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^{195}Pt NMR and Structural Studies of Platinum(II) *o*-Tolyl and Mesityl Complexes

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The syn and anti isomers of *cis*-Pt(o-tolyl)$_2$(PEt$_3$)$_2$ have distinguishable ^{195}Pt NMR spectra and have been separated chromatographically. ^{195}Pt and ^{1}H NMR spectra of these and a variety of related platinum complexes are reported, together with X-ray structures of four *o*-tolyl complexes: *trans*-Pt(o-tolyl)(PEt$_3$)$_2$Cl monoclinic, *Cc*, a = 14.412(3) Å, b = 11.615(3) Å, c = 14.818(3) Å, β = 106.14(2)°, Z = 4, V = 3282.8(8) Å^3, R = 0.030, R_w = 0.039 based on 2142 reflections with $I > \sigma(I)$; *trans*-Pt(o-tolyl)(PEt$_3$)$_2$Br, orthorhombic, *Pcmn*, a = 11.245(4) Å, b = 12.862(5) Å, c = 16.750(5) Å, Z = 4, V = 2422.5 (13) Å^3, R = 0.052, R_w = 0.056 based on 2075 reflections with $I > \sigma(I)$; *cis-syn*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, monoclinic, $P2_1/n$, a = 10.403(4) Å, b = 15.127(6) Å, c = 18.372(6) Å, β = 106.47(3)°, Z = 4, V = 2773(2) Å^3, R = 0.120, R_w = 0.134 based on 2075 reflections with $I > 3\sigma(I)$; *cis-anti*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, monoclinic, $P2_1/c$, a = 10.189(4) Å, b = 15.425(6) Å, c = 18.297(6) Å, β = 104.35(3)°, Z = 4, V = 2786(2) Å^3, R = 0.043, R_w = 0.036 based on 3264 reflections with $I > \sigma(I)$. All four structures show approximate square planar coordination about platinum but with significant distortions to maintain the Pt–CH$_3$ distance at approximately the sum of the van der Waals radii. Although electrochemical oxidations of the *o*-tolyl complexes are chemically irreversible, oxidation of *trans*-Pt(mesityl)(PEt$_3$)$_2$Cl apparently gives a short-lived monomeric Pt(III) species.

Introduction

In 1959, Chatt and Shaw[1] reported the synthesis of a series of platinum(II) compounds, L$_2$PtRX and L$_2$PtR$_2$, where L is a tertiary phosphine or arsine and R is an alkyl or aryl. The most stable of these compounds proved to be those where R is an ortho-substituted phenyl such as *o*-tolyl, presumably because of steric inhibition of attack at the Pt center. Although Chatt and Shaw pointed out the possibility of syn and anti isomers of *cis*- and *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, their characterization methods—elemental analysis, melting points, and dipole moment measurements—were incapable of distinguishing between them, and they believed that only one isomer was obtained. In fact, ^{195}Pt NMR clearly shows the presence of two isomers in preparations of both *cis*- and *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$. We have succeeded in separating the syn and anti isomers of the cis complex and report here X-ray crystal structures of both isomers.

These compounds attracted our attention as possible precursors to the relatively rare +3 oxidation state of platinum. Pt(II) and Pt(IV) complexes are well known to undergo, respectively, oxidative addition and reductive elimination reactions.[2] Chemical or electrochemical oxidations of Pt(II) complexes and reductions of Pt(IV) complexes generally follow the same course. In some cases, oxidation of a Pt(II) complex proceeds by one electron to form a formal Pt(III) species; however, with few exceptions, these have proven to be transient intermediates,[3] dimers or higher oligomers with Pt–Pt bonds[4] or complexes best described as Pt(IV) with an anion radical ligand.[5]

The best-characterized mononuclear Pt(III) species so far reported are the anion Pt(C$_6$Cl$_5$)$_4^-$ related to the isostructural Pt(II) dianion by a reversible one-electron oxidation[6] and several complexes with nitrogen[7] or sulfur[8] macrocyclic ligands. The stability of these species is thought to result from steric inhibition of nucleophilic attack or dimerization.

In addition to *cis*- and *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, we have prepared *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br, *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl, *cis*-Pt(mesityl)(PEt$_3$)$_2$Br, and *trans*-Pt(mesityl)(PEt$_3$)$_2$Cl. The structures of *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl and *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br have been determined and are reported here along with those of the syn and anti isomers of *cis*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$. ^{195}Pt and ^{1}H NMR data are reported for all compounds. Unfortunately, however, only *trans*-Pt(mesityl)(PEt$_3$)$_2$Cl showed any evidence of a reversible one-electron oxidation.

Experimental Section

Preparation of Platinum Compounds. *cis*-Pt(PEt$_3$)$_2$Cl$_2$ and *trans*-Pt(PEt$_3$)$_2$Cl$_2$ were prepared from K$_2$PtCl$_4$ and H$_2$PtCl$_6$·6H$_2$O, respectively, by the method of Jensen.[9,10]

cis-(mesityl)Pt(PEt$_3$)$_2$Br, 40%, mp 182–184 °C (lit.[1] mp 182–185 °C), was prepared, via the Grignard reagent, from bro-

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(10) A 94% yield of the trans isomer, mp 132–137 °C (lit.[9] mp 142–143 °C), was obtained after many days of standing exposed to the atmosphere; no reaction occurred when the mixture was stirred under argon.

