and an increased $^{1}J_{PP}$ coupling as compared to the other isomer. This, however, is not the case, and therefore structure **3a′** and **4a′** are ruled out.

Supplementary Material Available: Tables of crystal data, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (10 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Platinum(IV)–Azobenzene Cyclometalation Products and Related Species

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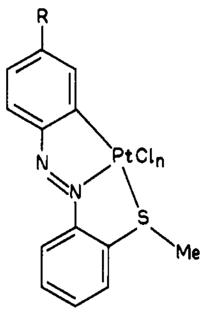
The first platinum(IV) cyclometalates of azobenzene, $Pt^{IV}(RL)Cl_3$ (R = H, Me), have been synthesized by oxidation of $Pt^{II}(RL)Cl$ by chlorine or *m*-chloroperbenzoic acid (Pt(RL) = cycloplatinated 2-(methylthio)azobenzene fragment). The X-ray structures of $Pt(MeL)Cl_3$ and Pt(MeL)Cl are reported. In both cases the organic moiety acts as a planar tridentate (C,N,S) ligand and the lattice consists of loose dimers held by nonbonded S···S interactions. The Pt–C distances are equal in the two molecules, but the other metal–ligand distances are longer (e.g., Pt–S by ~0.09 Å) in $Pt(MeL)Cl_3$. Weakening of back-bonding upon metal oxidation may be one of the reasons. In ^{1}H NMR spectra, the ^{3}J coupling constant between ^{195}Pt and ^{1}H(SMe) increases from 12.3 Hz in $Pt(MeL)Cl_3$ to 20.1 Hz in Pt(MeL)Cl, in accord with the increase in 6s character of the metal hybrid orbitals. The complexes Pt(MeL)Cl and Pd(MeL)Cl are isomorphous, with very similar bond parameters. However, chlorine and mCPBA, which oxidize the metal in Pt(RL)Cl, attack the Pd–C bond (in effect the coordinated ligand is attacked) in Pd(RL)Cl, leaving the metal oxidation state unchanged. The reactivity difference corresponds to the nucleophilicity orders $Pt^{II} \gg Pd^{II}$ and Pd–C ≫ Pt–C. Crystal data for $Pt(MeL)Cl_3$: space group $P2_1/n$; $a = 7.436$ (2) Å, $b = 18.613$ (4) Å, $c = 12.335$ (2) Å, $\beta = 104.66$ (2)°; $Z = 4$, $V = 1651.6$ (6) Å^3. Crystal data for Pt(MeL)Cl: space group $P\bar{1}$; $a = 7.421$ (5) Å, $b = 8.830$ (5) Å; $c = 11.083$ (6) Å, $\alpha = 105.44$ (4)°, $\beta = 92.05$ (5)°, $\gamma = 97.16$ (5)°; $Z = 2$, $V = 692.7$ (7) Å^3. Crystal data for Pd(MeL)Cl: space group $P\bar{1}$; $a = 7.424$ (3) Å, $b = 8.833$ (4) Å, $c = 11.127$ (4) Å, $\alpha = 105.44$ (3)°, $\beta = 93.26$ (3)°, $\gamma = 96.81$ (3)°; $Z = 2$, $V = 695.4$ (5) Å^3.

Introduction

Platinum(IV) organometallics containing Pt–C(aryl) bonds are rare.[1] In particular, ortho-metalated platinum(IV) species were virtually unknown until very recently and current knowledge is limited to just a few compounds synthesized by oxidative addition of halogens or halocarbons to platinum(II) precursors.[2-6] The platinum(II)–azobenzene system is as old as ortho metalation,[7] but platinum(IV) analogues remain unknown. Herein we describe the first examples of such species incorporating 2-(methylthio)azobenzene and having the coordination sphere $Pt(C,N,S)Cl_3$, which have been characterized by X-ray crystallography. Synthesis involves the treatment of the bivalent precursor Pt(C,N,S)Cl with chlorine or *m*-chloroperbenzoic acid in chlorocarbon solvents. These oxidants also react with Pd(C,N,S)Cl,[8] transforming the ligand without affecting the metal oxidation state. The origin of this reactivity divergence is examined. Structure determination has not revealed the presence of any gross mismatch between Pt(C,N,S)Cl and Pd(C,N,S)Cl in molecular shape or dimension.

