Competition between Intramolecular Oxidative Addition and Ortho Metalation in Organoplatinum(II) Compounds: Activation of Aryl–Halogen Bonds

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The ligands 2-$XC_6H_4CH{=}NCH_2CH_2NMe_2$ (1) react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (2) to give $[PtMe_2(2\text{-}XC_6H_4CH{=}NCH_2CH_2NMe_2)]$ (3), which then react either by ortho metalation to give CH_4 and $[PtMe(2\text{-}XC_6H_3CH{=}NCH_2CH_2NMe_2)]$ (4) or undergo oxidative addition of the C–X bond to give $[PtXMe_2(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ (5). These complexes, and related compounds with modified aryl substituents, have been characterized by NMR spectroscopy, and the derivative $[PtClMe_2(ClC_6H_3CH{=}NCH_2CH_2NMe_2)]$ (7b) has been characterized crystallographically. The complex $[PtMe(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ reacts with CD_3Br or MeI to give $[PtBrMe(CD_3)(C_6H_4CH{=}NCH_2CH_2NMe_2)]$ or $[PtIMe_2(C_6H_4CH{=}NCH_2CH_2NMe_2)]$, respectively, initially by trans oxidative addition. The ligands 2-$XC_6H_4CH{=}NR$ (R = Ph, Pr) react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give similar products of ortho metalation, $[PtMe(2\text{-}XC_6H_3CH{=}NR)(SMe_2)]$, or oxidative addition, $[PtXMe_2(C_6H_4CH{=}NR)(SMe_2)]$. The kinetics of the reaction of 3 to give 4 or 5 have been studied, and the reactions each follow first-order kinetics. The activation parameters for both types of reaction are similar, and since the ortho metalation is presumed to occur by concerted C–H oxidative addition followed by rapid reductive elimination of methane, it is suggested that the oxidative addition of aryl–bromide or aryl–chloride bonds also occurs by a concerted mechanism. The rates of reaction are C–Br > C–Cl > C–H, and internal competition reactions give the sequence C–Cl > C–H > C–F. Hence, the overall reactivity series is C–Br > C–Cl > C–H > C–F, the series of increasing C–X bond energies. These are the first examples of aryl–halogen bond activation by platinum(II) complexes.

Introduction

The complexes $[PtMe_2(NN)]$, where NN is a diimine ligand such as 2,2′-bipyridine or 1,10-phenanthroline, are among the most reactive transition-metal complexes in oxidative addition of alkyl halides. Several studies of reactivity and mechanism have been carried out, and both S_N2 and free-radical chain mechanisms have been established.[1,2] However, aryl halides fail to react either with these platinum(II) complexes or with many other square-planar d^8 complexes.[3,4] Therefore, most studies of oxidative addition of aryl halides have, of necessity, been concentrated on d^{10} complexes such as $[Ni(PEt_3)_4]$ and, most recently, on the d^6 complex $[W(CO)_3(MeCN)_3]$.[5,6] This paper describes the intramolecular oxidative addition of aryl halides to platinum(II) and a study of reactivity and mechanism in this reaction. While this work was in progress, Richmond has successfully used a similar approach to effect oxidative addition of aryl halides to tungsten(0) and Canty has independently discovered intramolecular oxidative addition of an aryl–halogen bond to platinum(II).[4,6] A preliminary account of part of this work has been published.[7]

Results and Discussion

The majority of the research described in this paper was carried out with imine ligands of formula $RCH{=}NCH_2CH_2NMe_2$, in which R is an *o*-halogenoaryl group. This ligand design was based on the hypothesis that substitution of the chelate nitrogen donor ligands onto a dimethylplatinum(II) center, giving a $PtMe_2N_2$ donor set, would lead to activation of a suitable group R.[8-10] Subsequently, it was found that the chelate nitrogen donor was not necessary and that similar activation of the group R would also occur in the simpler imine ligands $RCH{=}NR^1$, where R^1 = Ph or Pr. The synthesis, characterization, and

