Articles

Synthesis and Reactions of Mesitylplatinum Complexes. Molecular Structure of Bromo(mesityl)(1,5-cyclooctadiene)platinum(II)

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The reaction of [$PtCl_2$(cod)] with mesitylmagnesium bromide yields [PtBr(Mes)(cod)]. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 27.151 (5) Å, b = 7.987 (2) Å, c = 15.308 (2) Å, β = 96.24 (2)°, V = 3300.2 (11) Å^3, and Z = 8. Least-squares refinement converged at R = 0.0776 and R_w = 0.0641 on the basis of 4049 reflections with $F > 4.0\sigma(F)$. The cyclooctadiene may be displaced by PPh_3 or PEt_3 to give the *cis*-bis(phosphine) complexes, which isomerize slowly to their trans forms. Carbonylation of *trans*-[PtBr(Mes)(PEt_3)$_2$] leads to the corresponding aroyl complex, but the PPh_3 complex shows no tendency to undergo carbonyl insertion. Methylation of [PtBr(Mes)(cod)] yields the mixed organoplatinum complex [PtMe(Mes)(cod)]. Treatment with HCl results in cleavage of the platinum–mesityl bond exclusively. Reaction of [PtClBz(cod)] with MeMgBr produces [PtMeBz(cod)]. Displacement of the diene from these mixed organoplatinum species by PPh_3 or PEt_3 generates the corresponding *cis*-bis(phosphine) compound.

Introduction

Platinum complexes containing weakly bound ligands, such as olefins, thioethers, or nitriles, are used extensively as precursors to other compounds of interest. Diene complexes, particularly those of 1,5-cyclooctadiene, are usually the species of choice when an organoplatinum fragment is desired. Complexes of the types [PtR_2(cod)] and [PtClR(cod)] (cod = 1,5-cyclooctadiene) have been available for about 20 years,[1] and these represent conveniently prepared, stable starting materials. Their reactions with neutral ligands generally proceed by displacement of the cyclooctadiene to yield species of the type [PtR_2L_2] or [$PtClRL_2$].[2]

We have used complexes of the type [PtClR(cod)] as precursors to the dimeric platinum complexes [$Pt_2R_2(\mu$-$C_5H_4PPh_2)_2$] [R = Me, Et, Np (CH_2CMe_3), Bz (CH_2Ph), Ph].[3] In the course of this work we chose to investigate the use of the extremely bulky mesityl (Mes; 2,4,6-trimethylphenyl) group. In this paper we describe the preparation and molecular structure of [PtBr(Mes)(cod)], the first example of a mesitylplatinum complex to be characterized crystallographically. We also describe the preparation and reactions of the mixed organoplatinum species [PtMeR(cod)] (R = Mes, Bz).

Results and Discussion

Treatment of [$PtCl_2$(cod)] with excess (1.5–2.5 equiv) of mesitylmagnesium bromide results, after workup, in the isolation of a white solid, whose ^{1}H and ^{13}C NMR data (Table I) indicate a structure of the type [PtX(Mes)(cod)]; two sets of olefinic and methylene resonances are observed in each case. It has been identified as the bromide complex on the basis of elemental analysis and an X-ray structure determination. The bromide is formed presumably by halide exchange between the initial product [PtCl(Mes)(cod)] and the Grignard reagent or the magnesium halide salt formed. The failure to generate the dimesityl complex contrasts with other reactions of [$PtCl_2$(cod)] with Grignard or organolithium reagents. The reaction of [$PtCl_2$(cod)] with excess $MesSnMe_3$ has also been reported to give only [PtCl(Mes)(cod)], even after prolonged reaction times at 100 °C.[4] The dimesityl complexes *cis*-[$Pt(Mes)_2(PPh_3)_2$] and [$Pt(Mes)_2$(dppm)] have been prepared, however. This suggests that it is not steric crowding that prevents substitution of the second halide in the cyclooctadiene complexes (although cyclooctadiene is less sterically demanding than PPh_3 or dppm), but rather the inability of the trans ligand to promote that substitution.[5]