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Table I. Crystallographic Data

	1	2	3	4
formula	$PtClP_2C_{19}H_{37}$	$PtBrP_2C_{19}H_{37}$	$PtP_2C_{26}H_{44}$	$PtP_2C_{26}H_{44}$
color	pale yellow	pale yellow	pale yellow	pale yellow
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group (No.)	*Cc* (9)	*Pcmn* (62)	$P2_1/n$ (14)	$P2_1/c$ (14)
a/Å	14.412(3)	11.245(4)	10.403(4)	10.189(4)
b/Å	11.615(3)	12.862(5)	15.127(6)	15.425(6)
c/Å	14.818(3)	16.750(4)	18.372(6)	18.297(6)
β/deg	106.14(2)	90	106.47(3)	104.35(3)
V/Å^3	3282.8(8)	2422.5(1.3)	2773(2)	2786(2)
Z	4	4	4	4
ρ_{calc}/g cm^{-3}	1.555(1)	1.652(1)	1.470(1)	1.463(1)
λ/Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
tot. no. of uniq rflns	2173	2239	2577	3608
no. of uniq rflns	2143 ($I > \sigma(I)$)	2075 ($I > \sigma(I)$)	2075 ($I > 3\sigma(I)$)	3264 ($I > \sigma(I)$)
2θ range/deg	5–50	4–50	4–40	4–45
no. of params	115	118	108	262
R	0.030	0.052	0.120	0.043
R_w	0.039	0.056	0.134	0.036
goodness of fit	1.70	1.59	3.39	1.55

momesitylene (Aldrich), and *cis*-Pt(PEt$_3$)$_2$Cl$_2$, by the method of Chatt and Shaw.[1,11] *trans*-(mesityl)Pt(PEt$_3$)$_2$NO$_3$, 85%, mp 142–144 °C (lit.[12] mp 146–147 °C), and *trans*-(mesityl)Pt(PEt$_3$)$_2$Cl, 95%, mp 196–198 °C (lit.[12] mp 196.5–197.5 °C), were prepared from *cis*-Pt(mesityl)(PEt$_3$)$_2$Br by the method of Basolo et al.[12]

cis-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ was prepared by the method of Chatt and Shaw[1] from 2-bromotoluene (Aldrich), 2 M butyllithium in pentane (Aldrich), and *cis*-Pt(PEt$_3$)$_2$Cl$_2$. Recrystallization from petroleum ether gave yellowish crystals, mp 168–171 °C (lit.[1] mp 176–180 °C). ^{195}Pt NMR showed three Pt compounds, one of which, *trans*-Pt(PEt$_3$)$_2$Br$_2$, was removed by further recrystallization. The mixture was separated by column chromatography using Florisil packed in CCl$_4$ and ^{195}Pt NMR analysis of fractions eluted with 1:1 benzene/CCl$_4$. The first eluted fractions proved to be pure *cis-syn*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, mp 170–171 °C dec; later fractions contained pure *cis-anti*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, mp 169–170 °C dec.

We attempted to prepare *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ from *o*-tolylmagnesium bromide and *trans*-Pt(PEt$_3$)$_2$Cl$_2$ by following the general procedure of Chatt and Shaw.[1] The major product proved to be *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br, mp 134.5–135.5 °C, identified by its crystal structure. The isomers of *cis*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ were also formed along with two unidentified products, which showed ^{195}Pt resonances at −4632 (t, J_P = 2741 Hz), and −4540 ppm (dd, J_P = 839, 2150 Hz). A second attempt to prepare *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ was more successful: reaction of 2-bromotoluene, butyllithium, and *trans*-Pt(PEt$_3$)$_2$Cl$_2$, following another general method of Chatt and Shaw, gave four products which could be separated into two groups by fractional crystallization or chromatography. The two major products, identified by ^{1}H and ^{195}Pt NMR, were the syn and anti isomers of *trans*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, but we have not been able to separate them by chromatography despite many tries under various conditions. The two minor products were separated by chromatography on Florisil packed in hexane with fractions analyzed by ^{195}Pt NMR. Elution with hexane gave *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br, identical with the major product from the Grignard reactions. Elution with benzene gave *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl, mp 98–99 °C (lit.[1] mp 104–105 °C).

NMR Spectra. NMR spectra of the complexes dissolved in CDCl$_3$ at ambient temperature were obtained using a Bruker AM400WB spectrometer. ^{1}H spectra were referenced to TMS in CDCl$_3$; ^{195}Pt spectra were referenced to H$_2$PtCl$_6$ in water in a concentric internal tube. A macro program was written to allow examination of the whole ^{195}Pt frequency range, and care was taken that "fold-over" peaks were identified by checking the position of each peak at several different irradiating frequencies.

Table II. Atom Coordinates (×10^4) and Temperature Factors for *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl (1)[a]

atom	x	y	z	10^3U/Å^3
Pt	2500	2243(1)	2500	46(1)*
Cl	2498(8)	0167(2)	2453(6)	79(1)*
P(1)	1191(6)	2196(5)	3116(5)	55(2)*
P(2)	3797(6)	2188(5)	1915(4)	54(3)*
C(1)	889(8)	3613(8)	3517(9)	55(3)
C(2)	43(8)	3600(13)	3927(9)	67(4)
C(3)	137(8)	1640(12)	2209(7)	70(3)
C(4)	−189(24)	2325(20)	1314(13)	135(8)
C(5)	1548(8)	1390(10)	4230(6)	60(3)
C(6)	2437(10)	1786(17)	4966(9)	91(4)
C(7)	3777(9)	1141(10)	975(7)	76(4)
C(8)	2962(11)	1467(17)	133(10)	100(5)
C(9)	4813(9)	1296(11)	2583(8)	80(4)
C(10)	5225(14)	1829(19)	3537(10)	111(6)
C(11)	4362(8)	3529(8)	1665(9)	58(4)
C(12)	5237(8)	3434(14)	1303(9)	66(4)
C(13)	2589(12)	4005(5)	2579(6)	54(2)
C(14)	3113(8)	4483(3)	3436(4)	68(3)
C(15)	3167(8)	5679(6)	3548(5)	79(3)
C(16)	2705(10)	6398(4)	2801(4)	84(4)
C(17)	2188(9)	5921(6)	1941(5)	73(3)
C(18)	2122(8)	4724(6)	1834(6)	66(3)
C(19)	1593(11)	4285(14)	935(9)	95(4)

[a] Equivalent isotropic temperature factors U given in Tables III and V and those with asterisks in Tables II and IV are defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

Electrochemical Experiments. Cyclic voltammograms were obtained using platinum indicator and auxiliary electrodes and a Ag/AgCl/acetone reference electrode connected to the solution through a Luggin capillary filled with electrolyte solution. The cell was controlled with a PAR 173 Potentiostat connected to a PAR 175 universal programmer, a Nicolet NIC-310 digital oscilloscope, and a Bausch and Lomb Omnigraphic 2000 x-y recorder. Solutions were degassed with argon presaturated with solvent. Solvents were dried over calcium hydride and distilled under nitrogen. Electrolytes were recrystallized and dried under vacuum. All solutions were prepared just before use. Unless otherwise noted, the solvent was acetonitrile, the electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, and the working electrode was cleaned with polishing before each use.