Results and Discussion

Synthesis and Interconversion. The ortho-metalated fragment of interest in the present work is abbreviated Pt(RL). Cyclometalation of 2-(methylthio)azobenzenes by K_2PtCl_4 proceeds smoothly in hot aqueous ethanol, affording the brown Pt(RL)Cl (**1a**) in excellent yields. Orange-yellow $Pt(RL)Cl_3$ (**1b**) is isolated by oxidizing Pt(RL)Cl with chlorine in acetonitrile solution or, less efficiently, with *m*-chloroperbenzoic acid (mCPBA) in chlorocarbon solvents (vide infra).



R = H, Me

$Pt(RL)Cl_n$

1a, n=1

1b, n=3

The reduction of $Pt(RL)Cl_3$ back to Pt(RL)Cl can be achieved in several ways. In acetonitrile solution $Pt(MeL)Cl_3$ displays an irreversible cyclic voltammetric metal

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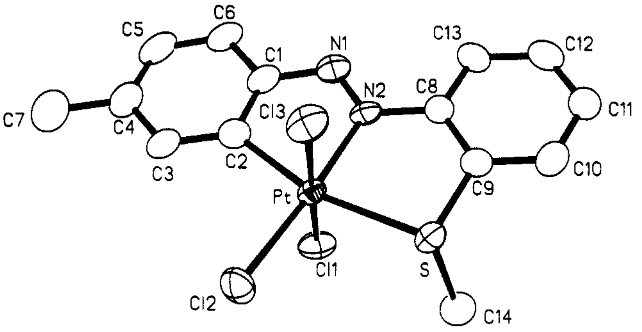

Figure 1. ORTEP diagram and atom labeling of the Pt(MeL)Cl_3 molecule. All atoms are represented by their 50% probability ellipsoids.

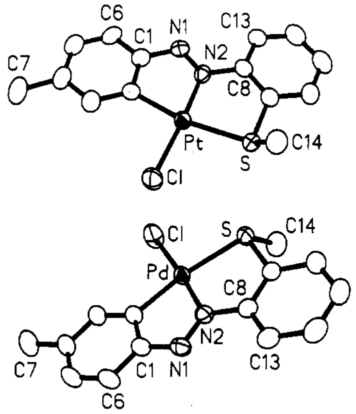

Figure 2. ORTEP diagrams and the atom labeling of Pt(MeL)Cl (top) and Pd(MeL)Cl (bottom). Atoms within each phenyl group are numbered consecutively in a cyclic fashion. All atoms are represented by their 50% probability ellipsoids.

reduction peak at −0.27 V vs the saturated calomel electrode. Upon coulometry at potentials less than this (typically −0.5 V), two electrons are consumed and Pt(MeL)Cl is produced quantitatively. The electrode reaction is coupled to rapid chloride loss (eq 1). The reduced complex is electroinactive in the voltage range ±0.7 V, and this explains the irreversible nature of the metal reduction voltammogram of Pt(MeL)Cl_3. The chemical reduction of Pt(MeL)Cl_3 to Pt(MeL)Cl can be achieved with hot ethanol or, more conveniently, with hydrazine hydrate in acetonitrile.

$$\mathrm{Pt(MeL)Cl_3} + 2e^- \rightarrow \mathrm{Pt(MeL)Cl} + 2\mathrm{Cl}^- \qquad (1)$$

Molecular Structures. The X-ray structures of Pt(MeL)Cl_3, Pt(MeL)Cl, and Pd(MeL)Cl have been determined. Views of molecules are shown in Figures 1 and 2, and selected bond parameters are listed in Tables I and II. Packing diagrams of Pt(MeL)Cl_3 and Pt(MeL)Cl (Pd(MeL)Cl packs similarly) are shown in Figure 3. In all three cases (i) the lattice consists of loose dimers held by nonbonded 3.4–3.6 Å long S···S interactions and (ii) the entire metalated azobenzene ligand, excluding C(14), constitutes a good plane with a mean deviation of ~0.04 Å. In Pt(MeL)Cl_3 the Pt(C,N,S)Cl_3 coordination sphere is distorted octahedral in which the tridentate ligand spans meridionally. The Pd(MeL)Cl complex is isomorphous with Pt(MeL)Cl with very closely similar dimensions of bond parameters.

