Platinum(II) Complexes with Monocoordinated 2,9-Dimethyl-1,10-phenanthroline and Phosphine Ligands. Exchange of the Donor Nitrogen and Rotation about the Pt–P and P–C Bonds Studied by NMR Spectroscopy: Arene Stacking as an Intramolecular Brake

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The structure and dynamic behavior of the platinum complexes *cis*- and *trans*-$[PtX_2(Me_2\text{-phen})(PPh_3)]$ (X = Cl (**1**), Br (**2**), I (**3**); cis isomer, **a**; trans isomer, **b**), *trans*-$[PtX(Me_2\text{-phen})(PPh_3)_2]X$ (X = Cl (**4**), Br (**5**), I (**6**)), and *trans*-$[PtX(Me_2\text{-phen})(PBu^n_3)_2]X$ (X = Cl (**7**), Br (**8**), I (**9**)) containing monocoordinated 2,9-dimethyl-1,10-phenanthroline (Me_2-phen) are reported. Exchange of the donor atom (flipping) for the singly bonded Me_2-phen and rotations about the Pt–P and P–C bonds of the phosphine have been investigated by NMR spectroscopy. For the first time the ΔG^* for flipping of a bidentate ligand with converging lone pairs of electrons has been measured and found to be strongly dependent upon the nature of the trans ligand (trans effect). The ΔG^* for rotation about the Pt–P bond is unusually high in the case of PPh_3 ligands ($\Delta G^* > 10$ kcal/mol) and does not change significantly among the different compounds examined, although the Pt–P bonds are 0.1 Å longer in complexes **4–6** (phosphine trans to another phosphine) than in complexes **1a–3a** (phosphine trans to a halogen atom). The PBu^n_3 complexes **7–9** exhibit much smaller ΔG^* values for phosphine rotation (<7 kcal/mol) but similar or slightly bigger ΔG^*'s for flipping of the Me_2-phen ligand. One phenyl ring of PPh_3 (the most shielded one) exhibits restricted rotation about the P–C_{ipso} bond with ΔG^* in the range 7.1–7.8 kcal/mol. The two remaining phenyls of PPh_3 are not equivalent, and for one of them restricted rotation about the P–C_{ipso} bond is also observed. The crystal structures of the complexes *cis*-$[PtCl_2(Me_2\text{-phen})(PPh_3)]$ (**1a**) and *trans*-$[PtCl(Me_2\text{-phen})(PPh_3)_2]Cl$ (**4**), as chloroform solvates, have been determined by X-ray diffraction methods. One phenyl of each phosphine ligand overlaps with the coordinated end of Me_2-phen, the C_{ipso} atom eclipsing the nitrogen atom of the phenanthroline; a second phenyl of the phosphine comes close to the second end of Me_2-phen. A stacking interaction between a phenyl ring of PPh_3 and the Me_2-phen aromatic system appears though to be responsible for the high-energy barrier to phosphine rotation, thus simulating an electromagnetic brake. Crystal data of **1a**·$CHCl_3$: space group $P2_1/n$, a = 15.996(6) Å, b = 17.996(6) Å, c = 12.314(4) Å, β = 111.23(2)°, Z = 4, 3726 reflections, R = 0.0322. Crystal data of **4**·$CHCl_3$: space group $P2_1$, a = 11.727(6) Å, b = 11.825(7) Å, c = 17.091(8) Å, β = 94.96(2)°, Z = 2, 4338 reflections, R = 0.0333.

Introduction

Phosphine ligands are very common in the coordination and organometallic chemistry of transition metals and are widely used in homogeneous catalysis.[1] Several studies have been devoted to establishing correlations between the steric requirements of the phosphine ligands and the coordination geometry and reactivity of the complexes,[2] but relatively few have dealt with interligand stereo and electronic effects influencing their intramolecular motions.[3] These dynamic processes have recently gained particular attention in view of producing micromachines, where the mechanical principles are applied to a molecular level.[4]

In a previous paper we have reported on the synthesis of $[PtX_2(Me_2\text{-phen})]$ complexes (X = Cl, Br, I; Me_2-phen = 2,9-dimethyl-1,10-phenanthroline) which add an extra ligand (L) to give $[PtX_2(Me_2\text{-phen})(L)]$ species, which can be either five- (L = alkene[5a] or alkyne[5b,c]) or four-coordinate (L = PPh_3, CO, PhNO, Me_2SO, NH_2Pr^n). In the latter case the phenanthroline ligand acts as monodentate toward platinum.[6]

We wish now to report on the synthesis and dynamic behavior of the mono- and bisphosphine complexes *cis*- and *trans*-$[PtX_2(Me_2\text{-phen})(PPh_3)]$ (X = Cl (**1**), Br (**2**), and I (**3**); cis isomer, **a**; trans isomer, **b**), *trans*-$[PtX(Me_2\text{-phen})(PPh_3)_2]X$ (X = Cl (**4**), Br (**5**), and I (**6**)), and *trans*-$[PtX(Me_2\text{-phen})(PBu^n_3)_2]X$

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(X = Cl (**7**), Br (**8**), and I (**9**)). Exchange of the donor atom for the singly bonded Me_2-phen and rotations about the Pt–P and P–C bonds of the phosphine have been investigated by NMR spectroscopy. A stacking interaction between the Me_2-phen ligand and one phenyl of PPh_3 was revealed by the X-ray investigation of complexes **1a** and **4**, and this appears to be responsible for the unusually high energy barriers for rotation about the Pt–P and P–C bonds.

Materials and Methods

Starting Materials. Commercial reagent grade chemicals 2,9-dimethyl-1,10-phenanthroline (Me_2-phen), triphenylphosphine, and tri-*n*-butylphosphine (Aldrich) were used without further purification. [PtX_2(Me_2-phen)] (X = Cl, Br, I) were prepared by previously reported procedures.[5a]

Preparation of *cis*- and *trans*-[PtX_2(Me_2-phen)(PPh_3)] (X = Cl (1), Br (2), I (3); Cis Isomer, a; Trans Isomer, b). A solution of PPh_3 (0.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of [PtX_2(Me_2-phen] (0.3 mmol) in the same solvent (15 mL). After 5 min of stirring, addition of diethyl ether to the mother solution caused the precipitation of a yellow-orange solid, which was collected, washed with diethyl ether, and dried in air, yield 90%. Anal. Calcd for $C_{32}H_{27}Cl_2N_2PPt$ (**1**): C, 52.2; H, 3.7; Cl, 9.5; N, 3.8. Found: C, 51.8; H, 3.8; Cl, 9.3; N, 3.6. Calcd for $C_{32}H_{27}Br_2N_2PPt$ (**2**): C, 46.7; H, 3.3; Br, 19.2; N, 3.4. Found: C, 46.5; H, 3.2; Br, 19.0; N, 3.3. Calcd for $C_{32}H_{27}I_2N_2PPt$ (**3**): C, 41.8; H, 3.0; I, 27.6; N, 3.0. Found: C, 41.6; H, 2.9; I, 27.3; N, 2.8.

***trans*-[PtX(Me_2-phen)(PPh_3)$_2$]X (X = Cl (4) Br (5) I (6)) and *trans*-[PtX(Me_2-phen)(PBu^n_3)$_2$]X (X = Cl (7), Br (8), I (9)).** These complexes were synthesized and isolated as yellow solids, in over 90% yield, by using the same procedure described above but a 2:1 molar ratio of phosphine and [PtX_2(Me_2-phen)]. Anal. Calcd for $C_{50}H_{42}Cl_2N_2P_2Pt$ (**4**): C, 60.1; H, 4.2; Cl, 7.1; N, 2.8. Found: C, 59.8; H, 4.0; Cl, 6.8; N, 2.7. Calcd for $C_{50}H_{42}Br_2N_2P_2Pt$ (**5**): C, 55.2; H, 3.9; Br, 14.7; N, 2.6. Found: C, 55.0; H, 3.7; Br, 14.2; N, 2.5. Calcd for $C_{50}H_{42}I_2N_2P_2Pt$ (**6**): C, 50.8; H, 3.6; I, 21.5; N, 2.4. Found: C, 50.5; H, 3.5; I, 21.1; N, 2.3. Calcd for $C_{38}H_{66}Cl_2N_2P_2Pt$ (**7**): C, 51.9; H, 7.6; Cl, 8.1; N, 3.2. Found: C, 51.6; H, 7.5; Cl, 7.9; N, 3.1. Calcd for $C_{38}H_{66}Br_2N_2P_2Pt$ (**8**): C, 47.2; H, 6.9; Br, 16.5; N, 2.9. Found: C, 47.1; H, 7.0; Br, 16.2; N, 2.8. Calcd for $C_{38}H_{66}I_2N_2P_2Pt$ (**9**): C, 43.0; H, 6.3; I, 23.9; N, 2.6. Found: C, 43.0; H, 6.3; I, 21.1; N, 2.6.