X-ray Crystal Structure Determinations. X-ray analyses were carried out using a Nicolet R3m/E single-crystal diffractometer, controlled by Nicolet software enhanced by modifications of Dr. Ward Robinson. ω scans were used for intensity data collection for all but compound **3**. Data reduction, structure determination, and refinement were carried out using the SHELXTL 5.1 program package. Crystallographic data are collected in Table I.

Clear chunky crystals of *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl (**1**) were grown from benzene/petroleum ether. A crystal approximately

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(11) The other major product was *trans*-Pt(PEt$_3$)$_2$Br$_2$, mp 129–130.5 °C (lit.[9] mp 134–135 °C). The identity was confirmed by a crystal structure which agreed with that reported by: Mesmer, G. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1775–1781.

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Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors for *trans*-Pt(*o*-tolyl)$(PEt_3)_2Br$ (2)

atom	*x*	*y*	*z*	$10^3U/Å^3$
Pt	2230(1)	7500	5786(1)	44(1)
Br	231(1)	7500	5057(1)	80(1)
P	2206(2)	5719(2)	5758(1)	52(1)
C(1)	2308(8)	5234(8)	4741(5)	75(4)
C(2)	3427(12)	5520(12)	4307(5)	107(6)
C(3)	799(8)	5143(8)	6092(6)	77(4)
C(4)	431(10)	5439(12)	6928(6)	132(6)
C(5)	3347(9)	5059(6)	6319(6)	77(4)
C(6)	3361(11)	3870(7)	6278(7)	99(5)
C(7)	3904(11)	7500	6290(6)	54(4)
C(8)	4879(11)	7500	5812(8)	69(5)
C(9)	6028(12)	7500	6111(9)	79(5)
C(10)	6214(14)	7500	6902(10)	91(6)
C(11)	5240(14)	7500	7403(10)	82(6)
C(12)	4059(12)	7500	7112(7)	66(5)
C(13)	3053(14)	7500	7694(7)	86(6)

$0.30 \times 0.38 \times 0.81$ mm^3 was cut from a larger block and used for all X-ray measurements. Numerical absorption corrections were applied, on the basis of the indexed and measured faces, for a linear absorption coefficient of 62 cm^{-1}; minimum and maximum transmission factors were 0.18 and 0.29. A Patterson map revealed the positions of the Pt atoms; the other atoms were located piecemeal on difference maps. Final refinement included Pt, Cl, and P atoms as anisotropic, carbon atoms as isotropic, hydrogen atoms in idealized positions as isotropic, and constraints to make the phenyl group regular and all ethyl groups alike; an empirical extinction correction with parameter 0.000 65 was applied to the data. Atomic coordinates and temperature factors are given in Table II, and representative bond lengths and bond angles are given in Table VI.

Large chunky crystals of *trans*-Pt(*o*-tolyl)$(PEt_3)_2Br$ (2) were grown from hexane by diffusion of acetone. A block of approximate dimensions $0.65 \times 0.70 \times 0.60$ mm^3 was cut from one of the crystals. Absorption corrections for indexed and measured faces and a linear absorption coefficient 76 cm^{-1} were applied; minimum and maximum transmission factors were 0.031 and 0.107. A Patterson map revealed the positions of the Pt and Br atoms; the other atoms were located piecemeal on difference maps. Final refinement included non-hydrogen atoms as anisotropic and hydrogen atoms in idealized positions as isotropic. Atomic coordinates and temperature factors are given in Table III, and representative bond lengths and bond angles are given in Table VI.

Crystals of *cis-syn*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (3) were grown from petroleum ether. The fibrous needlelike crystals were of poor quality; intensities fell off rapidly with increasing scattering angle, some twinning was always present, and the peaks were broad. A crystal of approximate dimensions $0.13 \times 0.22 \times 0.67$ mm^3 was selected and used for data collection by Wyckoff ω scans (7–11 points). Empirical absorption corrections were applied, on the basis of intensities measured in the same way for seven reflections over a complete range of 4 ψ angles for each; minimum and maximum transmission factors were 0.51 and 0.26. The structure was solved in part by direct methods and completed by successive difference syntheses. Final refinement included Pt and P atoms as anisotropic, carbon atoms as isotropic, hydrogen atoms in idealized positions as isotropic, and constraints to make both phenyl groups regular hexagons with ideal dimensions. Atomic coordinates and temperature factors are given in Table IV, and representative bond lengths and bond angles are given in Table VI.

Crystals of *cis-anti*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (4) were grown from CH_2Cl_2 by diffusion of petroleum ether and were stored in contact with solvent vapor. An irregular fragment approximately 0.35 $\times$ 0.37 $\times$ 0.54 mm^3 was cut from a large crystal for the X-ray study. Intensities of standard reflections decreased by about 12% over the course of data collection, and the initial pale yellow color became deeper. No absorption corrections could be applied because of the irregular shape of the crystal and the inaccessibility of reflections suitable for measurement at different ψ angles. A Patterson map revealed the positions of the Pt atoms; the other atoms were located piecemeal on difference maps. Final refinement of the structure included non-hydrogen atoms as anisotropic and hydrogen atoms in idealized positions as isotropic. Atomic coordinates and temperature factors are given in Table V, and representative bond lengths and bond angles are given in Table VI.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors for *cis-syn*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (3)

