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Overcrowded Organometallic Platinum(II) Complexes That Behave as Molecular Gears[**]

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The bottom-up approach to functional materials and the development of molecular-sized analogues of mechanical devices, such as shuttles,[1] rotors,[2] brakes,[3] ratchets,[4]

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gears,[5] and even molecular elevators,[6] constitute a challenge for chemists. All these nanosystems act on external chemical stimuli, such as pH changes, photoactivation, or charge injection.

We have recently reported on the fluxional motion of the 2,9-dimethyl-1,10-phenanthroline (dmphen) ligand between nonequivalent exchanging sites in cationic complex ions of the type $[Pt(Me)(dmphen)(L)]^+$, where L is a neutral S- or P-donor ligand.[7–9] The mechanism is switchable between associative and dissociative pathways. A fine-tuning of the rate and mechanism of the dynamic exchange of the coordinated dmphen ligand can be achieved by varying the solvent, the counterion, the nature and concentration of added nucleophiles, and the electronic and steric characteristics of the ligand L. The driving force for the fluxional motion is the steric distortion of the dmphen ligand, as measured by the dihedral angle between the dmphen plane and the coordination plane, the steric congestion at the metal, and a marked lengthening of the platinum–nitrogen bonds. A free-energy surface constructed for the reacting system by use of the quantitative analysis of ligand effects (QALE)[10] predicts a very fast flipping of dmphen when using phosphanes with a high cone angle. No restricted rotation was observed for any phosphane around the Pt–P or P–C_{ipso} bonds.

When we turned our interest to the dynamic behavior of $[Pt(Me)(dmphen)(PR_3)]^+$ complexes bearing bulky *o*-methoxyphenyl groups on the phosphorus donor atom we observed a very interesting phenomenon: contrary to our expectations, the fluxional motion of dmphen decreases with increasing steric congestion at PR_3, and for tris(2-methoxyphenyl)phosphane and bis(2-methoxyphenyl)phenylphosphane the rate of flipping of dmphen appears to be identical to that of phosphane rotation.

The rate of flipping of dmphen in **1** (see Figure 1 for structure) was monitored using the broadening of the signals of the substituent methyl groups in the 2- and 9-positions of the dmphen ligand (Me_a and Me_b, respectively, in Figure 2) as a probe. The rate of phosphane rotation was followed by monitoring the changes of the signals of the methyl groups of the *ortho*-methoxy groups (Me_x, Me_y, and Me_z in Figure 2). The rate constants of both the dynamic processes were determined separately or by a full line-shape analysis of the spectra (Figure 2) using the computer program gNMR 4.0,[11] and were found to be practically identical ($\Delta G^{\neq} = (55.4 \pm 0.3)\,kJ\,mol^{-1}$).

Compound **2** (Figure 1) has a static structure in solution as far as the planar 1,10-phenanthroline ligand is concerned, although its rate of phosphane rotation is essentially identical to that of compound **1** ($\Delta G^{\neq} = (55.6 \pm 0.2)\,kJ\,mol^{-1}$), the difference between the free-energies of activation being in the range of the statistical error at 340 K (see data in Table 1). The ^1H NMR resonance for Pt–Me of both **1** and **2** is practically unaffected by an increase of temperature, apart from a small shift to higher frequency and a sharpening of the ^{195}Pt satellites.[12]

The steric congestion in the coordination plane of the substrate is responsible for the two dynamic motions in compound **1** and for the restricted rotation around the Pt–P bond in **2**. As shown in the ORTEP view of compound **1** (Figure 1), two methoxy groups of the phenyl rings of the phosphane lie above and below the coordination plane in such a way that it resembles a "pseudo-octahedral" complex.[13] The steric clash between the bulky *ortho*-methoxy substituents and the adjacent methyl group of the phenanthroline ligand determines a tetrahedral distortion of the square-planar coordination geometry, a loss of planarity of the dmphen ligand, and, most remarkably, a rotation of the dmphen moiety around the N1–N2 vector to form a dihedral angle of 35.7(2)° with the mean-square coordination plane. A comparison with compound **2**, in which the unsubstituted phenanthroline moiety is coplanar with the coordination plane, shows that methyl substitution on dmphen is crucial in dictating its geometry and dynamic motion but hardly affects the rate of phosphane rotation. In other words, the two phosphane-containing moieties of **1** and **2** are identical from a structural and dynamic viewpoint, but the remaining two are totally different. The Pt–N1 and Pt–N2 bonds are somewhat longer in **1** than in **2** (2.156(4) and 2.134(4) vs. 2.139(5) and 2.105(5) Å, respectively).