Physical Measurements. Variable-temperature ^1H NMR spectra were recorded on a Bruker AM 300 instrument. The temperature of the probe was measured (±2 °C) by a thermocouple inserted in a NMR tube filled with toluene to the same depth as the solution in the sample tube. The sample concentration, in screw lid closed NMR tubes, was approximately 40 mmol L^{-1}, and provided that they were carefully filtered and degassed, it was possible to supercool the solutions at a temperature of ca. 20 °C below the freezing point of the solvent (CD_2Cl_2) for enough time to run the spectra.[3e] For lower temperatures a 1:1 mixture of CD_2Cl_2/CBr_2F_2 was used as solvent. The spectral simulation was performed using the SIM2 and SIM3 programs.[7] The methyl protons of the substituted phenanthroline and the ortho and meta protons of PPh_3 were used to analyze the head to tail rearrangement of the singly bonded Me_2-phen ligand (**A**), the rotation of the PPh_3 about the Pt–P bond (**B**), and the rotation of the Ph's about the P–C bonds (C_1, C_2, C_3). Satisfactory fit between simulated and observed spectra was judged by visual comparison. Values of ΔG^* were calculated using the Eyring equation. $\{^1H\}^{31}P$ NMR spectra were recorded on a Varian XL200 instrument operating at 80.96 MHz using 85% H_3PO_4 as external standard. $\{^1H\}^{195}Pt$ NMR spectra were recorded on a Bruker AM 300 instrument operating at 64.52 MHz using K_2PtCl_4 as external standard. IR spectra were recorded as KBr pellets on Perkin-Elmer 283 and FT 1600 spectrophotometers.

X-ray Crystallography. Crystals of **1a**·$CHCl_3$ and **4**·$CHCl_3$, suitable for the X-ray analyses, were obtained by crystallization from chloroform. Selected crystallographic data for both compounds are listed in Table 1. Data were collected at room temperature on Philips PW 1100 (**1a**·$CHCl_3$) and Siemens AED (**4**·$CHCl_3$) single-crystal diffractometers using the graphite-monochromated Mo Kα (**1a**·$CHCl_3$) and the niobium-filtered Mo Kα (**4**·$CHCl_3$) radiations. All reflections with θ in the range 3–25° (**1a**·$CHCl_3$) and 3–27° (**4**·HCl_3) were measured; of 6019 (**1a**·$CHCl_3$) and 5432 (**4**·$CHCl_3$) independent reflections, 3726 (**1a**·$CHCl_3$) and 4338 (**4**·$CHCl_3$), having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analyzed by following Lehmann and Larsen.[8] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied [maximum and minimum values for the transmission factors were 1.286 and 0.835 (**1a**·$CHCl_3$) and 1.288 and 0.760 (**4**·$CHCl_3$), respectively].[9] Only the observed reflections were used in the structure solution and refinement.

Table 1. Crystallographic Data for the Complexes 1a·$CHCl_3$ and 4·$CHCl_3$

	1a·$CHCl_3$	**4**·$CHCl_3$
mol formula	$C_{32}H_{27}Cl_2N_2PPt$·$CHCl_3$	$C_{50}H_{42}Cl_2N_2P_2Pt$·$CHCl_3$
mol wt	855.93	1118.22
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
diffractometer	Philips PW 1100	Siemens AED
radiatn (λ, Å)	graphite-monochromated Mo Kα (0.710 73)	Nb-filtered Mo Kα (0.710 73)
a, Å	15.996(6)	11.727(6)
b, Å	17.996(6)	11.825(7)
c, Å	12.314(4)	17.091(8)
β, deg	111.23(2)	94.96(2)
V, Å^3	3304(2)	2361(2)
Z	4	2
D_{calcd}, g cm^{-3}	1.721	1.573
F(000)	1672	1112
cryst dimens, mm	0.17 × 0.23 × 0.27	0.10 × 0.13 × 0.20
μ(Mo Kα), cm^{-1}	47.72	33.90
no. of unique tot. data	6019	5432
no. of unique obsd data	3726 [$I > 2\sigma(I)$]	4338 [$I > 2\sigma(I)$]
R^a	0.0322	0.0333
R_w^b	0.0396	0.0427

^{a} $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$. ^{b} $Rw = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w(F_o)^2]^{1/2}$.

Both structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares, initially with isotropic and in the last cycles with anisotropic thermal parameters for all the non-hydrogen atoms except the carbon atoms of the phenyl rings of the PPh_3 ligand(s). All hydrogen atoms were placed at their calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 291 (**1a**·$CHCl_3$) and 372 (**4**·$CHCl_3$) variables; after the last cycles, no parameters shifted by more than 0.4 (**1a**·$CHCl_3$) and 0.8 (**4**·$CHCl_3$) esd. The highest remaining peak in the final difference map was equivalent to about 0.5 (**1a**·$CHCl_3$) and 1.0 (**4**·$CHCl_3$) e/Å^3. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.296$ and $g = 0.0020$ (**1a**·$CHCl_3$) and $K = 1.000$ and $g = 0.0034$ (**4**·$CHCl_3$) at convergence. Final R and R_w values were 0.0322 and 0.0396 (**1a**·$CHCl_3$) and 0.0333 and 0.0427 (**4**·$CHCl_3$), respectively. Since the space group $P2_1$ leads to a chiral configuration in the structure, an independent final cycle of refinement for **4**·$CHCl_3$ was carried out using the coordinates $-x, -y, -z$ for the non-hydrogen atoms. A remarkable increase of the R value was observed [$R(x, y, z) = 3.74$, $R(-x, -y, -z) = 4.72$]. The former model was selected, and the reported data refer to this model. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 10. The SHELX-76 and SHELXS-86 systems of computer programs were used.[11] Final atomic coordinates for the non-hydrogen atoms are given in Table 2 (**1a**·$CHCl_3$) and Table 3 (**4**·$CHCl_3$). All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, Italy, and on the

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Table 2. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10⁴) for the Non-Hydrogen Atoms of Complex 1a·$CHCl_3$

atom	x/a	y/b	z/c	U
Pt	2912.2(2)	1481.8(2)	2254.9(2)	361(1)[a]
Cl(1)	1551(1)	2076(1)	1430(2)	530(8)[a]
Cl(2)	2548(1)	1222(1)	3925(2)	570(8)[a]
Cl(3)	5434(2)	3021(2)	-783(2)	881(12)[a]
Cl(4)	4225(2)	3189(2)	-3084(3)	1276(17)[a]
Cl(5)	5089(3)	4464(2)	-1760(5)	1605(27)[a]
P	3312(1)	1844(1)	780(2)	392(7)[a]
N(1)	4122(3)	988(3)	3127(4)	371(22)[a]
N(2)	2723(4)	31(3)	1761(5)	462(24)[a]
C(1)	4786(5)	1396(4)	3853(6)	484(31)[a]
C(2)	5642(5)	1096(5)	4445(7)	535(33)[a]
C(3)	5800(5)	378(5)	4316(7)	585(35)[a]
C(4)	5122(5)	-87(4)	3588(6)	496(32)[a]
C(5)	4280(4)	235(4)	3001(6)	413(28)[a]
C(6)	5298(6)	-842(5)	3466(8)	647(39)[a]
C(7)	4653(6)	-1276(5)	2754(8)	684(42)[a]
C(8)	3772(6)	-1003(4)	2158(7)	547(35)[a]
C(9)	3567(5)	-251(4)	2279(6)	458(30)[a]
C(10)	2076(5)	-417(4)	1135(6)	486(30)[a]
C(11)	2238(6)	-1173(5)	943(7)	627(38)[a]
C(12)	3067(7)	-1462(5)	1448(8)	707(41)[a]
C(13)	4615(6)	2192(4)	4056(7)	636(36)[a]
C(14)	1149(5)	-100(5)	644(8)	749(40)[a]
C(15)	3212(4)	2841(4)	509(6)	409(17)
C(16)	3132(5)	3321(4)	1335(7)	515(20)
C(17)	3113(5)	4095(5)	1136(7)	606(22)
C(18)	3157(5)	4359(4)	140(7)	553(21)
C(19)	3218(5)	3893(5)	-705(8)	633(23)
C(20)	3240(5)	3127(4)	-538(7)	525(20)
C(21)	2691(5)	1442(4)	-648(6)	482(18)
C(22)	3102(6)	1321(4)	-1472(8)	647(24)
C(23)	2582(6)	1069(6)	-2574(8)	812(29)
C(24)	1682(6)	927(5)	-2864(9)	749(27)
C(25)	1284(7)	1028(5)	-2067(8)	794(28)
C(26)	1794(6)	1287(4)	-942(8)	641(24)
C(27)	4477(5)	1640(4)	1032(6)	470(18)
C(28)	5134(5)	2179(5)	1418(7)	597(22)
C(29)	6031(6)	2000(6)	1669(8)	759(27)
C(30)	6253(7)	1289(5)	1503(8)	759(28)
C(31)	5616(6)	735(5)	1141(7)	707(25)
C(32)	4729(5)	920(4)	915(7)	566(21)
C(33)	5207(6)	3529(5)	-2029(8)	744(43)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Results

Synthesis and Configuration of the Complexes. [PtX_2(Me_2-phen)] complexes react instantaneously with 1 equiv of PPh_3 in CH_2Cl_2 solution to give the corresponding addition products [PtX_2(Me_2-phen)(PPh_3)] (X = Cl (**1**), Br (**2**), I (**3**)) as a mixture of cis (**a**) and trans isomers (**b**). In the presence of a second equivalent of PPh_3 the bisphosphine complexes [PtX(Me_2-phen)(PPh_3)$_2$]X (X = Cl (**4**), Br (**5**), I (**6**)) are obtained as pure trans isomers. Analogous reactions performed with PBu^n_3 in 1:2 Pt:P ratio afford the trans complexes [PtX(Me_2-phen)(PBu^n_3)$_2$]X (X = Cl (**7**), Br (**8**), I (**9**)). It is to be noted that the corresponding complexes with unsubstituted phenanthroline, [PtX_2(phen)], react with phosphines to give the substitution instead of the addition products, [$PtX(PR_3)$(phen)]X.[12] The peculiar behavior of the [PtX_2(Me_2-phen)] complexes stems from their highly distorted square planar geometry.[5] The steric interaction between the ortho substituents of the phenanthroline ligand and the cis halogen atoms favors the dissociation of one end of the chelate and formation of a three-coordinate intermediate, which can then add an extra ligand.[13]