atom	*x*	*y*	*z*	$10^3U/Å^3$
Pt	143(1)	7855(1)	2381(1)	41(1)*
P(2)	1984(10)	7006(7)	3025(5)	52(4)*
P(1)	−351(10)	8518(7)	3409(5)	51(4)*
C(1)	−1696(21)	8341(19)	1692(14)	62(11)
C(2)	−2736(21)	7727(19)	1572(14)	74(13)
C(3)	−3995(21)	7930(19)	1084(14)	133(21)
C(4)	−4213(21)	8746(19)	716(14)	111(18)
C(5)	−3173(21)	9360(19)	837(14)	89(15)
C(6)	−1914(21)	9157(19)	1325(14)	100(16)
C(7)	−845(44)	9741(31)	1416(27)	104(17)
C(8)	387(25)	7341(16)	1368(12)	55(11)
C(9)	−352(25)	6576(16)	1112(12)	72(12)
C(10)	−194(25)	6128(16)	479(12)	89(15)
C(11)	702(25)	6446(16)	102(12)	89(15)
C(12)	1441(25)	7211(16)	358(12)	87(14)
C(13)	1283(25)	7658(16)	991(12)	55(11)
C(14)	1976(40)	8489(29)	1204(24)	87(14)
C(15)	−1806(40)	9270(29)	3155(25)	83(14)
C(16)	−2158(51)	9721(38)	3796(29)	134(21)
C(17)	−801(43)	7835(30)	4088(26)	89(14)
C(18)	−1924(44)	7163(33)	3736(28)	108(17)
C(19)	990(40)	9190(27)	4028(24)	80(14)
C(20)	1440(54)	9955(39)	3595(32)	147(23)
C(21)	1624(39)	5841(26)	2835(24)	78(13)
C(22)	496(40)	5467(29)	3062(25)	90(15)
C(23)	3566(41)	7188(29)	2810(27)	91(15)
C(24)	4151(49)	8120(31)	2987(30)	120(20)
C(25)	2567(41)	7005(29)	4084(24)	84(14)
C(26)	3673(40)	6348(28)	4441(24)	88(14)

Table V. Atom Coordinates ($\times 10^4$) and Temperature Factors for *cis-anti*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (4)

atom	*x*	*y*	*z*	$10^3U/Å^3$
Pt	2218(1)	7307(1)	7485(1)	47(1)
P(1)	3651(2)	6639(1)	8513(1)	58(1)
P(2)	1001(2)	8203(2)	8105(1)	62(1)
C(1)	3100(9)	6609(6)	6775(4)	69(4)
C(2)	4105(13)	6865(10)	6509(7)	117(6)
C(3)	4831(17)	6377(13)	5977(9)	164(11)
C(4)	4158(17)	5650(14)	5860(9)	154(11)
C(5)	3070(16)	5258(10)	6078(8)	160(8)
C(6)	2578(11)	5749(8)	6542(5)	112(5)
C(7)	4772(11)	7687(9)	6709(7)	133(7)
C(8)	1028(7)	7823(5)	6482(4)	58(3)
C(9)	1477(8)	8589(5)	6176(4)	70(4)
C(10)	785(11)	8979(6)	5547(5)	91(5)
C(11)	−455(10)	8610(6)	5163(5)	97(5)
C(12)	−934(10)	7880(5)	5412(4)	87(4)
C(13)	−168(9)	7486(6)	6083(5)	77(4)
C(14)	−718(8)	6659(6)	6298(5)	86(4)
C(15)	4923(8)	5928(5)	8285(4)	80(4)
C(16)	5868(10)	5446(7)	8936(5)	126(6)
C(17)	4667(8)	7315(6)	9263(5)	82(4)
C(18)	5513(10)	7983(7)	8980(6)	119(6)
C(19)	2795(9)	5939(6)	9047(4)	89(4)
C(20)	1990(11)	5214(7)	8583(6)	134(6)
C(21)	1097(8)	9330(5)	7848(5)	84(4)
C(22)	2528(9)	9701(6)	8081(6)	115(5)
C(23)	−811(7)	8032(6)	7824(5)	87(4)
C(24)	−1241(10)	7183(7)	8108(5)	115(5)
C(25)	1365(8)	8259(6)	9138(4)	75(4)
C(26)	512(9)	8867(6)	9483(4)	97(5)

Results and Discussion

Electrochemical Studies. Cyclic voltammograms of *trans*-Pt(*o*-tolyl)$(PEt_3)_2Br$ and *trans*-Pt(*o*-tolyl)$_2(PEt_3)_2$

Table VI. Selected Bond Distances (in Å) and Bond Angles (in deg)

trans-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl (**1**)				*trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br (**2**)			
Pt–Cl	2.412(3)	Cl–Pt–P(1)	89.6(3)	Pt–Br	2.558(2)	Br–Pt–P	88.9(1)
Pt–P(1)	2.313(9)	Cl–Pt–P(2)	87.4(3)	Pt–P	2.291(2)	C–Pt–P	91.1(1)
Pt–P(2)	2.269(9)	C(13)–Pt–P(1)	92.6(5)	Pt–C(7)	2.06(1)	P–Pt–P	177.3(1)
Pt–C(13)	2.052(5)	C(13)–Pt–P(2)	90.3(5)	P–C(1)	1.82(1)	Br–Pt–C(7)	175.7(3)
P–C(av)	1.84(1)	P(1)–Pt–P(2)	177.0(2)	P–C(3)	1.84(1)	Pt–C(7)–C(12)	121.4(9)
		Cl–Pt–C(13)	176.6(5)	P–C(5)	1.80(1)	Pt–C(7)–C(8)	119.7(9)
		Pt–C(13)–C(14)	117.2(5)			C(7)–C(12)–C(13)	124(1)
		Pt–C(13)–C(18)	122.8(6)				
		C(13)–C(18)–C(19)	122.5(9)				