Table I. Selected Bond Distances (Å) and Angles (deg)[a] for Pt(MeL)Cl$_3$

	Bond Distances		
Pt–C(2)	2.002 (10)	Pt–Cl(2)	2.321 (2)
Pt–N(2)	2.000 (7)	Pt–Cl(3)	2.318 (3)
Pt–S	2.439 (2)	N(1)–N(2)	1.261 (11)
Pt–Cl(1)	2.321 (3)	S···S	3.567 (3)
	Bond Angles		
S–Pt–Cl(1)	94.7 (1)	Cl(1)–Pt–Cl(2)	91.4 (1)
S–Pt–Cl(2)	98.0 (1)	S–Pt–Cl(3)	85.8 (1)
Cl(1)–Pt–Cl(3)	176.8 (1)	Cl(2)–Pt–Cl(3)	91.7 (1)
S–Pt–C(2)	164.5 (3)	Cl(1)–Pt–C(2)	88.2 (3)
Cl(2)–Pt–C(2)	97.1 (3)	Cl(3)–Pt–C(2)	90.6 (3)
S–Pt–N(2)	85.3 (2)	Cl(1)–Pt–N(2)	89.0 (2)
Cl(2)–Pt–N(2)	176.6 (2)	Cl(3)–Pt–N(2)	87.9 (2)
C(2)–Pt–N(2)	79.5 (3)	Pt–S–C(9)	94.1 (3)
Pt–S–C(14)	111.9 (3)	C(9)–S–C(14)	101.8 (5)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table II. Selected Bond Distances (Å) and Angles (deg)[a] for M(MeL)Cl (M = Pt, Pd)

	Pt(MeL)Cl	Pd(MeL)Cl
	Bond Distances	
M–C(2)	1.999 (8)	1.980 (2)
M–N(2)	1.946 (8)	1.979 (2)
M–S	2.354 (3)	2.387 (1)
M–Cl	2.293 (3)	2.303 (1)
N(1)–N(2)	1.271 (10)	1.276 (3)
S···S	3.442 (3)	3.429 (1)
	Bond Angles	
S–M–Cl	97.2 (1)	98.8 (1)
Cl–M–N(2)	175.9 (2)	175.7 (1)
Cl–M–C(2)	97.4 (3)	96.5 (1)
S–M–N(2)	86.2 (2)	85.0 (1)
S–M–C(2)	165.0 (3)	164.2 (1)
N(2)–M–C(2)	79.1 (3)	79.5 (1)
M–S–C(9)	95.4 (3)	95.8 (1)
C(9)–S–C(14)	103.4 (5)	101.9 (1)
M–S–C(14)	111.1 (4)	111.3 (1)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

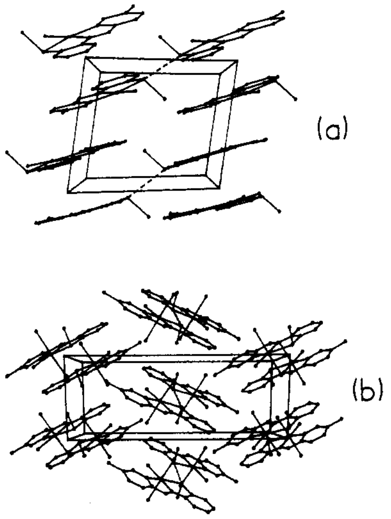

Figure 3. Packing diagrams of (a) Pt(MeL)Cl and (b) Pt(MeL)Cl_3, viewed down the *C* axis.

The radii of Pt(II) and Pt(IV) are virtually the same.[9,10] This is reflected in the Pt–C distances, which are equal within experimental error in Pt(MeL)Cl and Pt(MeL)Cl_3. The other metal–ligand distances are, however, longer in Pt(MeL)Cl_3. In particular, the Pt–S bond is longer by ~0.09 Å. This may arise at least in part from the stronger back-bonding (e.g., 5dπ(Pt)–3dπ(S)) in the bivalent complex. The normal Pt(II)–S(thioether) distance is ~2.25