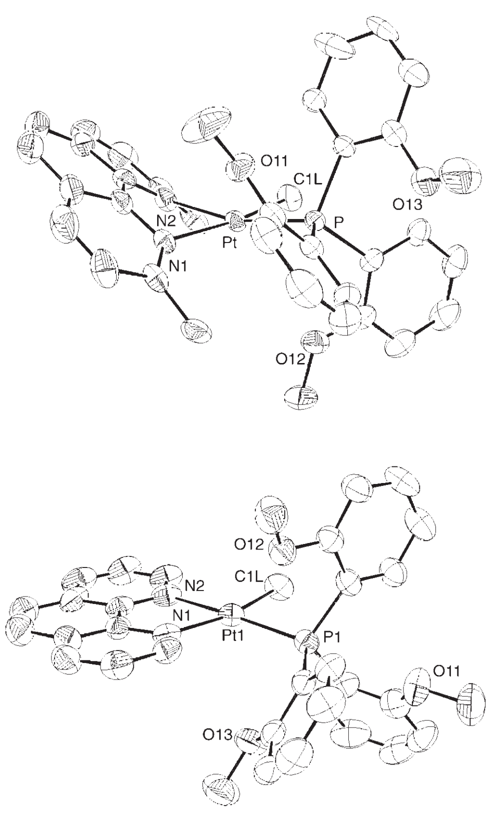


Figure 1. ORTEP drawings of the cationic complexes $[Pt(Me)(dmphen)\{P(2\text{-}MeOC_6H_4)_3\}]$ (**1**; top) and $[Pt(Me)(phen)\{P(2\text{-}MeOC_6H_4)_3\}]$ (**2**; bottom); thermal ellipsoids are at 50% probability. Selected bond lengths [Å] and bond and torsion angles [°] for compounds **1** and **2**, respectively: Pt1–C1L 2.057(5), 2.065(5); Pt1–P1 2.227(1), 2.242(2); Pt1–N1 2.156(4), 2.139(5); Pt1–N2 2.134(4), 2.105(5); N1-Pt1-N2 77.0(2), 78.1(2); P1-Pt1-C1L 83.3(2), 86.0(2); C1L-Pt1-N2 93.8(2), 91.5(2); P1-Pt1-N1 105.3(1), 104.7(1); Pt1-N1-N2-C10 36.8(5), 5.0(5).

When addressing the question of how the connection between the two dynamic motions in compound **1** is