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Table 3. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10⁴) for the Non-Hydrogen Atoms of Complex 4·$CHCl_3$

atom	x/a	y/b	z/c	U
Pt	3991.4(2)	2500.0(0)	2324.1(2)	319(1)[a]
Cl(1)	5376(2)	2388(4)	1427(1)	459(9)[a]
Cl(2)	9395(3)	3413(3)	6020(2)	619(10)[a]
Cl(3)	9647(4)	1223(4)	7934(3)	1102(19)[a]
Cl(4)	8517(5)	3155(4)	8493(3)	1172(21)[a]
Cl(5)	10940(4)	3162(4)	8461(3)	1103(18)[a]
P(1)	5467(2)	2350(3)	3316(1)	365(9)[a]
P(2)	2584(2)	2388(4)	1274(1)	370(8)[a]
N(1)	2773(5)	2501(13)	3130(4)	384(19)[a]
N(2)	3482(7)	4660(7)	2599(5)	467(27)[a]
C(1)	2311(12)	1523(11)	3393(9)	448(45)[a]
C(2)	1487(13)	1506(16)	3923(9)	539(49)[a]
C(3)	1167(8)	2470(19)	4282(5)	559(32)[a]
C(4)	1650(12)	3515(14)	4057(8)	446(39)[a]
C(5)	2442(12)	3516(42)	3436(8)	385(41)[a]
C(6)	1287(10)	4518(11)	4402(7)	614(41)[a]
C(7)	1760(11)	5515(12)	4220(7)	666(45)[a]
C(8)	2509(9)	5584(10)	3595(7)	583(39)[a]
C(9)	2836(11)	4620(12)	3207(9)	418(36)[a]
C(10)	3850(8)	5646(10)	2322(7)	562(38)[a]
C(11)	3593(10)	6653(10)	2754(8)	637(43)[a]
C(12)	2939(11)	6625(10)	3366(8)	690(47)[a]
C(13)	2690(12)	454(12)	3029(10)	562(50)[a]
C(14)	4471(12)	5686(10)	1604(8)	701(47)[a]
C(15)	6330(8)	1076(9)	3214(6)	415(21)
C(16)	5882(10)	185(11)	2762(7)	619(30)
C(17)	6545(11)	-797(12)	2685(8)	697(33)
C(18)	7582(11)	-875(12)	3078(8)	693(33)
C(19)	8081(13)	3(13)	3588(10)	675(44)
C(20)	7391(10)	959(10)	3630(7)	565(27)
C(21)	6496(8)	3516(8)	3413(5)	379(19)
C(22)	7200(9)	3631(10)	4111(7)	572(27)
C(23)	8004(10)	4507(11)	4174(7)	623(29)
C(24)	8028(13)	5291(14)	3502(9)	658(42)
C(25)	7393(10)	5129(11)	2882(7)	627(30)
C(26)	6597(9)	4261(8)	2806(6)	461(22)
C(27)	4974(7)	2257(7)	4298(5)	383(21)
C(28)	4573(8)	3241(9)	4635(6)	460(22)
C(29)	4099(9)	3188(10)	5349(7)	532(26)
C(30)	4039(9)	2189(9)	5729(8)	571(29)
C(31)	4407(10)	1228(12)	5410(7)	634(30)
C(32)	4868(9)	1230(10)	4683(6)	525(25)
C(33)	2633(8)	1141(10)	651(6)	420(24)
C(32)	4868(9)	1230(10)	4683(6)	525(25)
C(33)	2633(8)	1141(10)	651(6)	420(24)
C(34)	1899(12)	1062(12)	-22(8)	723(35)
C(35)	1910(13)	128(14)	-499(10)	878(43)
C(36)	2663(11)	-735(13)	-310(8)	689(34)
C(37)	3405(12)	-687(13)	356(8)	770(37)
C(38)	3385(10)	274(10)	826(7)	549(26)
C(39)	2613(9)	3540(10)	572(6)	435(24)
C(40)	1788(12)	4401(12)	526(8)	713(34)
C(41)	1901(14)	5330(15)	5(10)	894(45)
C(42)	2770(13)	5332(15)	-478(9)	813(41)
C(43)	3497(13)	4515(14)	-464(9)	869(43)
C(44)	3471(13)	3567(14)	61(9)	806(39)
C(45)	1129(6)	2338(7)	1607(5)	360(20)
C(46)	715(9)	3264(9)	1986(6)	486(23)
C(47)	-342(10)	3264(10)	2273(7)	535(26)
C(48)	-988(9)	2289(10)	2181(6)	585(32)
C(49)	-598(11)	1356(12)	1865(8)	659(32)
C(50)	468(9)	1385(10)	1568(7)	516(25)
C(51)	9667(10)	2679(16)	7987(7)	755(50)[a]

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Depending upon the electronic properties of the incoming ligand, the phenanthroline may remain monodentate (four-coordinate complex) or can recoordinate the second end (five-coordinate complex) (Scheme 1).[5,6]

The ^{31}P spectra of the monophosphine complexes [PtX_2(Me_2-phen)(PPh_3)] (X = Cl (**1**), Br (**2**), I (**3**)), Table 4, consist of two signals of different intensities both having ^{195}Pt satellites. The resonance at lower field shows a greater ^{195}Pt coupling constant

Scheme 1

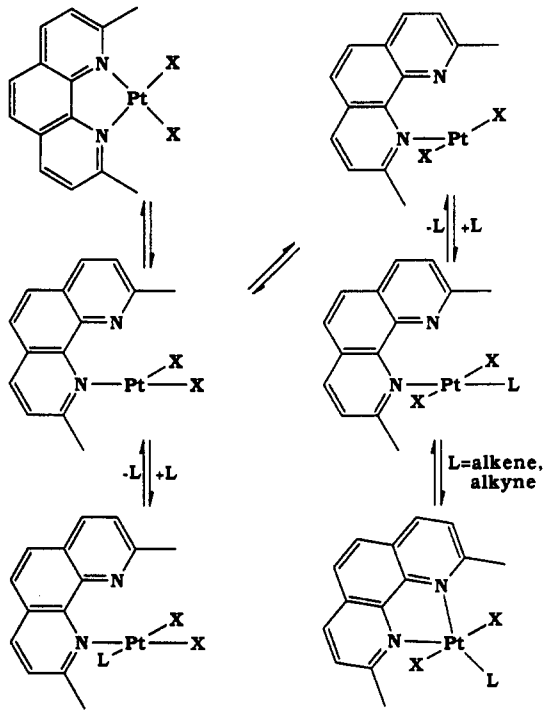

Table 4. ^{31}P NMR Data (δ, Downfield from H_3PO_4 (85% External Standard) and J(Pt–P) in Brackets; $CDCl_3$ Solvent) for $[PtX_2(Me_2\text{-phen})(PPh_3)]$ (X = Cl (**1**), Br (**2**), I (**3**)) and $[PtX(Me_2\text{-phen})(PR_3)_2]X$ (R = Ph, X = Cl (**4**), Br (**5**), I (**6**); R = Bu^n, X = Cl (**7**), Br (**8**), I (**9**))[a]

compd	cis isomer	trans isomer	compd	cis isomer	trans isomer
1	−2.67 [4289]	−5.07 [4193]	**6**		0.34 [2738]
2	−3.08 [4193]	−5.01 [4044]	**7**		−6.72 [2564]
3	−4.23 [3973]	−5.78 [3954]	**8**		−9.16 [2479]
4		3.16 [2860]	**9**		−12.55 [2444]
5		2.23 [2804]			

[a] Complexes **1–3** can have either the cis (**a**) or trans configuration (**b**). Complexes **4–9** always have the trans configuration.

and greater dependence of the chemical shift upon the nature of the halogen atom. In contrast, the signal at higher field has a smaller ^{195}Pt coupling constant and is very little affected by the nature of the halogen. These data are in agreement with the PPh_3 being trans to the halogen (cis isomer, **a**) and trans to the monocoordinated phenanthroline (trans isomer, **b**), respectively.[14] The cis/trans ratio strongly depends upon the nature of the halogen atoms (cis/trans = 0.7, 0.5, and <0.05 for **1–3**, respectively), the trans configuration being preferred over the cis by increasing the bulk of the halogen atoms.

The ^1H NMR spectra of complexes **1–3**, recorded at room temperature, show two sets of signals, which, on the basis of their relative intensities, resembling those of the ^{31}P signals, can be assigned to the cis and trans isomers, respectively (Table 5). For each set of resonances, the two methyls and the aromatic protons H_3 and H_8, H_4 and H_7, and H_5 and H_6 are chemically equivalent. In contrast, the crystal structures of both the cis (**1a**) and trans isomers (**3b**)[6] (see following Discussion) have shown that in the solid state the phenanthroline ligand is singly bonded to platinum. Therefore, the equivalence of both ends of Me_2-phen, on the NMR time scale at room temperature, stems from a dynamic process exchanging the two nitrogens at the same coordination site (flipping).