Table I. ^1H NMR Data for the Ligands $RCH^d{=}NCH^c_2CH^b_2N(CH^a_3)_2$[a]

R	δ(H^a)	δ(H^b)	δ(H^c)	$J(H^bH^c)$, Hz	δ(H^d)
2-BrC_6H_4	2.33	2.66	3.79	7.0	8.67
2-ClC_6H_4[b]	2.03	2.38	3.50	7.0	8.46
2,6-$Cl_2C_6H_3$	2.04	2.38	3.59	6.8	8.27
2-Cl,6-FC_6H_3	2.22	2.56	3.74	6.8	8.53
2-Cl,6-$NO_2C_6H_3$	2.20	2.47	3.70	6.8	8.59
2,3-$Cl_2C_6H_3$	2.21	2.56	3.77	6.0	8.71
C_6H_5[b]	2.31	2.67	3.81	7.0	8.73
2-FC_6H_4[c]	2.30	2.64	3.70	7.0	8.60
2-$NO_2C_6H_4$	2.31	2.65	3.75	7.0	8.32
2-NO_2,5-ClC_6H_3	2.22	2.59	3.78	6.6	8.64
2-$MeOC_6H_4$	2.10	2.14	3.56	6.7	8.58
2-HOC_6H_4	2.19	2.53	3.65	7.0	8.41
2-Cl,5-HOC_6H_4	2.21	2.56	3.70	6.5	8.45

[a] Solvent is acetone-d_6 unless otherwise noted. [b] Solvent is benzene-d_6. [c] Solvent is $CDCl_3$.

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Table II. ^{1}H NMR Data for [PtMe^{a}Me^b(Me^{c}NCH$^d_2$CH$^3_2$CH$^3_2$N=CH^{f}R)] in Acetone-d_6[a]

R	δ(H^a)	J(PtH^a)	δ(H^b)	J(PtH^b)	δ(H^c)	J(PtH^c)	δ(H^d)	δ(H^e)	J(H^{d}H^e)	δ(H^f)	J(PtH^f)
2-BrC$_6$H$_4$	0.40	84	0.12	92	2.73	21	2.65	4.10	6	9.32	50
2-ClC$_6$H$_4$	0.41	84	−0.11	90	2.7	21	2.6	4.11	6	9.22	49
2,6-Cl$_2$C$_6$H$_3$	0.35	84	−0.30	92	2.70	21	2.6	4.13	7	9.20	48
2-Cl,6-FC$_6$H$_3$	0.35	85	−0.26	92	2.70	21	2.62	4.13	8	9.22	52
2-Cl,6-NO$_2$C$_6$H$_3$	0.26	84	−0.47	92	2.68	21		4.20		9.44	52
2,3-Cl$_2$C$_6$H$_3$	0.40	85	−0.16	92	2.76	21	2.77	4.12	5.5	9.40	42
C$_6$H$_5$	0.43	84	0.06	92	2.7	20	2.65	4.07	7	9.2	47
2-FC$_6$H$_4$	0.43	84	−0.01	92	2.72	21	2.66	4.14	6	9.18	46
2-NO$_2$C$_6$H$_4$	0.34	85	−0.33	92	2.78	20	2.04	4.08	5	9.50	50
2-NO$_2$,5-Cl$_6$H$_3$	0.39	85	−0.27	91	2.76	21	1.80	4.10	5.5	9.02	42
2-MeOC$_6$H$_4$[b]	0.39	85	0.01	92	2.74	21	2.70	4.01	5.5	9.22	48

[a] *J* values in Hz. [b] δ(OCH$_3$) = 3.88.