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Table III. ^{1}H NMR Spectral Data in $CDCl_3$ for $Pt(MeL)Cl_3$ and Pt(RL)Cl[a]

compd	δ, ppm (*J*, Hz)										$^3J(^{195}Pt,^1H$-(SMe)), Hz
	3-H	4-H	5-H	6-H[c]	$7-CH_3$	10-H[c]	11-H[d]	12-H[d]	13-H[c]	SCH_3	
$Pt(MeL)Cl_3$	7.32[b]		7.64[c] (8.0)	8.12 (8.0)	2.61	7.64 (8.0)	7.80 (8.0)	7.80 (8.0)	8.32 (8.0)	3.04	12.3
Pt(HL)Cl	7.82[c] (8.5)	7.58[d] (9.0)	7.24[d] (9.0)	7.77 (8.0)		8.01 (8.0)	7.54 (8.5)	7.54 (8.5)	8.20 (8.0)	3.02	20.2
Pt(MeL)Cl	7.64[b]		7.06[c] (8.5)	7.76 (8.0)	2.32	7.90 (8.5)	7.54 (8.5)	7.54 (8.5)	8.18 (8.0)	3.02	20.1

[a] Atom-numbering scheme is as in Figures 1 and 2. [b] Singlet. [c] Doublet. [d] Triplet.

Table IV. UV-Vis Spectral Data[a] for $Pt(RL)Cl_3$ and Pt(RL)Cl

compd	UV-vis λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$Pt(HL)Cl_3$	570 (300),[b] 475 (4670), 385 (12 390), 280 (23 910)
$Pt(MeL)Cl_3$	580 (140),[b] 475 (7277), 455 (7673),[b] 400 (9195), 240 (13 561)
Pt(HL)Cl	575 (1400), 550 (1300),[b] 490 (2000), 445 (3300),[b] 415 (10 100), 385 (12 400), 365 (11 500), 350 (9300),[b] 265 (14 500)
Pt(MeL)Cl	575 (2500), 550 (2280),[b] 480 (2760), 415 (13 950), 375 (13 100), 355 (10 950), 340 (8500),[b] 270 (14 200),[b] 260 (15 960)

[a] In dichloromethane. [b] Shoulder.

Å.[5,11] In Pt(MeL)Cl this distances is 2.354 (3) Å due to the strong trans influence of the metalated carbon.[12,13]

Spectra. Both Pt(RL)Cl and $Pt(RL)Cl_3$ display well-resolved ^{1}H NMR spectra in $CDCl_3$, which have been assigned on the basis of chemical shifts, spin–spin structure, and the effect of substituents (Table III). The ^3J coupling constant between ^{195}Pt and ^{1}H(SMe) decreases from 20.1 to 12.3 Hz on going from Pt(MeL)Cl to $Pt(MeL)Cl_3$. This is in qualitative accord with the decrease in 6s character of the metal hybrid orbitals (dsp^2 to d^2sp^3).[12] The magnitude of ^3J in Pt(MeL)Cl is comparable to that (23.5 Hz) in *cis*-$PtPh_2(Me_2S)_2$.[14]

The Pt(RL) chromophore has distinctive absorption spectra for the bivalent and tetravalent metals (Figure 4 and Table IV). The oxidizability of Pt(MeL)Cl by bromine was examined spectrally. That oxidation occurs is clearly revealed by the spectra (Figure 4). The oxidized complex, presumably $Pt(MeL)Br_2Cl$, was, however, not isolated.

Reactivity Differences of M(RL)Cl (M = Pt, Pd). The divergent redox reactivities of isomorphous palladium(II) and platinum(II) organometallics is of current interest.[15] The M(RL)Cl pair provides one kind of example. Oxidation of Pt(RL)Cl with *m*-chloroperbenzoic acid in chlorocarbon solvents (CCl_4, $CHCl_3$, CH_2Cl_2 have been used) affords $Pt(RL)Cl_3$ in 40–50% yield. In the case of Pd(RL)Cl oxo insertion into the Pd–C bond occurs, yielding a phenolato complex.[8] On the other hand, chlorine cleaves[16] the Pd–C bond and the chlorinated ligand is liberated as detailed elsewhere.[17]