(14) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; pp 28–34.

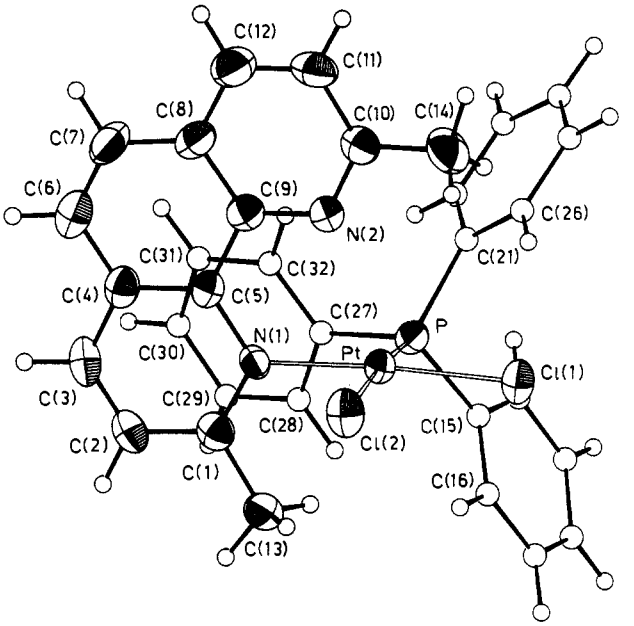

Figure 1. Molecular structure of the complex *cis*-$[PtCl_2(Me_2\text{-phen})(PPh_3)]$ (**1a**) with the atomic numbering scheme.

Compounds **1** and **2** ($CDCl_3$ solution) slowly decompose (1 week) to give an equilibrium mixture of Me_2-phen, *cis*- and *trans*-$[PtX_2(PPh_3)_2]$ (identified by $\{^1H\}^{31}P$ NMR),[14] and $[PtX_2(Me_2\text{-phen})]$ (starting complex). The decomposition of the iodo compound **3** is faster than those of compounds **1** and **2** and leads to the complete loss (24 h) of the Me_2-phen ligand and formation of $[PtI_2(PPh_3)]_2$ in a 1:5 cis/trans isomeric ratio. [The $\{^1H\}^{31}P$ and $\{^1H\}^{195}Pt$ NMR show typical AA'XX'spin systems characteristic of dimeric complexes of this type.[15] *cis*-$[PtI_2(PPh_3)]_2$: $\delta(^{31}P)$ = 15.8, ^1J(Pt,P) = 3642 Hz, ^3J(Pt,P) = 12 Hz, ^4J(P,P) = 5 Hz, ^2J(Pt,Pt) = 564 Hz; $\delta(^{195}Pt)$ = −5377. *trans*-$[PtI_2(PPh_3)]_2$: $\delta(^{31}P)$ = 11.7, ^1J(Pt,P) = 3690 Hz, ^3J(Pt,P) = 21 Hz, ^4J(P,P) = 10 Hz, ^2J(Pt,Pt) = 510 Hz; $\delta(^{195}Pt)$ = −5393]. The formation of iodo-bridged dimers *via* dissociation of sterically hindered chelate ligands appears to be of synthetic utility.[16]

Compounds **1–3** react with a second molecule of PPh_3 to give bisphosphine derivatives which are 1:1 electrolytes in chloroform, $[PtX(Me_2\text{-phen})(PPh_3)_2]X$ (X = Cl (**4**), Br (**5**), I (**6**)). These complexes are rather stable in chloroform solution and do not undergo the decomposition reaction observed for the monophosphine complexes **1–3**. The analogous complexes *trans*-$[PtX(Me_2\text{-phen})(PBu^n_3)_2]X$ (X = Cl (**7**), Br (**8**), I (**9**)) are obtained by reaction of $[PtX_2(Me_2\text{-phen})]$ with PBu^n_3 in molar ratio 1:2. The ^{31}P NMR spectra are in accord with equivalent phosphine ligands; moreover, the ^{31}P–^{195}Pt coupling constants, ranging from 2860 (**4**) to 2738 Hz (**6**), are typical of mutually trans phosphine ligands.[14] Therefore only one of the two possible isomers is formed. The ^1H NMR spectra of complexes **4–9** (Table 5), recorded at room temperature, show one set of signals for two equivalent phosphines and one set of resonances for a symmetrically bound Me_2-phen ligand (one chemical shift for the two methyls and for each couple of aromatic protons H_3 and H_8, H_4 and H_7, and H_5 and H_6). In contrast, the crystal structure of **4** has shown that, in the solid state, only one end of the phenanthroline is bound to platinum (see following Discussion). Again a flipping of the phenanthroline must take place in solution, rendering the two halves of the ligand equivalent on the NMR time scale.

Crystal Structure of 1a·$CHCl_3$. In the crystals of **1a**·$CHCl_3$, molecules of $[PtCl_2(Me_2\text{-phen})(PPh_3)]$ and $CHCl_3$ are present.

(15) Kiffen, A. A.; Masters, C.; Visser, J. P. *J. Chem. Soc., Dalton Trans.* **1975**, 1311–1315. Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 427–433. Clark, H. C.; Ferguson, G.; Jain, V. K.; Parvez, M. *Inorg. Chem.* **1985**, *24*, 1477–1482.

(16) Hartley, F. R.; Searle, G. W. *Inorg. Chem.* **1973**, *12*, 1949–1951.

Table 5. ^{1}H NMR Data (δ, Downfield from $SiMe_4$; CD_2Cl_2 Solvent) for $[PtX_2(Me_2\text{-phen})(PPh_3)]$ (X = Cl (**1**), Br (**2**), I (**3**)) and $[PtX(Me_2\text{-phen})(PR_3)_2]X$ (R = Ph, X = Cl (**4**), Br (**5**), I (**6**). R = Bu^n, X = Cl (**7**, Br (**8**), I (**9**))[a]

		Me_2-phen[a]				PPh_3[a]		
compd	T, K	Me	H(3,8)	H(4,7)	H(5,6)	H(2,6)	H(4)	H(3,5)
1a	293	3.42	7.47 d (8)	8.02 d (8)	7.60	7.35 m {6H}	7.28 m {3H}	7.09 m {6H}
	183	3.29	7.23 d (8)	7.82 d (8)	7.35 d (8)	5.85 m {2H}	6.75 m {1H}	6.32 m {2H}
		3.41	7.76 d (8)	8.20 d (8)	7.68 d (8)	7.59 m {2H}	7.57 m {1H}	7.28 m {2H}
1b	293	3.36 [5]	7.67 d (8)	8.28 d (8)	7.83	7.80 m {6H}	7.44 m {9H}	
2a	293	3.45	7.50 d (8)	8.02 d (8)	7.59	7.33 m {6H}	7.27 m {3H}	7.08 m {6H}
	173	3.32	7.28 d (8)	7.83 d (8)	7.28 d (8)	5.91 m {2H}	6.75 m {1H}	6.32 m {2H}
		3.42	7.77 d (8)	8.21 d (8)	7.70 d (8)	7.61 m {2H}	7.59 m {1H}	7.29 m {2H}
						8.21 m {2H}	7.50 m {1H}	7.53 m {2H}
2b	293	3.39 [5]	7.60 d (8)	8.17 d (8)	7.74	7.86 m {6H}	7.44 m {9H}	
3a	293	3.45	7.51 d (8)	8.03 d (8)	7.59	7.33 m {6H}	7.27 m {3H}	7.06 m {6H}
3b	293	3.37 [5]	7.67 d (8)	8.26 d (8)	7.85	7.86 m {6H}	7.43 m {9H}	
4	293	2.76	7.28 d (8)	8.14 d (8)	7.77	7.35 m {18H}		7.16 m {12H}
	183	2.32	6.84 d (8)	7.68 d (8)	7.44 d (8)	5.99 m {4H}	6.82 m {2H}	6.38 m {4H}
		2.85	7.79 d (8)	8.33 d (8)	7.83 d (8)	7.57 m {4H}	7.45 m {2H}	7.29 m {4H}
						8.17 m {4H}	7.71 m {2H}	7.66 m {4H}
5	293	2.77	7.32 d (8)	8.17 d (8)	7.77	7.34 m {18H}		7.15 m {12H}
	214	2.65	7.33 d (8)	8.11 d (8)	7.68	6.02 m {4H}	6.85 m {2H}	6.41 m {4H}
						7.87 m {8H}	7.67 m {4H}	7.47 m {8H}
	183	2.29	6.86 d (8)	7.68 d (8)	7.45 d (8)	5.98 m {4H}	6.81 m {2H}	6.63 m {4H}
		2.87	7.81 d (8)	8.37 d (8)	7.84 d (8)	7.54 m {4H}	7.43 m {2H}	7.27 m {4H}
						8.15 m {4H}	7.69 m {2H}	7.65 m {4H}
6	293	2.82	7.36 d (8)	8.18 d (8)	7.74	7.32 m {18H}		7.14 m {12H}
	183	2.62	7.35 d (8)	8.12 d (8)	7.65	5.97 m {4H}	6.77 m {2H}	6.33 m {4H}
						7.82 m {8H}	7.55 m {4H}	7.45 m {8H}
	153[b]	2.25	6.83	7.64	7.40	5.97 {4H}	6.69 {2H}	5.95 {2H}
		2.80	7.80	8.34	7.80			6.54 {2H}
						7.40 {4H}	7.40 {2H}	7.22 {4H}
						9.08 {2H}	7.67 {2H}	7.65 {4H}
						7.88 {2H}		