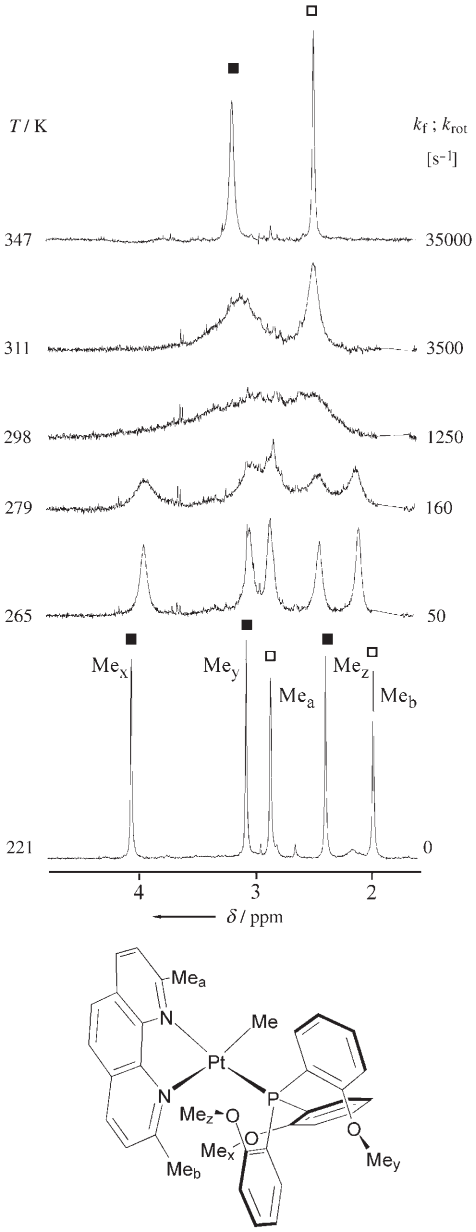


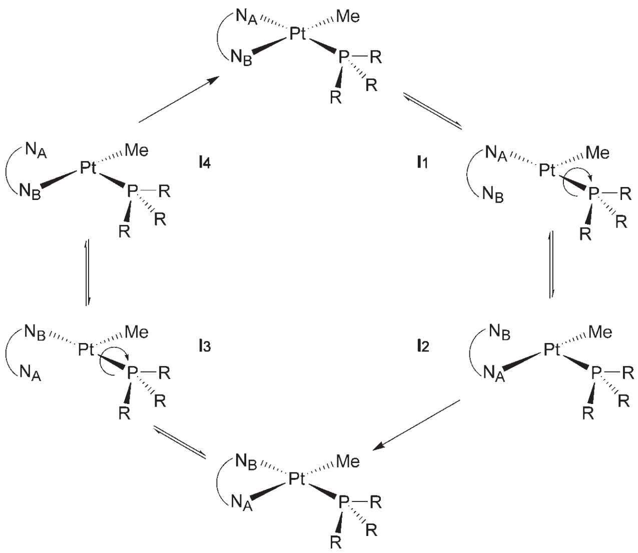
Figure 2. ^{1}H DNMR spectrum of **1** (300 MHz, CDCl$_3$, TMS) showing the phenanthroline methyl protons (open squares) and the methyl groups of the phosphane ligand (filled squares).

Table 1: Kinetic features for dynamic processes in the cationic [Pt(Me)(N-N)(PR$_3$)]$^+$ complexes in CDCl$_3$.

	N-N	PR$_3$	k_f[a] [10^3 s^{-1}]	k_{rot}[b] [10^3 s^{-1}]	$\Delta G^{\neq}$[c] [kJ mol^{-1}]
1	dmphen	P(2-MeOC$_6$H$_4$)$_3$	21.8 ± 0.2	21.8 ± 0.2	55.4 ± 0.3
2	phen	P(2-MeOC$_6$H$_4$)$_3$		19.0 ± 0.1	55.6 ± 0.2
3	dmphen	P(2-MeOC$_6$H$_4$)$_2$Ph	195 ± 1	195 ± 1	48.7 ± 0.1
4	dmphen	P(2-MeOC$_6$H$_4$)Ph$_2$	579 ± 2		46.2 ± 0.1

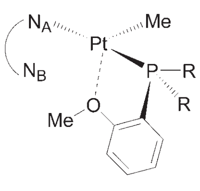
[a] Rate of N-N flipping at 340 K. [b] Rate of phosphane rotation at 340 K. [c] At 340 K.