Table III. ^{1}H NMR Spectra for [PtMe^a(Me$^b_2$NCH$^c_2$CH$^d_2$N=CHR)] in Acetone-d_6[a]

R	δ(H^a)	J(PtH^a)	δ(H^b)	J(PtH^b)	δ(H^c)	δ(H^d)	J(H^{c}H^d)	δ(H^e)	J(PtH^e)
C$_6$H$_4$	0.79	80	2.70	20	3.10	4.00	12	8.56	62
2-FC$_6$H$_3$	0.84	80	2.76	22	3.20	4.15[b]	12	8.96	62

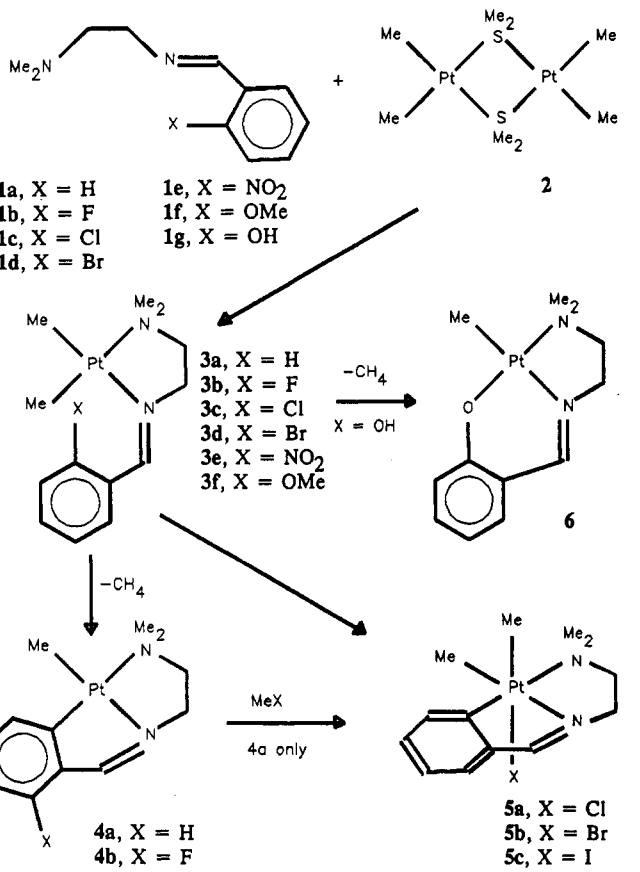
[a] *J* values in Hz. [b] *J*(PtH) = 20 Hz.

some reactions of the products obtained with these ligands are described first, followed by a description of studies of reactivity and mechanism.

Synthesis and Characterization of Complexes from the Ligands RCH=NCH$_2$CH$_2$NMe$_2$. These ligands were easily prepared by condensation reaction of Me$_2$NCH$_2$CH$_2$NH$_2$ with the corresponding aldehyde RCH=O. They were characterized by their ^{1}H NMR spectra (Table I) and, in many cases, by high-resolution mass spectrometry (Experimental Section). The ligands were formed as single isomers that are assumed to have anti stereochemistry about the C=N bond, as shown in structure **1** (Scheme I).

The chemistry with the ligands having R = 2-XC$_6$H$_4$ is shown in Scheme I. In each case, with X = Br, Cl, F, H, or NO$_2$, the reaction with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$][11] gave free SMe$_2$ and the substitution products **3**. These complexes were characterized spectroscopically (Table II) in all cases, but they could not usually be isolated in pure form, since further reaction occurred to give either the oxidative addition products **5** or the products of ortho metalation **4** (Scheme I). The substitution reaction that gives **3** actually occurs in two stages. The first stage, which is very rapid, gives 50% conversion to **3** and monomeric *cis*-[PtMe$_2$(SMe$_2$)$_2$].[11] Next a slower substitution occurs to give more **3** and free SMe$_2$. This reaction sequence was monitored by ^{1}H NMR spectroscopy. When X = OH, the reaction gave **6** (Scheme I) and no intermediate **3** could be detected. Selected spectroscopic data for the substitution products, **3**, are given in Table II. Each gave two methylplatinum resonances in the ^{1}H NMR spectrum with ^2J(PtH) = 84–85 Hz for PtMe^a trans to imine and ^2J(PtH) = 90–92 Hz for PtMe^b trans to NMe$_2$. These are typical values for methylplatinum(II) complexes.[1,24] The imine CH=N proton gave a peak at δ = 9.0–9.5 ppm with ^3J(PtH) = 42–52 Hz, while the MeN resonance was at δ = 2.68–2.76 ppm with ^3J(PtH) = 20–22 Hz.