		Me_2-phen[a]				PBu^n_3[a]			
compd	T, K	Me	H(3,8)	H(4,7)	H(5,6)	α-CH_2	β-CH_2	γ-CH_2	$-CH_3$
7	293	3.45	7.96 d (8)	8.60 d (8)	8.10	1.44 m {12H}	1.09 m {24H}		0.68t (6) {18H}
	200	3.09	7.79 d (8)	8.44 d (8)	8.02 d (8)	1.27 m {6H}	0.94 m {6H}	0.89 m {12H}	0.58t (6) {18H}
		3.65	8.01 d (8)	8.64 d (8)	8.09 d (8)	1.43 m {6H}	1.02 m {6H}		
8	293	3.46	7.96 d (8)	8.61 d (8)	8.10	1.50 m {12H}	1.08 m {24H}		0.68t (7) {18H}
	183	3.10	7.78 d (8)	8.44 d (8)	8.01 d (8)	1.31 m {6H}	0.90 m {6H}	0.84 m {12H}	0.57t (7) {18H}
		3.63	7.99 d (8)	8.63 d (8)	8.09 d (8)	1.46 m {6H}	1.00 m {6H}		
9	293	3.45	7.96 d (8)	8.60 d (8)	8.10	1.59 m {12H}	1.06 m {24H}		0.68t (7) {18H}
	153[b]	3.07	7.73	8.41	7.95	1.38 {12H}	1.06 m {18H}		0.50 {18H}
		3.58	7.93	8.58	8.04		0.92 {6H}		

[a] Values of J(H–H) (in parentheses) are given when assignable. Integral values are given in braces. [b] All signals are broad at this temperature.

The molecular structure of the complex is shown in Figure 1 together with the atomic numbering scheme. Relevant bond distances and angles are reported in Table 6. The platinum atom displays the expected square planar coordination with two cis positions occupied by two chlorine atoms and the other two by a nitrogen atom of Me_2-phen and the phosphorus atom of PPh_3. The phenanthroline molecule is roughly planar [the maximum deviation from the mean plane passing through all atoms except the methyl carbons is 0.071(7) Å for C(10)] and makes a dihedral angle of 88.7(1)° with the platinum coordination plane.

The values of the Pt–Cl bond distances are notably different [Pt–Cl(1) = 2.305(2), Pt–Cl(2) = 2.378(3) Å] reflecting the different trans influence of the N and P atoms. Only one nitrogen atom of phenanthroline is at a bond distance from platinum [Pt–N(1) = 2.046(5) Å], the second nitrogen atom of Me_2-phen, N(2), is at a much greater distance from Pt [2.673(6) Å]. A comparably long Pt–N(2) distance [2.661(18) Å] was found in the structure of **3b** [in the latter complex the Pt–N(1) bond length, 2.182(17) Å, was longer than in **1a**·$CHCl_3$ since the N(1) atom was trans to a P and not to a Cl atom].[6] The square planar coordination of Pt is slightly distorted toward a square pyramid, the Pt atom being out of the mean plane passing through the four coordinated atoms by 0.113(1) Å toward N(2).

The overlap with the Me_2-phen ligand of one phenyl ring of the PPh_3 ligand is worth noting. One phosphorus-bound carbon atom [C(27)] eclipses N(1), the other two [C(15) and C(21)] are staggered with respect to Cl(1) {τ[N(1)PtPC(27)] = -5.2(3), τ[Cl(1)PtPC(15)] = 53.2(3), τ[Cl(1)PtPC(21)] = -67.5(3)°}. Short distances between the stacked phenyl ring [C(27) and C(32) atoms] and the phenanthroline [C(1), N(1), and C(5) atoms] are C(27)···C(1) = 3.36(1), C(27)···N(1) = 3.07(1), C(32)···N(1) = 3.21(1), and C(32)···C(5) = 3.16(1) Å. The dihedral angle between this phenyl ring and the mean plane through the phenanthroline molecule is 20.8(2)°.

An intramolecular hydrogen bond involves the C(26) and Cl(1) atoms [C(26)···Cl(1) = 3.394(9) and H(26)···Cl(1) = 2.52 Å; C(26)H(26)Cl(1) = 146°]. Also the molecule of solvent is involved in a hydrogen bond with Cl(1) [C(33)···Cl(1) = 3.52(1) and H(33)···Cl(1) = 2.58 Å; C(33)H(33)Cl(1) =155°].

Crystal Structure of 4·$CHCl_3$. In the crystals of **4**·$CHCl_3$, $[PtCl(Me_2\text{-phen})(PPh_3)_2]^+$ cations, having an approximate C_s symmetry, Cl^- anions and $CHCl_3$ molecules of solvent are present. The molecular structure of the complex is shown in Figure 2 together with the atomic numbering scheme. Relevant bond distances and angles are reported in Table 6. The platinum atom displays square planar coordination with two trans positions occupied by the P atoms of two PPh_3 ligands and the other two positions by a N atom of Me_2-phen and a Cl atom. The phenanthroline molecule is roughly planar [the maximum deviation from the mean plane passing through all atoms excepting the methyl carbons is 0.13(1) Å for C(10)] and makes a dihedral angle of 87.4(1)° with the platinum coordination plane.

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complexes 1a·$CHCl_3$ and 4·$CHCl_3$

1a·$CHCl_3$		4·$CHCl_3$	
	Distances		
Pt–Cl(1)	2.305(2)	Pt–Cl(1)	2.331(3)
Pt–Cl(2)	2.378(3)		
Pt–N(1)	2.046(5)	Pt–N(1)	2.069(7)
Pt–N(2)	2.672(6)	Pt–N(2)	2.674(9)
Pt–P	2.231(2)	Pt–P(1)	2.322(2)
		Pt–P(2)	2.335(2)
P–C(15)	1.822(7)	P(1)–C(15)	1.83(1)
P–C(21)	1.827(7)	P(1)–C(21)	1.83(1)
P–C(27)	1.813(8)	P(1)–C(27)	1.83(1)
		P(2)–C(33)	1.82(1)
		P(2)–C(39)	1.82(1)
		P(2)–C(45)	1.84(1)
N(1)–C(1)	1.33(1)	N(1)–C(1)	1.37(2)
N(1)–C(5)	1.40(1)	N(1)–C(5)	1.38(2)
N(2)–C(9)	1.36(1)	N(2)–C(9)	1.34(2)
N(2)–C(10)	1.32(1)	N(2)–C(10)	1.34(1)
C(1)–C(2)	1.40(1)	C(1)–C(2)	1.38(2)
C(1)–C(13)	1.50(1)	C(1)–C(13)	1.49(2)
C(2)–C(3)	1.34(1)	C(2)–C(3)	1.36(3)
C(3)–C(4)	1.41(1)	C(3)–C(4)	1.42(3)
C(4)–C(5)	1.40(1)	C(4)–C(5)	1.47(2)
C(4)–C(6)	1.40(1)	C(4)–C(6)	1.41(2)
C(5)–C(9)	1.46(1)	C(5)–C(9)	1.45(2)
C(6)–C(7)	1.34(1)	C(6)–C(7)	1.35(2)
C(7)–C(8)	1.42(1)	C(7)–C(8)	1.44(2)
C(8)–C(9)	1.41(1)	C(8)–C(9)	1.39(2)
C(8)–C(12)	1.42(1)	C(8)–C(12)	1.40(2)
C(10)–C(11)	1.42(1)	C(10)–C(11)	1.45(2)
C(10)–C(14)	1.50(1)	C(10)–C(14)	1.48(2)
C(11)–C(12)	1.35(1)	C(11)–C(12)	1.35(2)
	Angles		
N(1)–Pt–N(2)	72.7(2)	N(1)–Pt–N(2)	72.8(3)
N(1)–Pt–P	93.4(2)	N(1)–Pt–P(1)	91.6(2)
		N(1)–Pt–P(2)	91.6(2)
		P(1)–Pt–P(2)	171.7(1)
Cl(1)–Pt–N(1)	174.9(2)	Cl(1)–Pt–N(1)	176.7(2)
Cl(2)–Pt–N(1)	86.7(2)		
Cl(1)–Pt–Cl(2)	89.1(1)		
Cl(1)–Pt–P	90.5(1)	Cl(1)–Pt–P(1)	87.6(1)
		Cl(1)–Pt–P(2)	88.7(1)
Cl(2)–Pt–P	173.8(1)		
Pt–P–C(27)	112.4(3)	Pt–P(1)–C(27)	113.6(3)
Pt–P–C(21)	116.9(3)	Pt–P(1)–C(21)	116.9(3)
Pt–P–C(15)	113.9(2)	Pt–P(1)–C(15)	112.1(3)
C(21)–P–C(27)	104.6(4)	C(21)–P(1)–C(27)	102.7(4)
C(15)–P–C(27)	104.4(4)	C(15)–P(1)–C(27)	105.1(4)
C(15)–P–C(21)	103.5(3)	C(15)–P(1)–C(21)	105.3(5)
		Pt–P(2)–C(45)	112.1(3)
		Pt–P(2)–C(39)	114.4(3)
		Pt–P(2)–C(33)	116.0(3)
		C(39)–P(2)–C(45)	107.4(4)
		C(33)–P(2)–C(45)	103.4(4)
		C(33)–P(2)–C(39)	102.5(5)
Pt–N(1)–C(5)	122.6(5)	Pt–N(1)–C(5)	119.1(7)
Pt–N(1)–C(1)	119.0(5)	Pt–N(1)–C(1)	122.3(7)

The Pt–P bonds, trans to one another, have very similar lengths [Pt–P(1) = 2.322(2), Pt–P(2) = 2.335(2) Å] and are much longer than those found in **1a**·$CHCl_3$ [Pt–P = 2.231(2) Å], in which the phosphorus atom is trans to a chlorine atom, and in **3b** [Pt–P = 2.187(6) Å], in which the phosphorus atom is trans to a nitrogen atom. The values of the Pt–Cl(1) and Pt–N(1) bond lengths [2.331(3) and 2.069(7) Å, respectively], mutually trans to one another, are slightly longer than corresponding values in **1a**·$CHCl_3$ [2.305(2) and 2.046(5) Å, respectively]. The distance between the second nitrogen atom of Me_2-phen [N(2)] and the platinum atom is 2.674(9) Å, a value very similar to that observed in **1a**·$CHCl_3$. As already observed in compound **1a**·$CHCl_3$, the square planar coordination of Pt is slightly distorted toward a square pyramid, with the Pt atom displaced from the mean plane passing through the four coordinated atoms by 0.145(1) Å toward N(2).