cis-syn-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ (**3**)				*cis-anti*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ (**4**)			
Pt–P(1)	2.32(1)	P(1)–Pt–P(2)	99.5(3)	Pt–P(1)	2.317(2)	P(1)–Pt–P(2)	100.0(1)
Pt–P(2)	2.33(1)	C(1)–Pt–P(1)	88.0(8)	Pt–P(2)	2.330(2)	C(1)–Pt–P(1)	89.7(2)
Pt–C(1)	2.10(2)	C(8)–Pt–P(2)	87.6(7)	Pt–C(1)	2.058(10)	C(8)–Pt–P(2)	86.5(2)
Pt–C(8)	2.10(2)	C(1)–Pt–C(8)	85.1(10)	Pt–C(8)	2.091(6)	C(1)–Pt–C(8)	83.9(3)
P(1)–C(15)	1.84(4)	C(1)–Pt–P(2)	166.8(8)	P(1)–C(15)	1.823(9)	C(1)–Pt–P(2)	170.4(2)
P(1)–C(17)	1.78(5)	C(8)–Pt–P(1)	173.0(7)	P(1)–C(17)	1.827(8)	C(8)–Pt–P(1)	173.5(2)
P(1)–C(19)	1.84(4)	Pt–C(1)–C(2)	113.3(8)	P(1)–C(19)	1.818(10)	Pt–C(1)–C(2)	125.8(9)
P(2)–C(21)	1.82(4)	Pt–C(1)–C(6)	126.5(8)	P(2)–C(21)	1.810(8)	Pt–C(1)–C(6)	118.5(7)
P(2)–C(23)	1.82(5)	C(1)–C(6)–C(7)	119(2)	P(2)–C(23)	1.809(8)	C(1)–C(2)–C(7)	123(1)
P(2)–C(25)	1.87(4)	Pt–C(8)–C(9)	114.4(7)	P(2)–C(25)	1.836(7)	Pt–C(8)–C(13)	125.0(6)
		Pt–C(8)–C(13)	125.4(7)			Pt–C(8)–C(9)	119.1(5)
		C(8)–C(13)–C(14)	121(2)			C(8)–C(13)–C(14)	122.2(7)

Table VII. ^{195}Pt NMR Data

compd	δ/ppm	^1J_P/Hz
cis-Pt(PEt$_3$)$_2$Cl$_2$	–4483 (lit.[a] –4490)	3528 (lit.[a] 3502)
trans-Pt(PEt$_3$)$_2$Br$_2$	–4479	2334
trans-Pt(PEt$_3$)$_2$Cl$_2$	–3925 (lit.[a] –3938)	2402 (lit.[a] 2394)
trans-Pt(mesityl)(PEt$_3$)$_2$NO$_3$	–4094	2945
cis-Pt(mesityl)(PEt$_3$)$_2$Br	–4516	1619, 4285
trans-Pt(mesityl)(PEt$_3$)$_2$Cl	–4303	2818
trans-Pt(*o*-tolyl)(PEt$_3$)$_2$Cl (**1**)	–4295	2806
trans-Pt(*o*-tolyl)(PEt$_3$)$_2$Br (**2**)	–4417	2781
cis-syn-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ (**3**)	–4489	1757
cis-anti-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ (**4**)	–4484	1748
trans-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$[b]	–4400, –4389	2837, 2850

[a] Reference 15. [b] Mixture of syn and anti isomers.

(mixture of isomers) showed chemically irreversible oxidation peaks at 0.88 and 0.68 V, respectively (vs ferrocene, 200 mV s^{-1}, room temperature). *cis*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$ (either the syn isomer or the mixture of syn and anti isomers) showed an irreversible oxidation at +0.81 V (200 mV s^{-1}, room temperature). Lowering the temperature to –27 °C, increasing the scan rate, or changing the solvent to dichloromethane resulted in no qualitative change. Cyclic voltammograms of *cis*-Pt(mesityl)(PEt$_3$)$_2$Br show a large absorption peak at 0.85 V (room temperature, 200 mV s^{-1}) followed by several poorly defined oxidation peaks with no hint of reversibility at lower temperatures or faster scan rates.

Cyclic voltammograms of *trans*-Pt(mesityl)(PEt$_3$)$_2$Cl show an oxidation peak at 0.83 V (room temperature, 200 mV s^{-1}) and a hint of a reduction peak on the reverse cathodic scan. Increasing the scan rate to 1 V s^{-1} or decreasing the temperature to –22 °C causes the oxidation to become more nearly chemically reversible, $i_{pc}/i_{pa} \approx 0.5$. Thus in this case, there is evidence for a short-lived Pt(III) intermediate in the oxidation of the Pt(II) complex.

NMR Studies. NMR data for the *o*-tolyl and mesityl complexes, as well as *cis*- and *trans*-Pt(PEt$_3$)$_2$Cl$_2$ and *trans*-Pt(PEt$_3$)$_2$Br$_2$, are given in Tables VII and VIII.

For *cis*-phosphines, $^2J_{PP}$ is small, "virtual coupling" is negligible, and the PEt$_3$ ^{1}H CH$_3$ and CH$_2$ resonances are expected to be doublets of triplets and quartets, usually appearing as 1:2:2:2:1 and 1:4:6:4:1 quintets, respectively, since $^3J_{HH} \approx {}^2J_{PH} \approx {}^3J_{PH}/2 \approx 7.5$ Hz.[13] A value of $^3J_{PH}$ on the order of 15 Hz implies rapid CH$_3$ rotation; in rigid systems trans and gauche protons show significantly different phosphorus couplings.[14] The spectra of *cis*-Pt(PEt$_3$)$_2$Cl$_2$ and *cis*-Pt(mesityl)(PEt$_3$)$_2$Br fulfill this expectation. For *trans*-phosphines with large $^2J_{PP}$, "virtual coupling" produces an approximate 1:2:1 triplet with spacing equal to $^1/_2|^2J_{PH} + {}^4J_{PH}|$. Since $^3J_{HH} \approx |^2J_{PH} + {}^4J_{PH}|$, the CH$_3$ and CH$_2$ resonances usually appear as 1:4:6:4:1 and 1:2:4:6:6:6:4:2:1 patterns, respectively,[13] entirely consistent with the spectrum of *trans*-Pt(PEt$_3$)$_2$Br$_2$.