Table I. ^{1}H and ^{13}C{^{1}H} NMR Parameters for [PtBr(Mes)(cod)][a]

	^{1}H NMR	^{13}C NMR
CH=	4.44 (75)	87.3 (205)
	5.78 (27)	114.8 (28)
CH_2	2.3 m	28.2 (22)
	2.6 m	32.0 (25)
o-CH_3	2.50	25.1 (50)
p-CH_3	2.21	20.5
m-CH	6.70	128.6 (37)
quaternary carbons		134.0, 138.9, 139.7

[a] Recorded in $CDCl_3$ solution. Couplings to ^{195}Pt in hertz are given in parentheses.

The molecular structure of [PtBr(Mes)(cod)] has been determined and is shown in Figure 1. Selected bond

(1) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973,** *59,* 411.
(2) For examples, see: Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981,** *20,* 1636 and 3607.
(3) Lin, M.; Fallis, K. A.; Anderson, G. K.; Rath, N. P.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992,** *114,* 4687.
(4) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1978,** 357.
(5) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985,** 1501.

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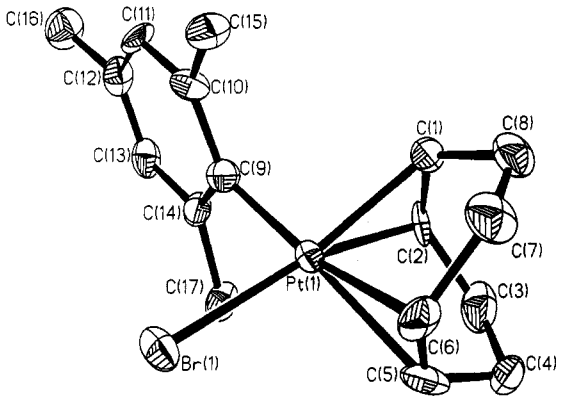


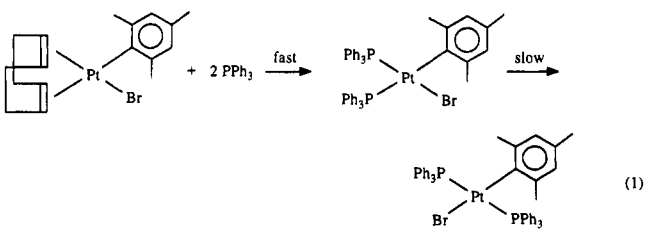
Figure 1. Projection view of the molecular structure of one molecule of [PtBr(Mes)(cod)], showing the atom labeling scheme.

Table II. Selected Bond Distances (Å) and Angles (deg) for [PtBr(Mes)(cod)]

Bond Lengths			
Pt(1)–Br(1)	2.429(3)	Pt(1)–C(1)	2.13(2)
Pt(1)–C(2)	2.13(2)	Pt(1)–C(5)	2.28(2)
Pt(1)–C(6)	2.31(2)	Pt(1)–C(9)	1.99(2)
C(1)–C(2)	1.42(3)	C(1)–C(8)	1.55(3)
C(2)–C(3)	1.46(3)	C(3)–C(4)	1.55(4)
C(4)–C(5)	1.52(4)	C(5)–C(6)	1.34(3)
C(6)–C(7)	1.53(3)	C(7)–C(8)	1.49(3)
Bond Angles			
Br(1)–Pt(1)–C(1)	162.6(6)	Br(1)–Pt(1)–C(2)	158.6(6)
Br(1)–Pt(1)–C(5)	94.6(6)	Br(1)–Pt(1)–C(6)	91.7(5)
Br(1)–Pt(1)–C(9)	89.4(5)	C(1)–Pt(1)–C(9)	91.8(7)
C(2)–Pt(1)–C(9)	90.0(8)	C(5)–Pt(1)–C(9)	163.9(8)
C(6)–Pt(1)–C(9)	161.8(8)	C(2)–C(1)–C(8)	122.5(18)
C(1)–C(2)–C(3)	129.0(19)	C(4)–C(5)–C(6)	125.7(22)
C(5)–C(6)–C(7)	126.6(21)		