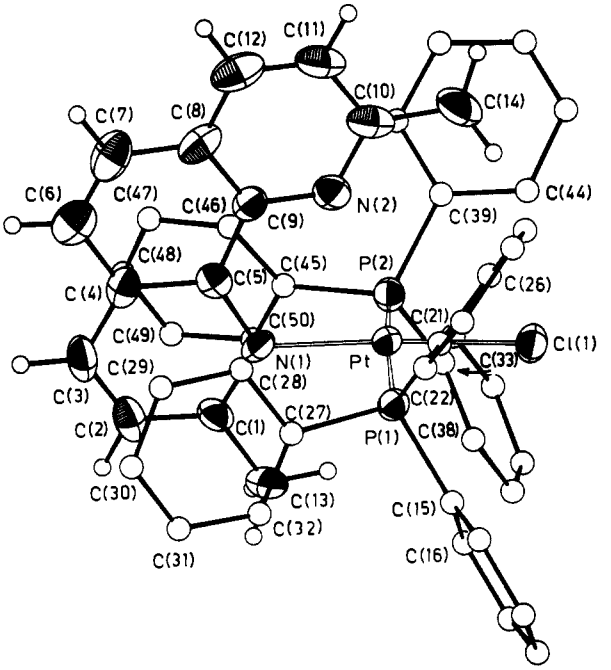

Figure 2. Molecular structure of the cationic complex *trans*-[PtCl(Me_2-phen)$(PPh_3)_2$]$^+$ (cation of **4**) with the atomic numbering scheme.

The conformations of the two PPh_3 ligands are very similar to that observed for the PPh_3 ligand in **1a**·$CHCl_3$. One phenyl of P(1) [phosphorus-bound carbon atom C(27)] and one phenyl of P(2) [phosphorus-bound carbon atom C(45)] eclipse the coordinated end of phenanthroline {τ[N(1)PtP(1)C(27)] = 1.8(4)° and τ[N(1)PtP(2)C(45) = 0.6(4)°}. The other two phenyls of P(1) [phosphorus-bound carbon atoms C(15) and C(21), respectively] and P(2) [phosphorus-bound carbon atoms C(33) and C(39), respectively] are staggered with respect to Cl(1) {τ[Cl(1)PtP(1)C(15)] = –56.2(4)° and τ[Cl(1)PtP(1)C(21) = 65.5(4)°; τ[Cl(1)PtP(2)C(33) = 57.7(4)° and τ[Cl(1)PtP(2)C(39) = –61.3(4)°}. The interaction of double stacking between the phenanthroline molecule and one phenyl ring for each phosphine is evidenced by the short distances between the phenyl rings [C(27) and C(28) for the phenyl of P(1); C(45) and C(46) for the phenyl of P(2)] and the phenanthroline [C(1), N(1), and C(5)]. These are C(27)···C(1) = 3.36(1), C(27)···N(1) = 3.14(1), C(28)···N(1) = 3.30(1), C(28)···C(5) = 3.11(2), C(45)···C(1) = 3.38(2), C(45)···N(1) = 3.11(1), C(46)···N(1) = 3.11(1), and C(46)···C(5) = 3.08(2) Å. The dihedral angles between these two phenyl rings and the phenanthroline molecule are 19.1(2) and 28.8(2)° for P(1) and P(2), respectively.

As observed for **1a**·$CHCl_3$, also in **4**·$CHCl_3$ there is a rather weak intramolecular hydrogen bond involving the C(26) and Cl(1) atoms [C(26)···Cl(1) = 3.45(2) and H(26)···Cl(1) = 2.69 Å; C(26)H(26)Cl(1) = 133°]. The solvent is also involved in hydrogen bonding with the Cl(2) anion [C(51)···Cl(2) = 3.46(2) and H(51)···Cl(2) = 2.47 Å; C(51)H(51)Cl(2) =169°].

Dynamic Processes. A detailed investigation of the dynamic processes involving the *cis*-monophosphine complexes **1a** and **2a** and the *trans*-bisphosphine complexes **4–9** was performed by ^1H NMR. The very low concentration of the *cis*-monophosphine complex **3a** (always in equilibrium with the much more stable trans isomer) prevented a detailed investigation of this species, while the *trans*-monophosphine complexes **1b–3b** did not show decoalescence of the ^1H NMR signals even at the lowest temperature reached in our experiments.

Figure 3 gives a schematic representation of the three types of intramolecular dynamic processes which can be conceived for these complexes: (i) flipping of the phen ligand (**A**); (ii) rotation about the Pt–P bond (**B**); (iii) rotation about the P–C_{ipso} bonds (C_1–C_3). The NMR spectrum of one of the compounds (**4**) and

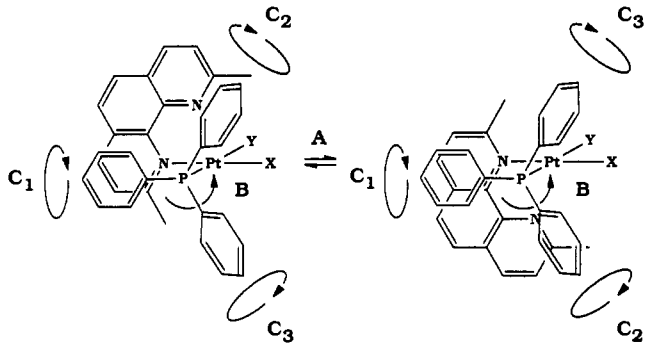

Figure 3. Schematic representation of the three types of intramolecular dynamic processes which can be conceived for complexes **1a–3a** and **4–6**: Flipping of the Me_2-phen ligand (**A**), rotation about the Pt–P bond (**B**), and rotation about the P–C_{ipso} bonds (C_1–C_3).

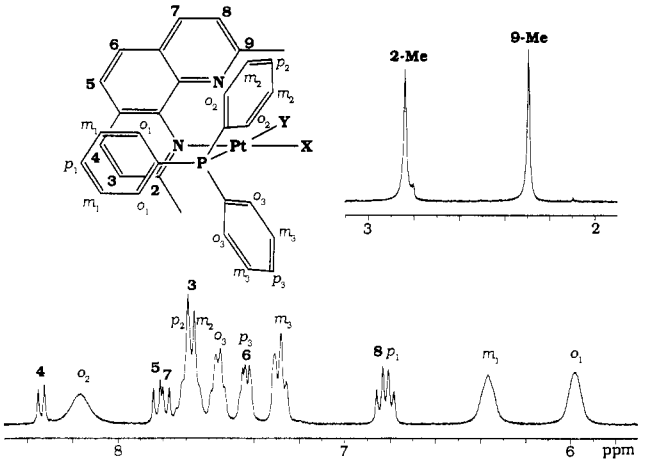

Figure 4. ^1H NMR spectrum of compound **4** (CD_2Cl_2 solution, 175 K, δ downfield of TMS) and relative assignments.

the relative assignment of the proton resonances (selective decoupling experiments) are given in Figure 4.

Compounds **4–6**, for which there is no complication arising from the simultaneous presence of the *cis* and *trans* isomers (as is the case for complexes **1–3**) will be discussed first. The ^1H NMR spectra of compound **5**, taken at different temperatures, are shown in Figure 5. At 293 K the two methyls and the aromatic protons H_3 and H_8, H_4 and H_7, and H_5 and H_6 are chemically equivalent indicating that the monocoordinated Me_2-phen ligand undergoes a fast head to tail rearrangement. The PPh_3 ligands exhibit only two multiplets which account for the ortho and for the meta and para protons, respectively.