generated, we must take into account two main observations: 1) the rate of phosphane rotation is not greatly influenced by the coordination environment or whether the phenanthroline is flat or distorted; rather, the contrary seems to be true, namely the fluxional motion of dmphen in **1** is controlled by the rotation rate of the crowded phosphane; 2) the fluxional motion of dmphen in compound **1** is not affected by the nature of the counterion, the solvent (including CD$_3$OD), or by deliberate addition of weak nucleophiles (sulfoxides or sulfides) to the solution;[8] no traces of free PR$_3$ were observed by ^{31}P{^{1}H} NMR spectroscopy. These observations are perfectly in keeping with the dissociative mechanism established for these compounds.[7–9] Scheme 1 shows the suggested steps for the coupled process: 1) platinum–nitrogen bond breaking and the formation of two T-shaped, three-coordinate intermediates **I1** and **I3** containing η^1-coordinated dmphen, 2) their isomerization into the corresponding intermediates **I2** and **I4**, and 3) final ring closure. During the oscillation of dmphen between the two nonequivalent exchanging sites, the phosphane ligand rotates by 120° around the platinum–phosphorus bond. Restricted rotation about a platinum–phosphorus bond is a well-known phenomenon which often depends on the bulk of the ligand, although other causes have been found to participate in this dynamic process.[14]



Scheme 1. A dissociative mechanism involving three-coordinate, T-shaped intermediates (**I1**–**I4**) for the coupled rotation/flipping motion.

A reasonable hypothesis is that one step of the dissociative mechanism, presumably ring closing of the monodentate three-coordinate intermediate complex [Pt(Me)(η^1-dmphen){P(2-MeO-C$_6$H$_4$)$_3$}]$^+$ (**I1** and **I3**), can be slowed down by the presence of methoxy groups on the phenyl rings of the phosphane projecting towards the metal center. The coordinative and electronic unsaturation of the 14-electron species[15] is somewhat compensated by a temporary electronic assistance from one oxygen of a methoxy group (Scheme 2) and, as a consequence, isomerization of the intermediate and the ring closing must await the



Scheme 2. Postulated interactions in the intermediates **I1** and **I3**.

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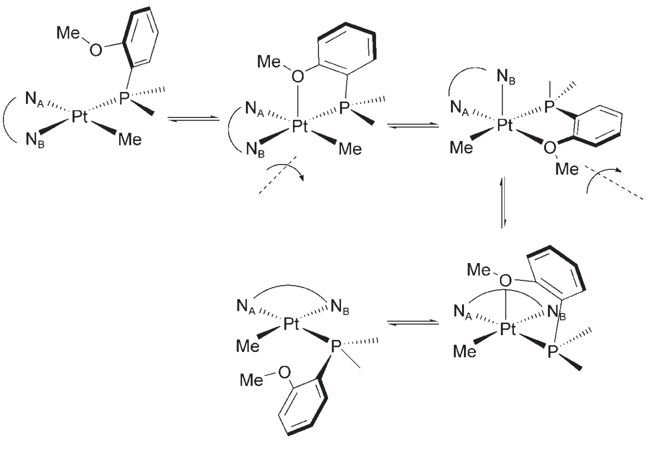
liberation of the coordination site from this oxygen atom before taking place.

This idea is supported by the steady increase in the coupled motion upon removal of one or two methoxy groups from the phosphane ligand. Table 1 shows that, on passing from P(2-MeOC$_6$H$_4$)$_3$ (in **1**) to P(2-MeOC$_6$H$_4$)$_2$Ph (in **3**) a tenfold increase in the value of the two rates can be measured. On going from P(2-MeOC$_6$H$_4$)$_2$Ph (in **3**) to P(2-MeOC$_6$H$_4$)Ph$_2$ (in **4**), we can no longer measure the rate of phosphane rotation. However, based on the free-energy surface that represents the way in which any single P-donor ligand can affect the energy of the transition state in the absence of any additional effect,[9] the value of $\Delta G^{\neq}$, (46.2 ± 0.1) kJ mol^{-1}, for the flipping of dmphen appears to be in the range expected from the value of the cone angle of P(2-MeOC$_6$H$_4$)Ph$_2$. Thus, we are inclined to conclude that the connection between the two motions in compound **4** is lost or becomes very weak.