distances and angles are presented in Table II. There are two independent molecules per unit cell. The structure reveals nearly square planar geometry about platinum, the two olefinic groups and the bulky mesityl moiety being approximately perpendicular to the molecular plane. The Pt–C distances trans to the mesityl group are longer than those trans to bromide, as expected on the basis of the relative trans influences of aryl and bromide ligands.[6]

Reaction of [PtBr(Mes)(cod)] with 2 equiv of PPh_3 produces a complex of the form $[PtBr(Mes)(PPh_3)_2]$, which is identified as the cis isomer on the basis of its ^{31}P NMR spectrum (Table III). It exhibits two doublets, one with a large coupling to platinum, assigned to the phosphorus atom lying trans to bromide, and one with a much smaller coupling. This complex is quite stable and may be isolated in pure form, but it is the kinetic product of the reaction. When a $CDCl_3$ solution of *cis*-$[PtBr(Mes)(PPh_3)_2]$ is allowed to stand at ambient temperature for 5 days, complete conversion to the trans isomer occurs (eq 1).

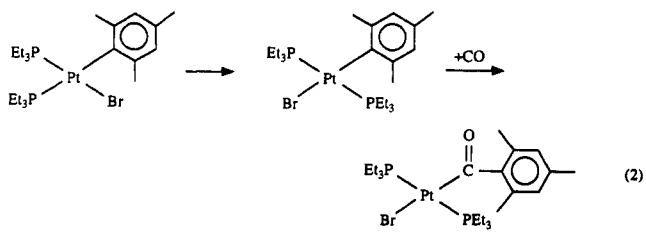


(1)

The rate of isomerization may be increased by heating the solution, but some decomposition takes place also. The trans isomer is characterized by a single resonance in its $^{31}P\{^1H\}$ NMR spectrum (Table III). The analogous reaction with PEt_3 leads to the isolation of *cis*-$[PtBr(Mes)(PEt_3)_2]$. This complex isomerizes more slowly than its triphenylphosphine counterpart, conversion being incomplete after 14 days at ambient temperature.

Neither *cis*- nor *trans*-$[PtBr(Mes)(PPh_3)_2]$ shows much tendency to undergo carbonylation. Treatment with 1 atm of carbon monoxide at temperatures of 25–100 °C does not lead to the aroyl product. In contrast, *trans*-$[PtBrPh(PPh_3)_2]$ reacts readily with CO at 25 °C.[7] Reaction of *cis*-$[PtBr(Mes)(PEt_3)_2]$ with 1 atm of CO at ambient temperature, however, produces the aroyl species *trans*-$[PtBr(COMes)(PEt_3)_2]$ (Tables III and IV). This complex exhibits a strong infrared absorption at 1585 cm^{-1} due to the inserted carbonyl group, and the expected shift to higher frequency of the mesityl group resonances in its ^1H NMR spectrum compared with those for *trans*-$[PtBr(Mes)(PEt_3)_2]$. When the reaction is performed using ^{13}CO, the ^{31}P resonance is split into a doublet, with a $^2J_{PC}$ coupling of 5 Hz.

The reaction of *trans*-$[PtBr(Mes)(PEt_3)_2]$ with CO also produces *trans*-$[PtBr(COMes)(PEt_3)_2]$, but the reaction is faster. When the reaction of the cis isomer with CO is monitored with time, a small amount of *trans*-$[PtBr(Mes)(PEt_3)_2]$ is observed, but there is no evidence for the formation of *cis*-$[PtBr(COMes)(PEt_3)_2]$. This suggests that the reaction proceeds by isomerization, followed by carbonylation of the trans isomer (eq 2). Carbonylation of *cis*-$[PtBr(Mes)(PEt_3)_2]$ is about 50% complete after 24 h, suggesting that the presence of CO also serves to enhance the rate of isomerization.