At lower temperature the PPh_3 signals become broader and then decoalesce (218 K) in one set of three signals upfield 7 ppm (at 6.8, 6.4, and 6.0 ppm, which account for 2, 4, and 4 protons, respectively) and one set of two signals downfield 7 ppm (at 7.8 and 7.5 ppm, which account for 8 and 12 protons, respectively). The decoalescence of the PPh_3 signals in two sets of multiplets, one above and the other below 7 ppm, is a consequence of the different environment which is felt by the phenyl rings of the PPh_3 ligands when the slow rotation about the Pt–P bond does not mediate the shielding anisotropy of the Me_2-phen ligand. The multiplets downfield 7 ppm account for the two phenyl rings of PPh_3 not overlapping with the Me_2-phen ligand, while the three multiplets upfield 7 ppm belong to the third ring of PPh_3 overlapping with the fused rings of Me_2-phen. The flipping of the Me_2-phen ligand is still fast on the NMR time scale and makes equivalent the two unshielded phenyls of PPh_3 which give coincident signals (one broad band for the ortho and one broad band for the meta and para protons, respectively). In complete accord with this conclusion are the signals related to the Me_2-phen ligand which are very little affected by the change of

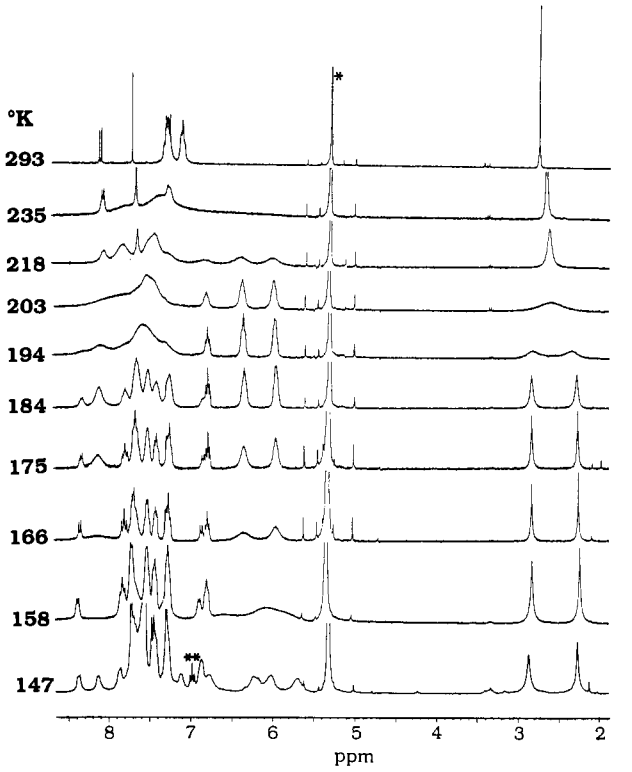

Figure 5. ^1H NMR spectra of compound **5** taken at different temperatures. Spectral changes (ranges of chemical shift and temperature) related to a specific motion are the following: **B**, 5.5–7.0 ppm, 293–203 K; **A**, 2.0–3.0 ppm, 218–175 K; C_1, 5.5–7.0 ppm, 175–147 K; C_2, 7.8–8.2 ppm, 175–147 °K. An asterisk indicates the resonance of $CHDCl_2$, and double asterisks indicate the resonance of CHF_2Br.

temperature, and down to 218 K they still consist of three, slightly broad, resonances for the aromatic protons and one broad signal for the two methyls.

As the temperature is lowered below 200 K, the signals of the phenanthroline ligand start to decoalesce. At 175 K the Me_2-phen ligand shows two singlets, one for each methyl, and six doublets, one for each aromatic proton. The two unshielded phenyls of the phosphines are no longer equivalent and give two separate sets of signals. Therefore, at this temperature both the rotation about the Pt–P bonds and the flipping of the phenanthroline ligand are frozen.

Below 175 K the signals of the ortho (5.8 ppm) and meta (6.4 ppm) protons of the shielded phenyl of PPh_3 and the ortho protons of one of the two unshielded phenyls of PPh_3 (8.2 ppm) broaden while the signals of the third phenyl of PPh_3 remain unchanged. At 147 K (solvent CD_2Cl_2/CBr_2F_2, 1:1 v/v) the ortho and meta protons of the shielded phenyl of PPh_3 give two well-separated multiplets each. Therefore we can conclude that the rates of rotation about the P–C_{ipso} bonds of the three phenyls of PPh_3 approach the NMR time scale in the order C_1 before C_2 before C_3. In our experimental conditions, complete decoalescence was attained only for the ^1H NMR signals related to the C_1 process, thus allowing the evaluation of the corresponding ΔG^* (Table 7). Note that the two trans PPh_3 ligands always give coincident signals indicating that the plane perpendicular to the P–P axis, which is also the plane of the Me_2-phen ligand, never loses its characteristic of plane of symmetry.

Figure 6 shows the NMR spectra of complexes **4–6**, taken at a temperature where the methyl signals of the phenanthroline have comparable decoalescence (which implies a comparable rate of motion **A**). It is interesting to note that process **A**, which strongly depends upon the nature of the halide ion, can approach the NMR time scale either before **B** and C_1 (**4**), or between **B** and C_1 (**5**), or finally after **B** and very close to C_1 (**6**).

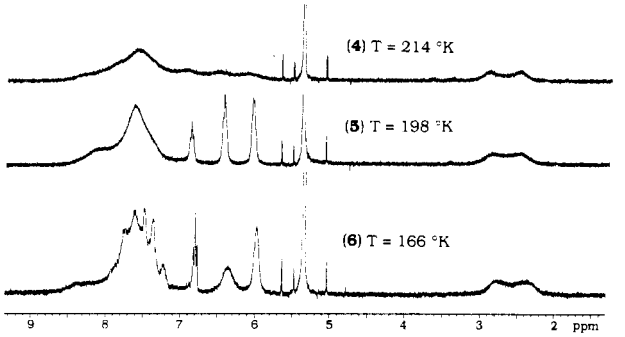

Figure 6. ^1H NMR spectra of complexes **4–6** taken at a temperature where they have comparable rate of motion **A** (equal decoalescence of the methyl signals): **4**, motions **B** and C_1 are still fast (very broad signals for o_1, m_1, and p_1 (5.8–7.0 ppm); **5**, motion **B** is slow and motion C_1 is still fast (well-separated signals for o_1, m_1, and p_1); **6**, motion **B** is slow and motion C_1 is approaching the NMR time scale (broadening of the o_1 signal).

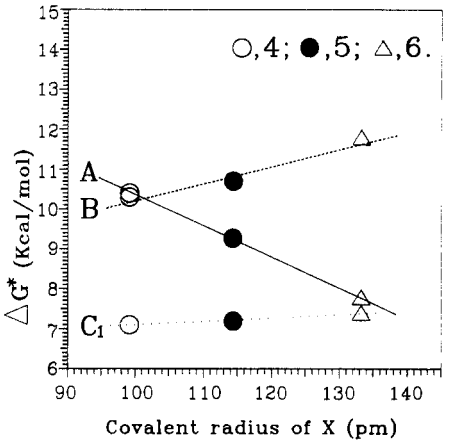

Figure 7. Plot of ΔG^* for the processes **A**, **B**, and C_1 against the covalent radii of the halogen ligands for complexes **4** (○), **5** (●), and **6** (△).

Table 7. ΔG^* (kcal/mol) for the **A**, **B**, and C_1 Dynamic Processes of *cis*-$[PtX_2(Me_2\text{-phen})(PPh_3)]$ (X = Cl (**1a**), Br (**2a**)) and *trans*-$[PtX(Me_2\text{-phen})(PR_3)_2]X$ (R = Ph, X = Cl (**4**), Br (**5**), I (**6**); R = Bu^n, X = Cl (**7**), Br (**8**), I (**9**))

compd	A	B	C_1
1a	11.6	10.2	7.2
2a	10.4	10.8	7.8
4	10.4	10.3	7.1
5	9.3	10.7	7.2
6	7.8	11.8	7.4
7	11.2		
8	9.9		
9	8.1		

Plots of ΔG^* for the processes **A**, **B**, and C_1, against the covalent radii of the halogen ligands, for complexes **4–6** are reported in Figure 7. The activation energy for the flipping of the Me_2-phen ligand (**A**) decreases considerably on going from the chloro to the iodo complex, while the activation energies for phosphine rotation (**B**) and phenyl ring rotation (C_1) increase slightly.

The monophosphine complexes **1a** and **2a** show essentially the same type of decoalescence phenomena already described for the bisphosphine compounds **4–6** The ΔG^*'s for the dynamic processes **A**, **B**, and C_1 are reported in Table 7. The activation energies for processes **B** and C_1 are very similar for the mono- and bisphosphine derivatives; that for process **A** is ca. 1 kcal/mol greater for the monophosphine than for the bisphosphine complexes.