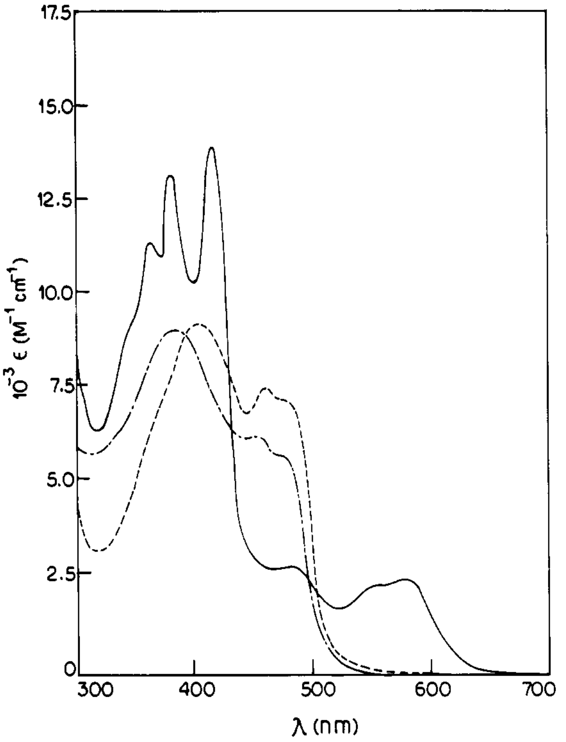
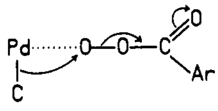


Figure 4. Electronic spectra of Pt(MeL)Cl (—), $Pt(MeL)Cl_3$ (- - -), and $Pt(MeL)Br_2Cl$ (–·–) in dichloromethane.

The reaction of Pd(RL)Cl with mCPBA involves electrophilic insertion of "O" into the Pd–C bond in the intermediate **2** (only the Pd–C bond of Pd(RL)Cl is shown).[8,18,19] The formation of $Pt(RL)Cl_3$ can be rationalized in terms of intermediate **3**. Here the Pt–C bond is not sufficiently nucleophilic for insertion of "O" but the metal itself is. Oxo species of types O=Pt^{IV}(RL)Cl are, however, expected to be unstable (d^n oxo system, n > 4).[18b,20] Either such species or "O" itself could oxidize the chlorocarbon solvent[21] to chlorine and other oxidants which are capable of oxidizing Pt(RL)Cl to $Pt(RL)Cl_3$.



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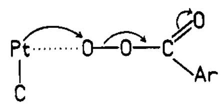

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The formation of $Pt(RL)Cl_3$ from Pt(RL)Cl and chlorine corresponds to electrophilic addition of chlorine to the

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Table V. Summary of Crystallographic Data for $Pt(MeL)Cl_3$, Pt(MeL)Cl, and Pd(MeL)Cl

	$Pt(MeL)Cl_3$	Pt(MeL)Cl	Pd(MeL)Cl
formula	$C_{14}H_{13}N_2SCl_3Pt$	$C_{14}H_{13}N_2SClPt$	$C_{14}H_{13}N_2SClPd$
fw	542.8	471.9	383.2
cryst syst	monoclinic	triclinic	triclinic
cryst dimens, mm	0.24 × 0.12 × 0.30	0.36 × 0.20 × 0.28	0.20 × 0.19 × 0.34
a, Å	7.436 (2)	7.421 (5)	7.424 (3)
b, Å	8.613 (4)	8.830 (5)	8.833 (4)
c, Å	12.335 (2)	11.083 (6)	11.127 (4)
α, deg		105.44 (4)	105.44 (3)
β, deg	104.66 (2)	92.05 (5)	93.26 (3)
γ, deg		97.16 (5)	96.81 (3)
V, $Å^3$	1651.6 (6)	692.7 (7)	695.4 (5)
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
D_{calc}, g/cm^3	2.183	2.262	1.830
F(000)	1024	444	380
μ(Mo Kα), cm^{-1}	91.89	105.59	16.41
temp, °C	23	23	23
$2\theta_{max}$, deg	55	55	50
no. of observns ($I > 3\sigma(I)$)	2749	2866	2225
scan type	ω	θ–2θ	ω
residuals: R,[a] R_w,[b] %	4.45, 5.75	4.7, 5.93	1.84, 2.41
goodness of fit indicator	1.17	1.57	1.32

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0010$ for $Pt(MeL)Cl_3$, 0.008 for Pt(MeL)Cl, and 0.0001 for Pd(MeL)Cl.

metal.[2b,5] On the other hand, electrophilic insertion of chlorine into the Pd–C bond expectedly leads to the liberation of the chloro-substituted ligand, since the aromatic chloro function is a poor coordinating agent.