(2)

The fact that the PEt_3 complexes undergo carbonyl insertion, whereas their PPh_3 analogues do not, is somewhat surprising. The rate of carbonylation of complexes of the type *trans*-$[PtXR(PR_nPh_{3-n})_2]$ generally decreases

Table III. $^{31}P\{^1H\}$ NMR Data for the Bis(phosphine) Complexes[a]

complex	δ_P	$^1J_{PtP}$	$^2J_{PP}$
cis-$[PtBr(Mes)(PPh_3)_2]$	16.5 d	4530	15
	18.9 d	1575	
trans-$[PtBr(Mes)(PPh_3)_2]$	21.5 s	3138	
cis-$[PtBr(Mes)(PEt_3)_2]$	1.3 d	4258	16
	8.8 d	1610	
trans-$[PtBr(Mes)(PEt_3)_2]$	9.9 s	2783	
trans-$[PtBr(COMes)(PEt_3)_2]$	10.8 s	3191	
cis-$[PtMe(Mes)(PPh_3)_2]$	24.9 d	1742	11
	25.0 d	1978	
cis-$[PtMe(Mes)(PEt_3)_2]$	6.0 d	1924	13
	9.9 d	1748	
cis-$[PtMeBz(PPh_3)_2]$	25.4 d	1833	9
	28.4 d	1964	
cis-$[PtMeBz(PEt_3)_2]$	9.1 d	1912	11
	9.5 d	1857	

[a] Recorded in $CDCl_3$ solution. Coupling constants are in hertz.

(6) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(7) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

Table IV. ^{1}H NMR Data for the Bis(phosphine) Complexes[a]

complex	*o*-CH_3	*p*-CH_3	*m*-CH	other signals
cis-[PtBr(Mes)(PPh_3)$_2$]	2.49	2.01	6.24	7.0–7.7 Ph
trans-[PtBr(Mes)(PPh_3)$_2$]	1.93	1.90	5.88	7.1–7.7 Ph
cis-[PtBr(Mes)(PEt_3)$_2$]	2.45	2.18	6.63	1.64, 2.06 m PCH_2CH$_3$ 1.03, 1.17 m PCH$_2$$CH_3$
trans-[PtBr(Mes)(PEt_3)$_2$]	2.48	2.17	6.58	1.70 m PCH_2CH$_3$ 1.03 m PCH$_2$$CH_3$
trans-[PtBr(COMes)(PEt_3)$_2$]	2.84	2.22	6.79	1.81 m PCH_2CH$_3$ 1.09 m PCH$_2$$CH_3$
cis-[PtMe(Mes)(PPh_3)$_2$]	2.44	2.13	6.40 (18)	0.48 (70) PtCH_3 6.9–7.9 Ph
cis-[PtMeBz(PPh_3)$_2$]				0.52 (67) PtCH_3 2.69 (92) PtCH_2 6.7–7.4 Ph

[a] Recorded in $CDCl_3$ solution. Couplings to ^{195}Pt are in hertz and are given in parentheses.

Table V. ^{1}H and ^{13}C{^{1}H} NMR Data for [PtMe(Mes)(cod)] and [PtMeBz(cod)][a]