The CH$_3$ resonances in spectra of the other mesitylene and *o*-tolyl derivatives reproduce the expected patterns, but the CH$_2$ resonance is considerably more complicated. In the spectrum of *trans*-Pt(*o*-tolyl)(PEt$_3$)$_2$Br, for example, the CH$_2$ resonance contains at least 21 nearly equally spaced features. Irradiation of the CH$_3$ multiplet collapsed the CH$_2$ resonance to a quartet; each feature was an approximate 1:2:1 triplet, consistent with an AB pattern ($^2J_{HH} = 10.9$ Hz, $\delta = 0.056$ ppm), split by ^{31}P coupling with $^2J_{PH} + {}^4J_{PH} = 7.3$ Hz. In the spectrum of *cis-syn*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$, the CH$_2$ resonance consists of two sets of seven approximately equally spaced features which can be interpreted in terms of an AB pattern ($^2J_{HH} = 14.8$ Hz, $\delta = 0.074$ ppm), split by ^{31}P and CH$_3$ protons with $^3J_{HH} \approx {}^2J_{PH} = 7.5$ Hz. Although it is tempting to invoke restricted rotation to explain this effect, it may be a simple reflection of the stereochemical nonequivalence of the CH$_2$ protons. Somewhat similar effects have been observed in the spectra of *cis-trans-cis*-Pt(C$_6$F$_5$)$_2$(PEt$_3$)$_2$Cl$_2$.[15]

The aromatic proton resonances in spectra of the *o*-tolyl compounds appear as a straightforward ABCX pattern (the H-6 resonance is well separated from the other three). Assignments were confirmed by double resonance experiments on *cis-syn*-Pt(*o*-tolyl)$_2$(PEt$_3$)$_2$. The chemical shifts in Table VIII have been corrected for small second-order effects. The H-6 resonance in spectra of the *o*-tolyl

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Table VIII. ^1H NMR Data

compd	δ/ppm and J/Hz: $P(CH_2CH_3)_3$	δ/ppm and J/Hz: aryl protons[a]
cis-$Pt(PEt_3)_2Cl_2$	1.184 (CH_3), 2.06 (CH_2), $^3J_H = 7.6$, $^3J_P = 17.3$, $^2J_P + {}^4J_P = 9.8$, $^3J_{Pt} = 26$	
trans-$Pt(PEt_3)_2Br_2$	1.153 (CH_3), 2.030 (CH_2), $^3J_H = 7.6$, $^3J_P = 16.5$, $^2J_P + {}^4J_P = 7.2$, $^3J_{Pt} \approx 18$	
cis-Pt(mesityl)$(PEt_3)_2Br$	1.030 (CH_3), 1.64 (CH_2), $^3J_H = 7.6$, $^3J_P = 16.4$, $^2J_P + {}^4J_P = 9.4$, 1.169 (CH_3), 2.06 (CH_2), $^3J_H = 7.5$, $^3J_P = 15.6$, $^2J_P + {}^4J_P = 7.6$	2.181 (4-CH_3), 2.456 (2,6-CH_3), $^4J_{Pt} = 10.3$, 6.625 ($H_{3,5}$)
trans-Pt(mesityl)$(PEt_3)_2NO_3$	1.042 (CH_3), 1.53 (CH_2), $^3J_H = 7.6$, $^3J_P = 16.0$	2.167 (4-CH_3), 2.585 (2,6-CH_3), 6.566 ($H_{3,5}$)
trans-Pt(mesityl)$(PEt_3)_2Cl$	1.049 (CH_3), 1.62 (CH_2), $^3J_H = 7.6$, $^3J_P = 15.9$	2.159 (4-CH_3), 2.488 (2,6-CH_3), 6.575 ($H_{3,5}$), $^4J_{Pt} = 13.4$
trans-Pt(*o*-tolyl)$(PEt_3)_2Cl$ (**1**)	1.071 (CH_3), 1.61 (CH_2), $^3J_H = 7.6$, $^3J_P = 16.2$	2.447 (CH_3), $^4J_{Pt} = 6$, 6.878 (H_3), $J_{34} = 7.6$, $^4J_{Pt} = 16.5$, 6.727 (H_4), 6.792 (H_5), $J_{45} = 7.0$, 7.359 (H_6), $J_{56} = 7.4$, $^3J_{Pt} = 68.8$
trans-Pt(*o*-tolyl)$(PEt_3)_2Br$ (**2**)	1.060 (CH_3), 1.66 (CH_2), $^3J_H = 7.7$, $^3J_P = 16.2$	2.428 (CH_3), $^4J_{Pt} = 6$, 6.884 (H_3), $J_{34} = 7.9$, $^4J_{Pt} = 18$, 6.744 (H_4), 6.804 (H_5), $J_{45} = 7.0$, 7.349 (H_6), $J_{56} = 7.5$, $^3J_{Pt} = 70.9$
cis-syn-Pt(*o*-tolyl)$_2(PEt_3)_2$ (**3**)	1.066 (CH_3), 1.47 (CH_2), $^3J_H = 7.5$, $^3J_P = 15.0$	2.430 (CH_3), $^4J_{Pt} = 5.4$, 6.76 (H_3), $J_{34} = 7.4$, $^4J_{Pt} = 16$, 6.65 (H_4), 6.75 (H_5), $J_{45} = 6.9$, 7.38 (H_6), $J_{56} = 7.4$, $^4J_P = 4.9$, $^3J_{Pt} = 55.6$
cis-anti-Pt(*o*-tolyl)$_2(PEt_3)_2$ (**4**)	1.073 (CH_3), 1.48 (CH_2), $^3J_H = 7.5$, $^3J_P = 14.9$	2.572 (CH_3), $^4J_{Pt} = 5.4$, 6.76 (H_3), $J_{34} = 7.4$, $^4J_{Pt} = 15$, 6.64 (H_4), 6.71 (H_5), $J_{45} = 7.0$, 7.38 (H_6), $J_{56} = 7.6$, $^4J_P = 4.9$, $^3J_{Pt} = 58.2$
trans-Pt(*o*-tolyl)$_2(PEt_3)_2$[b]	0.987, 0.982 (CH_3), 1.27, 1.26 (CH_2), $^3J_H = 7.6$, $^3J_P = 15.2$	2.534, 2.523 (CH_3), $^4J_{Pt} \approx 5$, ~6.83 (H_4), ~6.93 ($H_{3,5}$), 7.40, 7.49 (H_6), $J_{56} = 6.8, 7.2$, $^3J_{Pt} = 32, 33$

[a] Ring carbon 1 attached to platinum. [b] Mixture of syn and anti isomers; first values given correspond to dominant isomer.