A reasonable mechanistic alternative to dissociation could be a direct intramolecular attack at the metal center by the oxygen atom of the methoxy group. A variety of associative mechanisms could then be envisaged that involve 1) a sequence of nucleophilic substitution reactions that take place with retention of configuration, or 2) an intramolecular rearrangement from a five-coordinate intermediate, such as a Berry pseudorotation or a "turnstile" mechanism, as shown in Scheme 3.



Scheme 3. Turnstile mechanism involving simultaneous rotation of ligands on the triangular faces of a square-pyramidal adduct.

No distinction can be made among the possible reaction pathways on the basis of the kinetic data alone. However, we observe that 1) the flipping motion of dmphen in these complexes features an uncatalyzed intramolecular geometrical isomerization that, in platinum(II) complexes, is known to proceed with a dissociative mechanism very similar to that described in Scheme 1,[16] 2) if the addition of a fifth ligand is a prerequisite for the occurrence of the process we would have expected activation of fluxional motion of phen in **2** and an acceleration and a catalytic effect in **1**, **3**, and **4** by the addition of external nucleophiles that are much stronger than the oxygen of the methoxy group,[8] and 3) an associative attack should be facilitated by the number of oxygen atoms on the phosphane ligand, while the rates increase sharply along the series of complexes in the order **1** < **3** < **4**. Therefore, we conclude that release of steric congestion in these compounds confers a further impetus to ring opening, as expected from the results of previous studies, but ring closing is impeded by the contemporary slow rotation about the Pt−P bond.

The fascinating synchronism between the two motions—the fluxionality of dmphen and the rotation of the phosphane ligand—in complexes **1** and **3**, together with the possibility of being able to fine-tune the rates and the activation pathways, opens the way to the design of molecular gears whose dynamics can be controlled by intrinsic stereoelectronic properties (dissociative mechanism) or by external chemical stimuli (associative mechanism).

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[13] Crystal data for **1**$(SbF_6)\cdot H_2O$: $C_{36}H_{38}F_6N_2O_4PPtSb$, $M_r = 1024.48$, triclinic, space group $P\bar{1}$, $a = 10.3925(7)$, $b = 11.9207(8)$, $c = 16.264(1)$ Å, $\alpha = 73.956(2)$, $\beta = 76.621(2)$, $\gamma = 84.545(2)°$, $V = 1882.8(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.804$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 45.41$ cm^{-1}. 22382 Reflections were collected at room temperature with a Bruker SMART CCD diffractometer, of which 8975 were unique ($R_{int} = 0.0394$). An empirical absorption correction was applied using the program SADABS (transmission factors in the range 1.000–0.606). Structure solution was by Patterson and Fourier methods and refinement by full-matrix least-squares on F^2 (programs WinGx ver. 1.70 and SHELX-PC), using anisotropic displacement parameters for all atoms except the hydrogens (in calculated positions), which were treated as riding atoms. Final agreement factors were $R_1 = 0.0406$, $wR_2 = 0.0967$ for 6916 observed reflections ($I \geq 2\sigma(I)$) and 459 refined parameters; GOF = 1.052. Crystal data for **2**(PF_6): $C_{34}H_{32}F_6N_2O_3P_2Pt$, $M_r = 887.65$, triclinic, space group $P\bar{1}$, $a = 8.717(3)$, $b = 12.286(3)$, $c = 15.654(4)$ Å, $\alpha = 91.40(3)°$, $\beta = 96.65(4)°$, $\gamma = 96.52(3)°$, $V = 1653.2(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.783$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 45.13$ cm^{-1}. 5766 Independent reflections were collected at room temperature with a NONIUS CAD4 diffractometer. An empirical absorption correction was applied using the azimuthal (Ψ) scans of three reflections (transmission factors in the range 1.000–0.676). The structure solution was by Patterson and Fourier methods and refined as described above. Final agreement factors were $R_1 = 0.0310$, $wR_2 = 0.0726$ for 4463 observed reflections ($I \geq 2\sigma(I)$] and 433 refined parameters; GOF = 1.008. CCDC-299811 and -299812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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