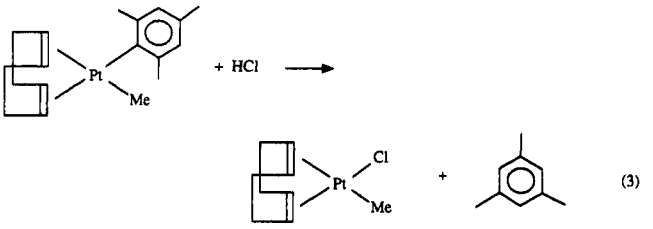
	^{1}H NMR	^{13}C NMR	
[PtMe(Mes)(cod)]	0.70 (82)	0.7 (767)	$PtCH_3$
	2.40	29.7	*o*-CH_3
	2.20	30.2	*p*-CH_3
	6.73 (18)	127.5 (54)	*m*-CH
	4.71 (40)	99.1 (54)	CH=
	5.04 (40)	101.4 (50)	CH=
	2.3–2.45	20.7, 25.9	CH_2
		132.2, 140.4, 154.9	quaternary C
[PtMeBz(cod)]	0.77 (87)		$PtCH_3$
	2.92 (120)		$PtCH_2$
	4.63 (39)		CH=
	4.82 (42)		CH=
	2.1–2.4		CH_2
	6.9–7.2		Ph

[a] Recorded in $CDCl_3$ solution. Couplings to ^{195}Pt are in hertz and are given in parentheses.

as the phenyl substituents on phosphorus are replaced by alkyl groups.[7] In the present instance, involving the very bulky mesityl group, it may be that steric factors are more important than electronic ones, and the platinum center in [PtBr(Mes)(PPh_3)$_2$] is simply too crowded to permit attack by the CO ligand.

Treatment of [PtBr(Mes)(cod)] with methylmagnesium bromide results, as expected, in formation of the mixed organoplatinum species [PtMe(Mes)(cod)], which has been characterized by elemental analysis and ^{1}H and ^{13}C{^{1}H} NMR spectrocopy (Table V). The fact that this species is accessible, whereas the dimesityl is not, indicates that the difficulty lies in introducing the second mesityl group, and not in a lack of reactivity of [PtBr(Mes)(cod)] itself. In fact, [PtMe(Mes)(cod)] may be prepared alternatively by reaction of [PtClMe(cod)] with MesMgBr. The ^{1}H and ^{13}C{^{1}H} NMR spectra of [PtMe(Mes)(cod)] reveal the presence of the expected two sets of olefinic resonances, as well as those associated with the methyl and mesityl groups. The ^{1}H NMR data show a marked solvent dependence. On changing from $CDCl_3$ to C_6D_6 solution, the methyl signal shifts by 0.42 ppm to higher frequency. The mesityl resonances also move to higher frequency, and the olefinic resonances move much closer together (4.53 and 4.66 ppm).

Reaction of [PtMe(Mes)(cod)] with HCl in C_6D_6 solution results in preferential cleavage of the platinum–mesityl bond (eq 3) to generate [PtClMe(cod)] and mesitylene (δ_H 2.15 and 6.71). Treatment with excess HNO_3 in $CDCl_3$ solution also produces [PtClMe(cod)], presumably formed in this case by interaction with the solvent, and $C_6H_3(CH_3)_3$. In contrast, addition of HNO_3 to a C_6D_6 solution of [PtMe(Mes)(cod)] results in partial reaction to give a



(3)

new species, which we assign as [Pt(NO_3)Me(cod)] [δ_H 1.0 (CH_3), 3.6, 5.2 (olefinic CH)], and mesitylene. When such a solution is evaporated and the residue dissolved in $CDCl_3$, examination of the ^{1}H NMR spectrum reveals the presence of both [PtClMe(cod)] and [PtMe(Mes)(cod)], the former again formed by reaction with the chlorinated solvent. In the absence of acid the unreacted [PtMe(Mes)(cod)] remains. These results are consistent with those reported previously for the reaction of [PtMe(*p*-tol)(cod)] with HCl, in which cleavage of the platinum–tolyl bond occurs exclusively.[8] In contrast, reactions of *cis*-[PtMeAr($PMePh_2$)$_2$] (Ar = Ph, *p*-tol)[8] or *cis*-[PtMeAr(PEt_3)$_2$] (Ar = Ph, Mes)[9] proceed by cleavage of the platinum–methyl linkage, indicating that the course of the reaction is strongly dependent on the nature of the supporting ligand(s).