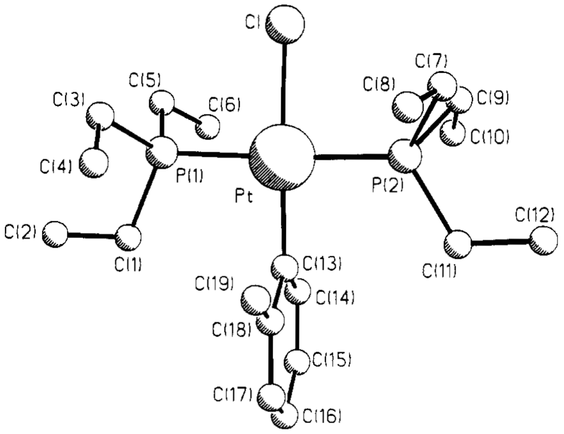

Figure 1. X-ray molecular structure of *trans*-Pt(*o*-tolyl)$(PEt_3)_2Cl$ (**1**). Hydrogen atoms are omitted for clarity.

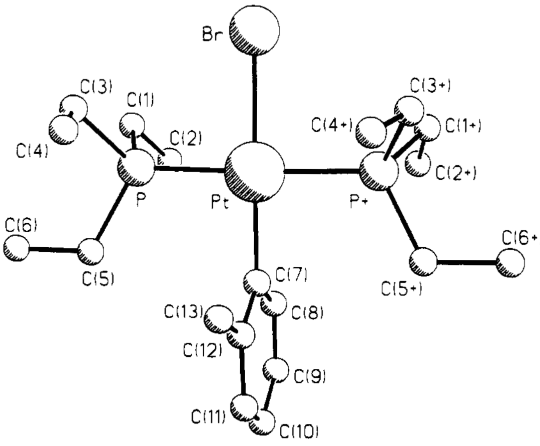

Figure 2. X-ray molecular structure of *trans*-Pt(*o*-tolyl)$(PEt_3)_2Br$ (**2**). Hydrogen atoms are omitted for clarity.

compounds shows ^{195}Pt satellites; the coupling constants, $^3J_{PtH}$, show a significant trans-effect but range around the value (59.2 Hz) found for H-2,6 in $[cis\text{-}PtPh(CO)Cl_2]^-$.[16]

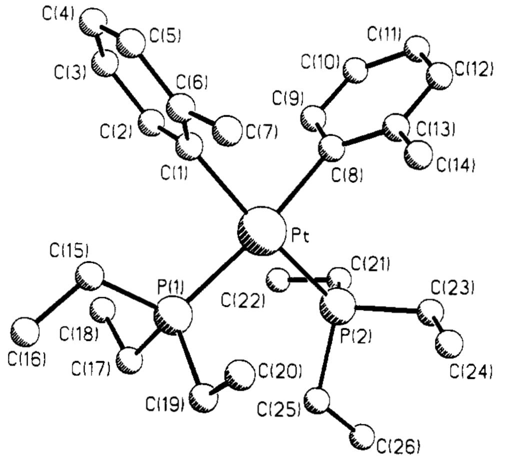

Figure 3. X-ray molecular structure of *cis-syn*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (**3**). Hydrogen atoms are omitted for clarity.

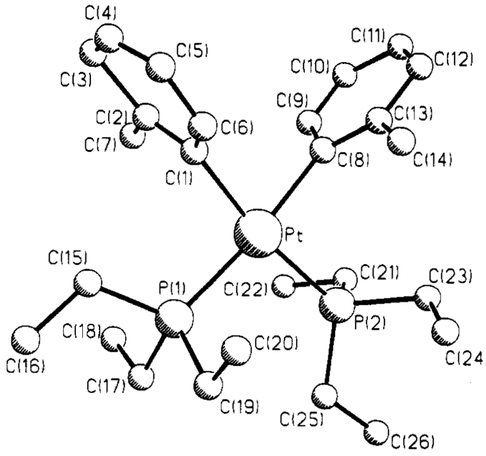

Figure 4. X-ray molecular structure of *cis-anti*-Pt(*o*-tolyl)$_2(PEt_3)_2$ (**4**). Hydrogen atoms are omitted for clarity.

More surprisingly, ^{195}Pt satellites were found on the H-3 resonances for the *o*-tolyl compounds and the H-3,5 resonances for the mesityl derivatives, $^4J_{PtH} = 13\text{–}18$ Hz,[17] as well as the ring *ortho*-methyl resonances, $^4J_{PtH} \approx 6\text{–}10$ Hz.[18]

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Table IX. Distances (Å) from Mean Pt Coordination Plane

	Pt	L1		L2		L3		L4		av
1	0.027	P(1)	0.009	Cl	−0.021	P(2)	0.010	C(13)	−0.025	0.018
2	0.058	P(1)	0.000	Br	−0.026	P(2)	0.000	C(7)	−0.032	0.029
3	0.079	P(1)	0.076	C(1)	−0.140	C(8)	0.101	P(2)	−0.116	0.102
4	0.001	P(1)	0.004	C(1)	−0.005	C(8)	0.005	P(2)	−0.004	0.004
5	−0.032[a]	P(2)	−0.028	C(11)	0.054	C(21)	−0.036	P(4)	0.042	0.038
6	0.001	P(1)	−0.059	C(1)	0.078	C(8)	−0.079	P(2)	0.058	0.055
7	0.002	P(1)	−0.014	C(10)	0.016	C(1)	−0.017	P(2)	0.012	0.012
8	0.020	P(1)	0.027	C(12)	−0.045	C(1)	0.034	P(2)	−0.036	0.032

[a] Pt(2).

