Being that the nuclei are fixed during the CSOV analysis, the change in the dipole moment reflects the amount of electron transfer for each bonding mechanism,  $\sigma$  donation or  $\pi$  back-donation. A positive  $\Delta\mu$  indicates charge flow from L to the metal, *vice versa* for a negative  $\Delta\mu$ . All ligands considered resulted to be good  $\sigma$ -donors (as expected since the oxidation state of the metal is 2+), on the contrary the  $\pi$ -accepting capability varied dramatically along the series C<sub>2</sub>H<sub>4</sub> > CO > PH<sub>3</sub> > ONMe.

These results provide strong evidence that five-coordination stems from the ability of the L ligand to reduce the electron density on the metal centre. The structural changes from four- to five-coordination are almost entirely restricted to the equatorial plane of the trigonal-bipyramid in which one finds the same electron concentrations which are located above and below the plane of the square-planar geometry.<sup>11</sup> The C<sub>2</sub>H<sub>4</sub> ligand, because of its side on coordination, is the most efficient in lowering these electron concentrations so that the metal can receive electron charge from an extra donor atom. PH<sub>3</sub> and ONMe, differently from C<sub>2</sub>H<sub>4</sub>, are poor  $\pi$ -acceptors; CO is intermediate between the two extremes. As a consequence, the dmphen ligand is doubly bonded in **1**, singly bonded in **3** and **4**, and intermediately bonded in **2**.

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