When a $CDCl_3$ solution of [PtMe(Mes)(cod)] is treated with 2 equiv of PPh_3, the bis(phosphine) complex *cis*-[PtMe(Mes)(PPh_3)$_2$] is formed. In this case the two doublets in the ^{31}P NMR spectrum are almost coincident, and each exhibits a relatively small coupling to ^{195}Pt (Table III). The smaller coupling (1742 Hz) is assigned to the phosphine lying trans to the mesityl group, and the larger (1978 Hz) to that lying trans to the methyl group.[10,11] [PtMe(Mes)(cod)] reacts analogously with PEt_3 to yield *cis*-[PtMe(Mes)(PEt_3)$_2$].[9]

We anticipated that the steric bulk in the methyl(mesityl)platinum species might be sufficient to promote methane elimination and metalation of the mesityl group. Such a reaction has been reported for *cis*-[PtMe(8-$MeC_{10}H_6$)(PPh_3)$_2$],[12] whereas isomerization of a mesityliridium complex to the corresponding 3,5-dimethylbenzyliridium species has also been demonstrated in the presence of ethylene at 90 °C.[13] Heating toluene solutions

(8) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332.
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(10) Eaborn, C.; Kundu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933.
(11) Reamey, R. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1984**, *106*, 81.
(12) Duff, J. A.; Shaw, B. L.; Turtle, B. L. *J. Organomet. Chem.* **1974**, *66*, C18.
(13) Cleary, B. P.; Eisenberg, R. *Organometallics* **1992**, *11*, 2335.

of [PtMe(Mes)(cod)] or *cis*-[PtMe(Mes)(PPh_3)$_2$] to 100 °C for 14 days causes no reaction, however.

Methyl(benzyl)platinum compounds may also be prepared by the above methods. Methylation of [PtClBz(cod)], or treatment of [PtClMe(cod)] with benzylmagnesium chloride, leads to the isolation of [PtMeBz(cod)]. Its ^{1}H NMR spectrum reveals the presence of methyl- and benzylplatinum groups, the CH_3 and CH_2 hydrogens each exhibiting a substantial coupling to ^{195}Pt, in addition to two closely-spaced olefinic resonances (Table V). Treatment of [PtMeBz(cod)] with 2 equiv of PPh_3 or PEt_3 leads to a complex of the type *cis*-[PtMeBz(PR_3)$_2$]. Each exhibits two doublets in its ^{31}P{^{1}H} NMR spectrum, but the presence of two alkyl groups in this case results in the two $^1J_{PtP}$ couplings being more nearly equal.

Experimental Section

All reactions were carried out under an atmosphere of argon, and the products were worked up in air, unless otherwise stated. NMR spectra were recorded on a Varian XL-300 spectrometer, operating in the FT mode. ^{1}H and ^{13}C chemical shifts were measured relative to the residual solvent resonance and are reported in δ units (δ(TMS) = 0), and ^{31}P shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA. [PtClBz(cod)] was prepared from [PtBz$_2$(cod)] by treatment with CH_3COCl/CH_3OH in ether.[1] Previously unreported ^{13}C{^{1}H} NMR data follow (couplings to ^{195}Pt in hertz are given in parentheses). [PtBz$_2$(cod)]: δ_C 29.4 CH_2; 33.2 (739) PtCH_2; 100.2 (66) CH; 122.8 (19) *m*; 127.6 (15) *p*; 128.2 (32) *o*; 149.3 *ipso*. [PtClBz(cod)]: δ_C 27.9 CH_2; 29.1 (575) PtCH_2; 31.7 CH_2; 86.1 (232) *C*H trans to Cl; 113.5 (30) *C*H cis to Cl; 124.4 (10) *p*; 128.0 (9) *m*; 129.0 (19) *o*; 145.0 *ipso*.