Scheme I



The only case in which **3** was stable was then X = NO$_2$ (**3e**). No oxidative addition or ortho metalation occurred in this case. The ^{1}H NMR spectrum of **3e** is given in Figure 1 and is typical for these complexes.

Complexes **3a** and **3b** decomposed slowly in solution to give **4a** and **4b**, respectively, together with methane. These are examples of the well-known ortho-metalation reactions[12] and serve to show that the aromatic C–H bond is more reactive than the C–F bond toward the dimethylplatinum(II) center. ^{1}H NMR data for complexes **4** are

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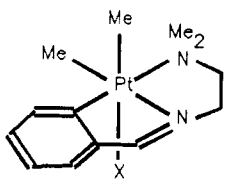
Table IV. ^{1}H NMR Spectra for [PtXMe^{a}Me^b(Me^{c}Me^{d}NCH^e$_2$H^f$_2$N=CH^{g}R)] in Acetone-d_6[a,b]

R, X	δ(H^a)	J(PtH^a)	δ(H^b)	J(PtH^b)	δ(H^c)	J(PtH^c)	δ(H^d)	J(PtH^d)	δ(H^g)	J(PtH^g)
C_6H_4, Br	0.63	74	1.00	64	2.61	16	2.00	11	8.70	48
C_6H_4, Cl	0.54	74	0.92	64	2.64	16	2.94	11	8.70	45
6-ClC_6H_3, Cl	0.55	73	0.92	63	2.63	16	2.91	11	9.00	48
6-FC_6H_3, Cl	0.55	73	0.94	64	2.63	16	2.91	11	8.90	48
6-$NO_2C_6H_3$, Cl	0.38	66	1.07	62	2.65	17	2.76	11	9.20	48
3-C_6H_3, Cl	0.72	74	1.38	62	2.58	18	2.82	13	8.83	42

[a] J values in Hz. [b] Resonances due to H^e and H^f appeared as complex multiplets in the region δ = 3.4–5.4 ppm.

given in Table III and define the structures unambiguously. Thus, there was a single MePt resonance with δ = 0.83–1.09 ppm and ^2J(PtH) = 77–80 Hz, a single Me_2N resonance with δ = 2.70–2.78 ppm and ^3J(PtH) = 20–24 Hz, and an imine resonance with δ(C*H*=N) = 8.56–9.11 ppm and ^3J(PtH) = 60–62 Hz. Compared to the complexes **3**, the coupling constant ^2J(PtCH$_3$) is smaller and ^3J(PtN=CH) is larger in **4**. However, these parameters are still well within the range expected for platinum(II) complexes, and the differences are probably due to geometric changes on ortho metalation.

In contrast to the above reactions, complexes **3c** and **3d** rearranged in solution to give **5a** and **5b**, respectively. There was some difficulty in distinguishing between the two possible structures with the favored *fac*-PtC$_3$ stereochemistry **5** and **5′** for these products. Structure **5** was



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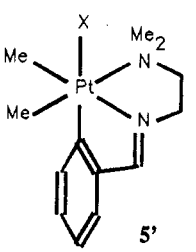
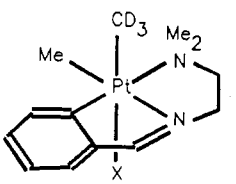