The reactivity differences qualitatively correspond to the nucleophilicity orders: (i) Pd–C ≫ Pt–C and (ii) Pt^{II} ≫ Pd^{II}. Subtle changes in the energetics of the metal oxidation states and the metal–carbon bonds could produce these orders. The close structural similarity of Pt(MeL)Cl and Pd(MeL)Cl does not stand in contradiction to the observed reactivity differences.

Concluding Remarks

The synthesis and characterization of the first cyclometalated azobenzene (2-(methylthio)-substituted) complexes of platinum(IV), $Pt(RL)Cl_3$, having the meridional coordination sphere $Pt(C,N,S)Cl_3$ are described. The X-ray structures of $Pt(MeL)Cl_3$, its synthetic precursor Pt(MeL)Cl, and Pd(MeL)Cl have been determined. Nonbonded S···S interactions are observed in all three cases. Metal–ligand bond distances in the $Pt(MeL)Cl_3$–Pt(MeL)Cl pair reveal interesting variations.

In spite of very close structural similarities, the reactivities of Pt(RL)Cl and Pd(RL)Cl toward chlorine and mCPBA are very different. The former undergoes metal oxidation, affording $Pt(RL)Cl_3$, but in the latter the Pd–C bond is attacked and the ligand is oxidized. A partial rationalization has been offered, and further studies are in progress.

Experimental Section

Materials. Dipotassium tetrachloroplatinate(II) was prepared by a reported method.[22] Commercial mCPBA was purified by a known procedure and was used after determining active oxygen content by iodometric titrations.[23] 2-(Alkylthio)azobenzenes and the Pd(MeL)Cl complex were prepared by a reported procedure.[8] All other chemicals and solvents used for the preparative works were of reagent grade and were used without further purification. Dry acid-free dichloromethane was prepared by the usual methods. Commercially available BDH silica gel (60–120 mesh) was used for column chromatography.

Instrumentation. Visible and ultraviolet spectra were taken with a Hitachi 330 spectrophotometer fitted with a thermostated cell compartment, and ^1H NMR data were collected in $CDCl_3$ solvent with the help of Varian XL 200 and Bruker 270- and 500-MHz FTNMR spectrometers. Electrochemical measurements were performed with a PAR Model 370-4 electrochemistry system, as reported elsewhere.[24] Elemental analyses were obtained by using a Perkin-Elmer 240C elemental analyzer.

Synthesis of Pt(MeL)Cl. To an aqueous solution (10 mL) of K_2PtCl_4 (0.10 g, 0.24 mmol) was added slowly an ethanolic solution of 2-(methylthio)azo-*p*-toluene (0.054 g, 0.22 mmol). The mixture was stirred for 24 h. The brown-red solution was evaporated in air, and the residue was washed thoroughly with water and then with 50% ethanol/50% water (v/v). The dark brown residue was chromatographed on silica gel with 10% acetonitrile/90% benzene (v/v) as eluent. A brown band was collected, which yielded 0.075 g (72%) of Pt(MeL)Cl. Anal. Calcd for $C_{14}H_{13}N_2SClPt$: C, 35.63; H, 2.76; N, 5.94. Found: C, 35.77; H, 2.76; N, 5.83.

Pt(HL)Cl was prepared similarly, and the yield was 71%. Anal. Calcd for $C_{13}H_{11}N_2SClPt$: C, 34.09; H, 2.40; N, 6.12. Found: C, 34.20; H, 2.39; N, 6.22.

Synthesis of $Pt(MeL)Cl_3$. (a) Chlorine as Oxidant. To an acetonitrile solution (50 mL) of Pt(MeL)Cl (0.10 g, 0.21 mmol) was added dropwise 20 mL of acetonitrile saturated with chlorine. The reaction mixture was stirred for $^1/_2$ h and then evaporated in air. The solid was dissolved in dichloromethane, and the solution (10 mL) was chromatographed on silica gel with benzene as eluent. An orange-yellow band was collected, which yielded 0.080 g (70%) of $Pt(MeL)Cl_3$. Anal. Calcd for $C_{14}H_{13}N_2SCl_3Pt$: C, 30.97; H, 2.40; N, 5.16. Found: C, 31.03; H, 2.42; N, 5.19.