Preparation of [PtBr(Mes)(cod)]. An ether solution of mesitylmagnesium bromide (3.05 mL, 1.0 M, 3.05 mmol) was added to a stirred suspension of [PtCl$_2$(cod)] (0.760 g, 2.03 mmol) in ether (100 mL) at 0 °C over a period of 5 min. The ice bath was removed, and the contents of the flask were allowed to warm to room temperature. After stirring for an additional 2 h, the reaction mixture was quenched with a saturated solution of NH_4Cl (15 mL). The ethereal layer was separated and dried by stirring over anhydrous $MgSO_4$, and the solvent was evaporated. The resulting solid was washed with hexanes, leaving the product as a white solid (0.919 g, 90%). Anal. Calcd for $C_{17}H_{23}BrPt$: C, 40.65; H, 4.62. Found: C, 40.51; H, 4.84. Colorless needles were obtained from ether solution, from which a crystal suitable for an X-ray diffraction study was chosen.

Preparation of *cis*-[PtBr(Mes)(PPh_3)$_2$]. [PtBr(Mes)(cod)] (0.024 g, 0.048 mmol) and PPh_3 (0.025 g, 0.096 mmol) were placed together in a 25-mL round-bottomed flask, and CH_2Cl_2 (10 mL) was added by syringe. The solution was stirred for 1 h, and then the solvent was evaporated. The residue was washed with pentane, and then ether, and dried *in vacuo* to leave the product as a white solid (0.040 g, 92%). Anal. Calcd for $C_{45}H_{41}BrP_2Pt$: C, 58.83; H, 4.50. Found: C, 58.41; H, 5.07.

Preparation of *cis*-[PtBr(Mes)(PEt_3)$_2$]. This complex was prepared as above from [PtBr(Mes)(cod)] (0.016 g, 0.033 mmol) and PEt_3 (0.010 mL, 0.068 mmol) and isolated as a white solid (0.017 g, 93%). Anal. Calcd for $C_{21}H_{41}BrP_2Pt$: C, 40.00; H, 6.55. Found: C, 40.10; H, 6.52.

Preparation of [PtMe(Mes)(cod)]. An ether solution of methylmagnesium bromide (0.060 mL, 3.0 M, 0.18 mmol) was added dropwise to a stirred suspension of [PtBr(Mes)(cod)] (0.076 g, 0.15 mmol) in ether (100 mL) at 0 °C. When the addition was complete, the reaction mixture was allowed to warm to ambient temperature and stirred for 3 h. After quenching with NH_4Cl solution (5 mL, 1.0 M), the ethereal layer was decanted and dried over anhydrous $MgSO_4$. Following filtration, the solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2, and addition of pentane resulted in precipitation of the product as a white powder (0.058 g, 88%). Anal. Calcd for $C_{18}H_{26}Pt$: C, 49.42; H, 5.99. Found: C, 49.49; H, 6.05.

Table VI. Crystallographic Data for [PtBr(Mes)(cod)]

formula	$C_{17}H_{23}BrPt$
mol wt	502.4
color, habit	colorless, needles
space group	$P2_1/c$
a, Å	27.151(5)
b, Å	7.987(2)
c, Å	15.308(2)
β, deg	96.24(2)
cell vol, Å^3	3300.2(11)
Z	8
D(calcd), Mg/m^3	2.022
temp, K	298
radiation	graphite monochromated, Mo Kα (λ = 0.710 73 Å)
cryst dimens, mm	0.6 × 0.1 × 0.1
abs coeff, mm^{-1}	10.911
2θ range, deg	3.5–60.0
scan speed, deg/min	4.0–14.7
scan range (ω), deg	0.60 plus Kα separation
independent rflns	9572
obs rflns ($F > 4.0\sigma(F)$)	4049
absorption correction	semiempirical
min/max transmission	0.0706/1.0000
no. of refined params	343
R	0.0776
R_w	0.0641
goodness of fit	1.41

Preparation of *cis*-[PtMe(Mes)(PPh_3)$_2$]. [PtMe(Mes)(cod)] (0.038 g, 0.086 mmol) and PPh_3 (0.045 g, 0.17 mmol) were mixed in a round-bottomed flask. CH_2Cl_2 (20 mL) was added by syringe, and the mixture was stirred for 30 min. The solvent was evaporated, and the residue was washed with pentane to leave the product as a white solid (0.068 g, 93%). Anal. Calcd for $C_{46}H_{44}P_2Pt$: C, 64.71; H, 5.19. Found: C, 64.08; H, 5.91. The triethylphosphine analogue of the above was prepared similarly and characterized in solution.