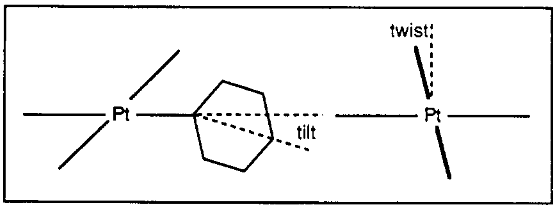

Figure 5. Definition of ring tilt and twist angles.

Table X. Ring Tilt and Twist Angles (deg) and Pt–Methyl Distances (Å)

compd	ring tilt	ring twist	Pt–Me
1	4.1	3.5	3.32
2	5.1	0.7	3.33
3	12.4, 5.6	4.1, 8.7	3.36, 3.40
4	2.5, 3.6	3.0, 0.5	3.31, 3.38
5	1.0, 5.9	1.3, 21.7	3.40, 3.52
6	4.4, 4.1	6.3, 3.6	
7	1.6, 3.0	6.3, 1.8	
8	1.1, 4.0	0.4, 3.5	

Hill et al.[19] have found that $^{1}J_{\rm PtP}$ is larger in *cis*-Pt$(PR_3)_2X_2$ (X = Cl^-, Br^-, I^-) than in the corresponding trans isomers but noted ambiguities when X = NO_2^- or R_2S. When X = *o*-tolyl, the relation is reversed with $J_{\rm trans} > J_{\rm cis}$. Otherwise, comparison of ^{195}Pt chemical shifts and ^{31}P coupling constants for cis and trans isomers or for related chloro and bromo compounds shows trends as expected from previous work.[20,21] Clark and Nicholas[22] have noted that the ^{195}Pt resonance shifts downfield when the size of phosphines is increased; they suggest that this is a deshielding effect associated with a lengthening of Pt–P bonds. This result apparently cannot be generalized: *trans*-Pt(mesityl)$(PEt_3)_2$Cl should be more crowded than *trans*-Pt(*o*-tolyl)$(PEt_3)_2$Cl, and *syn-cis*-Pt$(o\text{-tolyl})_2(PEt_3)_2$, more crowded than the anti isomer; in these pairs, the more crowded molecule has the ^{195}Pt resonance at higher field. As we will see below, however, the steric demands of an *o*-tolyl group result in a variety of distortions, so that the qualitative concept of steric crowding is of little predictive value in these cases.

Structural Studies. The molecular structures of *trans*-Pt(*o*-tolyl)$(PEt_3)_2$Cl, **1**, *trans*-Pt(*o*-tolyl)$(PEt_3)_2$Br, **2**, *cis-syn*-Pt$(o\text{-tolyl})_2(PEt_3)_2$, **3**, and *cis-anti*-Pt$(o\text{-tolyl})_2(PEt_3)_2$, **4**, are shown in Figures 1–4. In discussing these structures, it is instructive to compare them with the related compounds, *syn*-$(o\text{-tolyl})_2$Pt(μ-dppm)$_2$PtMe$_2$, **5**,[23] *cis-anti*-Pt(2-methoxyphenyl)$_2(PPh_3)_2$, **6**,[24] *cis-anti*-Pt(2-nitrophenyl)$_2(PPh_3)_2$, **7**,[25] and *cis-anti*-Pt(7-methyl-1-naphthyl)$_2(PPh_3)_2$, **8**.[26] In all eight cases, the platinum coordination geometry is approximately square planar, but there are small in-plane distortions to open the C–Pt–P bond angles in **1** and **2** and the P–Pt–P bond angle in **3**–**8**. Distortions from planarity (Table IX) are generally small except in **3** and **5** (the two cis-syn structures) and in **6**. The cis-anti structures (**4**, **6**–**8**) have Pt nearly in the mean plane as expected, but in **1**–**3**, the Pt atom is out of the plane *toward* the *o*-tolyl methyl groups; in **5**, the Pt atom is out of plane in the opposite direction.

The benzene rings are tilted away from the Pt coordination plane by up to 12° (see Figure 5 and Table X); in **1**–**5**, **7**, and **8**, the tilt is such as to move the ortho substituent away from Pt, but the methoxy groups of **6** move toward Pt. The *ortho*-methyl groups in **1**–**5** and the nitro groups in **7** are bent away from Pt, but the methoxyl groups in **6** are bent toward Pt. The benzene rings are all nearly perpendicular to the Pt coordination plane, but significant twists are seen for **3** and **5**. The Pt–Me distance is nearly constant in **1**–**5** at 3.38 ± 0.06 Å; as Hutton et al.[5] have pointed out, this distance is comparable to the sum of the van der Waals radii of Pt and Me. Since the Pt–Me distance dependence on ring tilt is about 0.06 Å deg^{-1} and ring tilts ranging from 1 to 12° are found, the constancy of the Pt–Me distance is quite remarkable. Apparently distortion of the coordination plane, ring tilt, ring twist, and bending of the methyl groups combine in various ways to keep the Pt–Me distance nearly constant.

Acknowledgment. We thank J. Van Epp for technical assistance with the NMR spectra and R. J. Goodfellow and R. G. Lawler for helpful discussions.

Supplementary Material Available: Crystallographic data including complete tables of bond distances and angles, positions of hydrogen atoms, thermal parameters, and torsion angles for *trans*-Pt(*o*-tolyl)$(PEt_3)_2$Cl, *trans*-Pt(*o*-tolyl)$(PEt_3)_2$Br, *cis-syn*-Pt$(o\text{-tolyl})_2(PEt_3)_2$, and *cis-syn*-Pt$(o\text{-tolyl})_2(PEt_3)_2$ (14 pages). Ordering information is given on any current masthead page.

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[17] ^{195}Pt satellites may be present on the H-5 resonance in spectra of the *o*-tolyl derivatives but, if so, are obscured by neighboring lines.

[18] The ^{195}Pt satellites appear as shoulders in spectra of the *trans*-mesityl derivatives but are resolved for the other compounds.

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