5′



5b-d_3

expected to be most stable due to the preference of the metalated imine ligand to be approximately planar, and this preference was also indicated by molecular mechanics calculations, which indicated that **5** was more stable than **5′** by approximately 8.1, 8.6, and 9.3 kcal mol^{-1} when X = Cl, Br, and I, respectively. The complexes each gave two MePt resonances and two MeN resonances in the ^{1}H NMR spectra (Table IV). The coupling constants ^2J(PtCH$_3$) were 66–74 Hz for the MePt group trans to halogen and 60–64 Hz for the MePt group trans to the imine nitrogen. However, neither these data nor the corresponding ^{13}C NMR data disprove the alternative structure **5′**. Some further support for structure **5** was obtained by reaction of **4a** with CD_3Br to give **5b-d_3**, X = Br, monitoring the reaction by ^{1}H NMR spectroscopy. The reaction initially gave a complex with a ^{1}H NMR spectrum identical with that of **5b** but with the methylplatinum resonance at δ = 0.63 ppm, ^2J(PtH) = 74 Hz, missing. This is the resonance for **5b** assigned as the MePt group trans to halogen. After 1 h at room temperature, the ^{1}H NMR spectrum contained both methylplatinum resonances for **5b** with equal intensities (half-intensity of unlabeled complex), indicating that scrambling between CH_3Pt and CD_3Pt groups had occurred. This probably occurs by dissociation of the

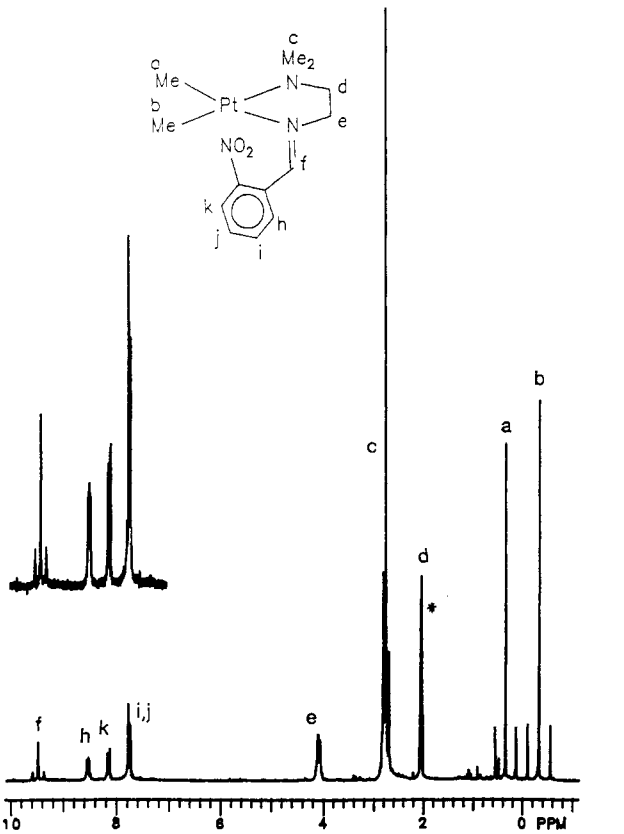


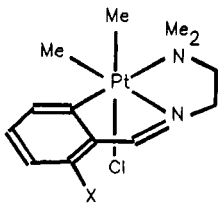
Figure 1. ^{1}H NMR spectrum (200 MHz) of complex **3e**. The resonance due to H^d overlaps with the solvent resonance, and protons H^i and H^j overlap at ca. δ = 7.7 ppm.

dimethylamino group from platinum followed by pseudorotation within the 5-coordinate intermediate and recoordination. Now, since oxidative additions of methyl halides to platinum(II) complexes occur with trans stereochemistry,[1] the stereochemical observation strongly indicates that the structure **5** is correct. Final proof was obtained by an X-ray structure determination on a substituted derivative (see later).

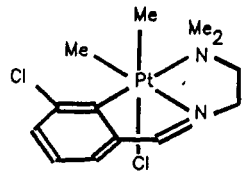
The oxidative addition of the aryl–halogen bond to give **5** occurs with cis stereochemistry at platinum. However, since **5** is the thermodynamically most stable isomer, some caution must be exercised in drawing mechanistic conclusions from this. It is conceivable, though improbable, that trans oxidative addition occurs to give **5′** and that rapid isomerization to give **5** occurs subsequently.