The bisphosphine complexes **7–9** exhibit only the dynamic process **A**. The activation energies are slightly bigger than those observed for complexes **4–6** and have a similar dependence upon the covalent radii of the halogen ligands (Table 7). ^1H NMR

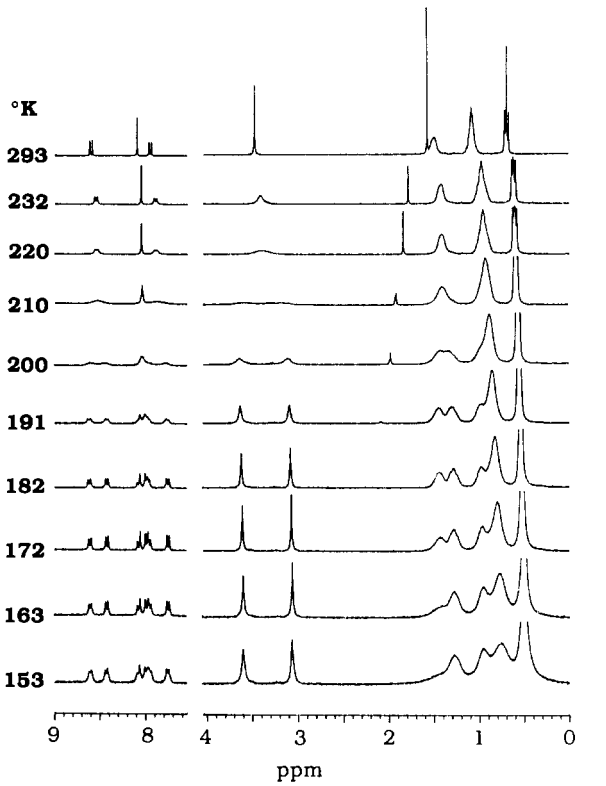

Figure 8. ^1H NMR spectra of compound **8** taken at different temperatures (CD_2Cl_2 solvent).

spectra of compound **8**, taken at different temperatures, are shown in Figure 8. As the flipping of the phenanthroline ligand becomes slow on the NMR time scale, the metallic center becomes stereogenic causing a diastereotopic splitting of the methylene protons of the *n*-butyl radicals. In the whole range of temperatures the three *n*-butyl groups remain equivalent and give one set of resonances which become broad below 172 K but do not decohalesce in different signals even at a temperature as low as 153 K. This indicates that ΔG^* for the dynamic process **B** is much smaller for complexes **7–9** than for complexes **1a–2a** and **4–6**. An upper limit of 7 kcal/mol can be estimated on the basis of the lowest temperature reached and of the maximum variation of chemical shift expected.

Discussion

Flipping of the Phenanthroline Ligand. The flipping of a bidentate ligand has been previously investigated for platinum complexes of formula *cis*-$[PtCl(PR_3)_2(L)][BF_4]$, with L = phenanthroline, bipyridine, naphthyridine, pyridazine, or phthalazine and PR_3 = PEt_3, PMe_2Ph, or PPh_3. The flipping process could only be frozen in the case of potentially bidentate ligands with parallel (naphthyridine) or diverging (pyridazine and phthalazine) lone pairs of electrons and not in the case of phenanthroline and bipyridine; therefore ΔG^* for the fluxional process could only be related to the different orientations of the lone pairs of the chelate.[17] All the complexes mentioned above had a phosphine ligand trans to the potentially bidentate ligand, and in this respect, they are similar to our complexes **1b–3b**, for which we too have been unable to show by NMR spectroscopy any dissymmetry in the coordinated phenanthroline, even at a

(17) (a) Alvarez, S.; Bermejo, M. J.; Vinaixa, J. *J. Am. Chem. Soc.* **1987**, *109*, 5316-5323. (b) Bushnell, G. W.; Dixon, K. R.; Khan, M. A. *Can. J. Chem.* **1978**, *56*, 450–455. (c) Bushnell, G. W.; Dixon, K. R. *Can. J. Chem.* **1978**, *56*, 879–883. (d) Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618–2624. (e) Dixon, K. R.; Moss, K. C.; Smith, M. A. R. *Can. J. Chem.* **1974**, *52*, 692–695. (f) Bushnell, G. W.; Dixon, K. R.; Khan, M. A. *Can. J. Chem.* **1974**, *52*, 1367-1376. (g) Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1973**, *51*, 618–623.

temperature as low as 148 K, although the solid-state structure of **3b** has definitely proven that the phenanthroline ligand is singly bonded to platinum.[6]

The activation energy for the flipping of a singly bonded phenanthroline becomes considerably greater than in the above quoted examples and can be measured by NMR spectroscopy when the ligand in trans position is a halogen instead of a phosphine ligand (compounds **1a**, **2a**, and **4–9**). The values of ΔG^* increase in the order $PPh_3 \ll I < Br < Cl$ and therefore are inversely proportional to the labilizing effect of the trans ligands. The linear correlation shown in Figure 7 also indicates that the covalent radius of the halogen is a good index of its trans effect. The decrease of activation energy observed on going from the neutral (**1a**, **2a**) to the +1 charged species (**4–6**) can be related to an increased electrophilicity of the platinum nucleus in the latter series of complexes, which stabilizes the transition state with both ends of the phenanthroline ligand bonded to the metal. Finally the slightly bigger activation energy observed for compounds **7–9** (PBu^n_3 ligands) with respect to compounds **4–6** (PPh_3 ligands) could be related to the greater basicity of PBu^n_3 with respect to that of PPh_3.

Rotation about the Metal–Phosphorus Bond. The rotation about the metal–phosphorus bond has already been investigated in the case of square planar compounds carrying phosphine ligands with two bulky *tert*-butyl substituents such as *trans*-$[MX_2(PRBu^t_2)_2]$ (M = Pt, Pd; X = Cl, Br, I; R = H, Ph)[3d,n] and *trans*-$[MX(CO)(PRBu^t_2)_2]$ (M = Rh, Ir: X = Cl, R = H, Me, Et, Pr^n, Ph; X = Br, I, R = H, Me).[3d,h,m,n] The measured values of activation energy were of the order of 10 kcal/mol.[3d,h] Restricted rotation about the Pt–P bond was also observed in the complex $[Pt(\eta^3\text{-}C_3H_5)(PCy_3)_2][PF_6]$, but substitution of PPh_3 for PCy_3 restored the free rotation.[3k] More recently an energy barrier of 8–10 kcal/mol for rotation about a M–PPh_3 bond has been reported for chromium(0) and molybdenum(0) complexes of formula $[M(\eta^6\text{-}C_6R_6)(CO)_2(PPh_3)]$ (R = Me, Et, Pr^n)[3e,g] and for the Iron(II) complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(COMe)]$.[3a] Also in these complexes the activation energy is believed to stem from steric rather than electronic factors (steric interaction between PPh_3 and the arene substituents in the chromium and molybdenum complexes; overcrowding of the metal center in the iron complex).

In contrast with the previous reports, the ΔG^* values for rotation about the M–PPh_3 bond, observed in the series of complexes **1a**, **2a**, and **4–6**, are greater than 10 kcal/mol and appear to be particularly high if compared with those found for rotation of phosphines with much greater cone angle such as $PRBu^t_2$ and PCy_3 in platinum(II) complexes.[2] Moreover no great steric effects can be expected from the Me_2-phen ligand which exchanges the donor atom *via* a trigonal bipyramidal transition state with the phenanthroline ligand confined into the plane perpendicular to the platinum–phosphorus axis. Also the cis halogen atom is not expected to create steric hindrance to the rotation of the phosphine as clearly shown by the small increase of ΔG^* observed on going from chloro to iodo species. A stacking interaction between one phenyl ring of PPh_3 and the aromatic system of the Me_2-phen ligand appears to be the most likely explanation for the high-energy barrier to rotation about the M–P bond experienced in the series of compounds **1a–2a** and **4–6**. This hypothesis is strongly supported by several facts: (i) The very similar values of ΔG^* observed in the two series of complexes **1a–2a** and **4–6** in spite of the fact that the Pt–P bond lengths are significantly different in the two cases (0.1 Å); (ii) the very small dependence of ΔG^* upon the bulk of the halogen atom; (iii) the much smaller activation energy for rotation observed in compounds **7–9** for which no stacking interaction between the phenanthroline and the PBu^n_3 can take place. Therefore the arene stacking between Me_2-phen and one phenyl of PPh_3 can be viewed as a type of intramolecular brake.

Rotation about the P–C_{ipso} Bonds. The stacking interaction can also account for the restricted rotation about the P–C_{ipso} bond of the most shielded phenyl of PPh_3. Since the stacked phenyl overlaps with the coordinated end of Me_2-phen, the two remaining phenyls of PPh_3 are not equivalent and one of them, probably being close to the uncoordinated end of the phenanthroline ligand, is also restricted in its rotation about the P–C_{ipso} bond. Compounds **1a**, **2a**, and **4–6** are the first for which an energy barrier greater than 7 kcal/mol has been observed for rotation of a phenyl group of PPh_3; these values of activation energy are significantly greater than the upper limit of 5 kcal/mol calculated from conformational analysis[3a] and suggest that the stacking interaction contributes significantly to the energy barrier of this process.[18] As already observed for Pt–P rotation, also ΔG^*'s for P–C_{ipso} rotation remain almost unchanged in the two sets of compounds **1a–2a** and **4–6** in spite of the changes in Pt–P bond lengths.

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Supplementary Material Available: Hydrogen atom coordinates and isotropic thermal parameters (Tables SI and SII), thermal parameters for the non-hydrogen atoms (Tables SIII and SIV), complete bond distances and angles (Tables SV), and crystallographic data (Table SVI) (8 pages). Ordering information is given on any current masthead page.

(18) High-energy barriers have been reported for the rotation about the P–C bond of a *tert*-butyl ([$M(CO)_5(PPh_2Bu^t)$], 8.3 kcal/mol),[3l] phenyl (PBu^t_2-Ph, 10.5 kcal/mol),[3d] and *ortho*-tolyl groups ([$Cr(CO)_5\{P(o\text{-tolyl})_3\}$] and [$Fe(CO)_4\{P(o\text{-tolyl})_3\}$], 9–11 kcal/mol).[3b] In all cases steric rather than electronic factors, related to the presence of the sterically demanding *tert*-butyl or *ortho*-tolyl groups, are responsible for such a high-energy barrier.