Preparation of [PtMeBz(cod)]. An ether solution of MeMgBr (0.13 mL, 3.0 M, 0.39 mmol) was added to an ether solution of [PtClBz(cod)] (0.109 g, 0.025 mmol) at 0 °C. After allowing to warm to room temperature, the solution was stirred for 2 h. The reaction was quenched with NH_4Cl solution, and the ether layer was separated, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated, leaving the product as a light yellow solid (0.095 g, 92%). Anal. Calcd for $C_{16}H_{22}Pt$: C, 46.94; H, 5.42. Found: C, 46.88; H, 5.47.

Preparation of *cis*-[PtMeBz(PPh_3)$_2$]. [PtMeBz(cod)] (0.039 g, 0.096 mmol) and PPh_3 (0.051 g, 0.19 mmol) were mixed in a round-bottomed flask. CH_2Cl_2 (20 mL) was added by syringe, and the mixture was stirred for 30 min. The solvent was evaporated, and the residue was washed with pentane to leave the product as a white solid (0.075 g, 95%). Anal. Calcd for $C_{44}H_{40}P_2Pt$: C, 63.99; H, 4.88. Found: C, 63.29; H, 4.99. The triethylphosphine analogue of the above was prepared similarly and characterized in solution.

X-ray Structure Determination. A single crystal of [PtBr(Mes)(cod)] was mounted on a glass fiber in random orientation. Preliminary examination was carried out with Mo Kα radiation using a Siemens R3 automated four-circle diffractometer. Final cell parameters and orientation matrices were obtained by least-squares refinement of 25 automatically centered reflections (20° < 2θ < 25°). Axial photographs of the three axes were taken to confirm cell lengths and the lattice symmetry. ω-scans of representative reflections indicated acceptable crystal quality.

Data were collected using the θ–2θ scan technique, and the intensities of three standard reflections were measured every 50 reflections. As no significant variation in intensities of the standard reflections was observed during data collection, no decay correction was applied. An empirical absorption correction was applied to the data using 6 ψ curves for reflections with 83° < χ < 89°.

Data reduction and structure solution was achieved using the SHELXTL PLUS structure solution software package.[14] The structure was solved by the Patterson method in the monoclinic space group $P2_1/c$ and was refined successfully in this space group. The remaining non-hydrogen atoms were located from subsequent difference Fourier maps. Full matrix least-squares refinement was carried out by minimizing the function $w(F_o - F_c)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Hydrogen atoms were included in their idealized calculated positions and were held fixed. The final difference Fourier map had strong residual peaks (maximum electron density of 5.12 e/Å^3) at 0.9 Å from the platinum atom, possibly due to the presence of bromine atoms and ineffective absorption correction using the ψ scan technique on a needle-shaped crystal. Summaries of crystal data, intensity collection parameters, and final structure refinement parameters are presented in Table VI. All calculations were performed on a VAX Station 3100 computer using SHELXTL PLUS software.

(14) Sheldrick, G. M. Siemens Analytical X-ray Division, Madison, WI, 1989.

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Supplementary Material Available: A figure showing the atom numbering scheme in both molecules of [PtBr(Mes)(cod)] (Figure S1) and tables of atomic coordinates (Table S1), bond lengths and bond angles (Tables S2 and S3), anisotropic displacement coefficients for non-hydrogen atoms (Table S4), calculated hydrogen atom coordinates and isotropic displacement coefficients (Table S5) (6 pages). Ordering information is given on any current masthead page.

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