A number of more highly substituted derivatives were studied, all containing the 2-chlorophenyl unit. All led to oxidative addition of the aryl–chloride bond to platinum(II). Thus, the imine derivatives with aryl groups 2-Cl, 6-FC_6H_3, 2-Cl, 6-$NO_2C_6H_3$, and 2,6-$Cl_2C_6H_3$ gave the complexes **7** and that with aryl = 2,3-$Cl_2C_6H_3$ gave **8**.

These complexes were characterized spectroscopically, as described for **5**, and complex **7b** was also characterized crystallographically. None of the complexes **5**, **7**, or **8** gave good single crystals, but the crystals of **7b** were just good



7a, X = F
7b, X = Cl
7c, X = NO_2



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enough to allow structure solution. Crystallographic data are given in Table V, atomic coordinates are in Table VI, and bond distances and angles are in Table VII. The structure is shown in Figure 2 and confirms the geometry predicted from the spectroscopic studies and molecular mechanics calculations (although it is the enantiomer opposite of that depicted in **7b**). In particular the tridentate ligand (donors C1, N1, N2) adopts an almost planar geometry and the three carbon donors adopt the *fac*-PtC_3 geometry. All bond distances are in the expected range after making allowance for the strong trans influence of the carbon donor ligands. The distance Pt–NMe_2 of 2.254 (11) Å is significantly longer than the imine Pt–NCH distance of 2.045 (13) Å, consistent with the relatively weak ligating ability of tertiary amines for platinum. Most bond angles at platinum are close to the ideal 90°, and the greatest distortions involve the tridentate ligand. Thus, the angles N1–Pt–N2 = 81.2 (4)° and N1–Pt–C1 = 81.7 (5)° are less than 90° due to the chelate effect and N2–Pt–C13 = 99.3 (5)° and C1–Pt–C13 = 97.8 (6)° are correspondingly greater than 90°.

Synthesis and Characterization of Complexes from the Ligands 2-XC_6H_4CH=NR, R = Ph or Pr. The chemistry of these ligands with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ is similar in many ways to the chemistry of the ligands 2-XC_6H_4RCH=$NCH_2CH_2NMe_2$, but there are also significant differences. The major differences was that intermediate coordination complexes were not detectable by ^1H NMR spectroscopy, but only the overall conversions to products of ortho-metalation or oxidative addition were observed. The chemistry is summarized in Scheme II.

The reactions of 2-XC_6H_4CH=NPh, when X = H, F, or NO_2, with $[PtMe_4(\mu\text{-}SMe_2)_2]$ occurred slowly to give the products of ortho metalation **10a–c**. It is significant that the nitro derivative gave ortho metalation, since the corresponding reaction of 2-$NO_2C_6H_4CH$=$NCH_2CH_2NMe_2$ gave only a coordination complex. In these reactions, the dimethyl sulfide ligand remains coordinated in the products **10a–c** as is clearly shown in the ^1H NMR data.

The reaction of 2-ClC_6H_4CH=NPh with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gave the product of oxidative addition $[PtMe_2Cl(SMe_2)(C_6H_4CH$=NPh)], as shown clearly by the ^1H and ^{13}C NMR data. However, these data do not distinguish between the two possible stereochemistries **11a** or **12a** (Scheme II). The difficulty is that **11** and **12** differ in having a methyl group trans to SMe_2 or trans to halogen, respectively, and since these ligands have similar trans influences, little difference in the coupling constants $^2J(PtCH_3)$ is expected. Molecular mechanics calculations suggest that **11** should be slightly more stable than **12** [ΔH for the equilibrium = 1.5 and 1.8 kcal mol^{-1} for R = Ph and X = Cl or Br, respectively, and 2.1 and 2.0 kcal mol^{-1} for R = Pr and X = Cl or Br, respectively, but the errors involved in such calculations are not known and so this should be regarded with caution. That the energies of **11** and **12** are similar is shown by the reaction of 2-BrC_6H_4CH=NPh with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give an equilibrium mixture of both isomers **11b** and **12b**, each giving the expected two methylplatinum resonances. The two isomers were formed in a ratio of ~4:1, but it is not possible to determine which is the major isomer (NMR assignments are made under the assumption that the major isomer is **11**). The ligands **9f** and **9g** gave very similar products **11c**, **12c** and **11d**, **12d**, respectively (Scheme II), but since these were oils, they were characterized only by