(b) mCPBA as Oxidant. To a dichloromethane solution (25 mL) of Pt(MeL)Cl (0.10 g, 0.21 mmol) was added mCPBA (0.10 g, 40 mmol) in one portion. The reaction mixture was stirred for $^1/_2$ h and then evaporated to dryness. The residue was washed thoroughly with 50% ethanol/50% water (v/v) and then with diethyl ether. It was then dissolved in dichloromethane, and the solution (10 mL) was chromatographed on silica gel with benzene as eluent. The orange-yellow band was collected and yielded 0.045 g (40%) of $Pt(MeL)Cl_3$ upon evaporation.

Crystallographic Analyses. Crystals suitable for diffraction analyses were grown by slow diffusion of dichloromethane solutions into hexane at 298 K. Data collection was performed on

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Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Pt(MeL)Cl_3

	x	*y*	*z*	*U*(eq)[a]
Pt	392 (1)	811 (1)	2422 (1)	28 (1)
S	1242 (3)	-203 (1)	1402 (2)	32 (1)
Cl(1)	3095 (4)	1452 (1)	2488 (2)	44 (1)
Cl(2)	-1231 (4)	1472 (1)	889 (2)	47 (1)
Cl(3)	-2232 (3)	149 (1)	2455 (2)	45 (1)
N(1)	1795 (12)	551 (4)	4748 (7)	38 (3)
C(1)	853 (14)	1204 (5)	4667 (8)	37 (3)
C(2)	-68 (15)	1466 (5)	3610 (8)	37 (3)
N(2)	1732 (11)	282 (4)	3801 (6)	30 (2)
C(9)	2396 (14)	-675 (5)	2638 (8)	33 (3)
C(13)	3468 (14)	-768 (5)	4666 (9)	36 (3)
C(8)	2558 (13)	-393 (4)	3721 (8)	32 (3)
C(5)	-75 (18)	2231 (6)	5550 (10)	51 (4)
C(12)	4226 (15)	-1435 (5)	4531 (9)	44 (4)
C(10)	3143 (16)	-1357 (6)	2531 (9)	47 (4)
C(14)	3157 (14)	15 (6)	795 (9)	43 (4)
C(6)	845 (16)	1582 (5)	5655 (9)	45 (4)
C(4)	-1026 (18)	2492 (5)	4500 (11)	53 (5)
C(3)	-1035 (17)	2108 (5)	3529 (9)	46 (4)
C(11)	4062 (16)	-1721 (5)	3493 (9)	45 (4)
C(7)	-2094 (21)	3191 (6)	4401 (11)	85 (8)

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

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Pt(MeL)Cl

	x	*y*	*z*	*U*(eq)[a]
Pt	2135 (1)	1845 (1)	3984 (1)	34 (1)
S	1107 (3)	3757 (2)	5631 (2)	40 (1)
Cl	1873 (5)	3144 (3)	2463 (2)	58 (1)
N(2)	2306 (9)	599 (8)	5182 (7)	35 (2)
N(1)	2772 (10)	-783 (8)	4874 (7)	39 (2)
C(9)	1399 (12)	2720 (10)	6794 (8)	40 (3)
C(6)	3547 (13)	-2718 (10)	3028 (10)	46 (3)
C(8)	1968 (11)	1237 (10)	6474 (8)	37 (3)
C(4)	3573 (13)	-2106 (10)	1067 (9)	45 (3)
C(2)	2903 (11)	-130 (9)	2896 (8)	35 (2)
C(1)	3083 (12)	-1223 (10)	3597 (8)	40 (3)
C(5)	3770 (13)	-3161 (10)	1789 (9)	48 (3)
C(13)	2111 (13)	412 (11)	7358 (8)	42 (3)
C(10)	1043 (13)	3409 (12)	8022 (9)	46 (3)
C(3)	3156 (12)	-595 (10)	1638 (9)	42 (3)
C(12)	1720 (15)	1083 (13)	8564 (9)	54 (4)
C(14)	2773 (16)	5501 (11)	6153 (10)	55 (4)
C(11)	1189 (15)	2573 (14)	8907 (9)	55 (4)
C(7)	3770 (18)	-2601 (13)	-351 (11)	65 (4)