Table V. Crystallographic Details

formula	$C_{13}H_{20}Cl_2N_2Pt$
fw	470.3
$F(000)$	896
cryst dimens	0.42 × 0.34 × 0.61 mm
radiation	Mo Kα (λ = 0.710 73 Å)
temp	21 ± 1 °C
space group	orthorhombic, $P2_12_12_1$
cell dimens	a = 8.337 (4) Å
	b = 11.816 (4) Å
	c = 15.370 (4) Å
cell vol.	1514 (2) Å^3
Z	4
D_c	2.06 g cm^{-3}
μ	97.1 cm^{-1}
monochromator	graphite
scan type	ω–2θ
scan width	$(0.7 + 0.35 \tan \theta)°$
max 2θ	54
minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)$
least-squares weights	$1/(\sigma(F_o)^2 + 0.047(F_o)^2)$
param refined	163
unweighted agreement factor	0.033
weighted agreement factor	0.037
highest peak in final diff map	0.81 (18) e/Å^3

Table VI. Positional and Thermal Parameters and Their Esd's[a]

atom	x	y	z	B, Å^2
Pt	0.18989 (6)	−0.04425 (4)	0.30769 (3)	2.157 (7)
Cl1	0.0049 (4)	−0.0436 (4)	0.1834 (2)	3.53 (7)
Cl2	−0.2680 (6)	0.2034 (4)	0.4813 (3)	6.3 (1)
N1	0.153 (1)	0.126 (1)	0.3234 (7)	3.6 (3)
N2	0.386 (1)	0.0207 (9)	0.2202 (7)	3.1 (2)
C1	−0.000 (1)	−0.053 (1)	0.3866 (8)	2.7 (3)
C2	−0.075 (2)	−0.143 (1)	0.424 (1)	3.8 (3)
C3	−0.208 (2)	−0.125 (1)	0.4752 (9)	4.8 (3)
C4	−0.268 (1)	−0.021 (2)	0.4942 (9)	4.0 (4)
C5	−0.197 (2)	0.071 (1)	0.4611 (8)	3.2 (3)
C6	−0.058 (1)	0.061 (1)	0.4058 (7)	2.5 (3)
C7	0.025 (1)	0.154 (1)	0.3689 (8)	2.8 (3)
C8	0.262 (2)	0.200 (1)	0.278 (1)	4.1 (4)
C9	0.328 (2)	0.135 (1)	0.200 (1)	4.3 (3)
C10	0.545 (2)	0.027 (2)	0.263 (1)	5.0 (4)
C11	0.402 (2)	−0.042 (2)	0.139 (1)	5.3 (4)
C12	0.327 (2)	−0.043 (1)	0.4172 (9)	4.5 (3)
C13	0.227 (2)	−0.216 (1)	0.293 (1)	3.9 (3)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

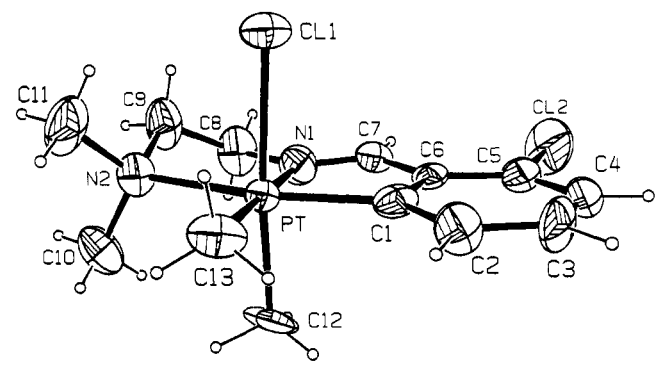


Figure 2. View of the structure of complex **7b**.