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

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Pd(MeL)Cl

	x	*y*	*z*	*U*(eq)[a]
Pd	2153 (1)	1836 (1)	3965 (1)	31 (1)
S	1112 (1)	3755 (1)	5628 (1)	37 (1)
Cl	1896 (1)	3101 (1)	2413 (1)	58 (1)
N(2)	2343 (3)	595 (2)	5197 (2)	33 (1)
N(1)	2769 (3)	-805 (2)	4864 (2)	36 (1)
C(8)	1963 (3)	1212 (3)	6456 (2)	34 (1)
C(4)	3579 (3)	-2111 (3)	1075 (3)	42 (1)
C(10)	1044 (3)	3387 (3)	8005 (2)	42 (1)
C(1)	3087 (3)	-1216 (3)	3607 (2)	35 (1)
C(9)	1426 (3)	2722 (3)	6786 (2)	34 (1)
C(5)	3739 (3)	-3160 (3)	1790 (3)	45 (1)
C(11)	1217 (4)	2559 (3)	8891 (2)	49 (1)
C(6)	3501 (3)	-2733 (3)	3048 (3)	43 (1)
C(13)	2082 (3)	371 (3)	7348 (2)	41 (1)
C(12)	1717 (4)	1056 (4)	8550 (3)	50 (1)
C(7)	3786 (5)	-2586 (4)	-302 (3)	61 (1)
C(14)	2788 (5)	5490 (3)	6201 (3)	55 (1)
C(2)	2906 (3)	-125 (3)	2904 (2)	34 (1)
C(3)	3159 (3)	-590 (3)	1643 (2)	39 (1)

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

a Nicolet R3m/V automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Significant crystal data and data collection parameters are listed in Table V. All calculations for data reduction and structure solution were done on a MicroVAX II computer with the programs of SHELXTL-PLUS.[25] The position of the metal atom in each case was determined by heavy-atom methods. All non-hydrogen atoms were located by subsequent difference Fourier syntheses and made anisotropic. Hydrogen atoms were affixed at their idealized positions and were refined isotropically with fixed thermal parameters. Final convergent refinement gave residuals as summarized in Table V.

Pt(MeL)Cl_3 crystallized in the monoclinic crystal system as orange parallelepiped crystals. Unit cell constants were determined by a least-squares fit of up to 25 reflections selected from rotation photographs with $6.0 < 2\theta < 26.0°$. Lattice dimensions and Laue groups were checked by axial photography. The space group $P2_1/n$ was identified uniquely from systematic absences observed during the collection of data. Both Pt(MeL)Cl and Pd(MeL)Cl crystallized in the $P\bar{1}$ space group as dark brown prismatic and orange parallelepiped crystals, respectively. Unit cell constants were determined from 22 and 20 machine-centered reflections with $17 < 2\theta < 31°$ and $14 < 2\theta < 29°$, respectively. Two check reflections were measured after every 98 reflections over 39 h (Pt(MeL)Cl_3), 29 h (Pt(MeL)Cl), and 19 h (Pd(MeL)Cl) of data collection to monitor the crystal stability; all data were corrected for decay (decay correction ranges on intensities were 0.9488–1.0012 for Pt(MeL)Cl_3, 0.7783–1.0269 for Pt(MeL)Cl, and 0.9736–1.0103 for Pd(MeL)Cl) and Lorentz and polarization effects. An empirical absorption correction was done on the basis of azimuthal scans[26] of eight reflections with the diffractometer angle χ set at 270–290°. The highest difference Fourier peaks were 1.10, 1.31, and 0.25 e $Å^{-3}$ for Pt(MeL)Cl_3, Pt(MeL)Cl, and Pd(MeL)Cl, respectively, all lying close to the metal centers. Atomic coordinates and isotropic thermal parameters are collected in Tables VI–VIII.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms (12 pages); listings of calculated and observed structure factors (35 pages). Ordering information is given on any current masthead page.

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