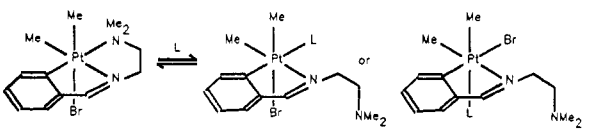
Table VII. Molecular Dimensions

	(a) Bond Lengths (Å)		
Pt-Cl1	2.456 (3)	N2-C10	1.478 (18)
Pt-N1	2.045 (13)	N2-C11	1.463 (19)
Pt-N2	2.254 (11)	C1-C2	1.361 (20)
Pt-C1	1.999 (12)	C1-C6	1.455 (20)
Pt-C12	2.036 (13)	C2-C3	1.377 (20)
Pt-C13	2.068 (15)	C3-C4	1.362 (24)
Cl2-C5	1.704 (14)	C4-C5	1.339 (21)
N1-C7	1.318 (6)	C5-C6	1.439 (18)
N1-C8	1.450 (19)	C6-C7	1.420 (19)
N2-C9	1.470 (19)	C8-C9	1.521 (21)
	(b) Bond Angles (deg)		
Cl1-Pt-N1	89.6 (3)	Pt-N2-C11	113.8 (9)
Cl1-Pt-N2	89.5 (3)	C9-N2-C10	110 (1)
Cl1-Pt-C1	88.5 (3)	C9-N2-C11	108 (1)
Cl1-Pt-C12	175.3 (4)	C10-N2-C11	109 (1)
Cl1-Pt-C13	90.8 (4)	Pt-C1-C2	131 (1)
N1-Pt-N2	81.2 (4)	Pt-C1-C6	109.9 (9)
N1-Pt-C1	81.7 (5)	C2-C1-C6	119 (1)
N1-Pt-C12	88.8 (5)	C1-C2-C3	120 (1)
N1-Pt-C13	179.4 (5)	C2-C3-C4	123 (2)
N2-Pt-C1	162.8 (5)	C3-C4-C5	119 (1)
N2-Pt-C12	94.6 (5)	Cl2-C5-C4	121 (1)
N2-Pt-C13	99.3 (5)	Cl2-C5-C6	118 (1)
C1-Pt-C12	86.8 (5)	C4-C5-C6	121 (1)
C1-Pt-C13	97.8 (6)	C1-C6-C5	117 (1)
C12-Pt-C13	90.8 (6)	C1-C6-C7	118 (1)
Pt-N1-C7	116 (1)	C5-C6-C7	124 (1)
Pt-N1-C8	116.3 (9)	N1-C7-C6	114 (1)
C7-N1-C8	128 (1)	N1-C8-C9	107 (1)
Pt-N2-C9	101.3 (8)	N2-C9-C8	115 (1)
Pt-N2-C10	113.9 (9)		

NMR spectroscopy and were not studied further.

The reactions of Scheme II demonstrate that both ortho metalation and oxidative addition of aryl-chloride and aryl-bromide bonds can be achieved by using simple imine ligands of general formula 2-$XC_6H_4CH{=}NR$, R = phenyl or propyl, and hence that the use of chelate ligands 2-$XC_6H_4CH{=}NCH_2CH_2NMe_2$ is not necessary in order to activate the aryl group R. One advantage of the chelate ligands is that the intermediate coordination complexes **3** (Scheme I) can be formed in solution. This simplifies kinetic studies of the subsequent ortho metalation or oxidative addition reactions as described below.

Reversible Displacement of the Dimethylamino Ligand in 5b. Complex **5b** reacts with the donor ligands L = SMe_2 or PPh_3 according to eq 1.



(1)

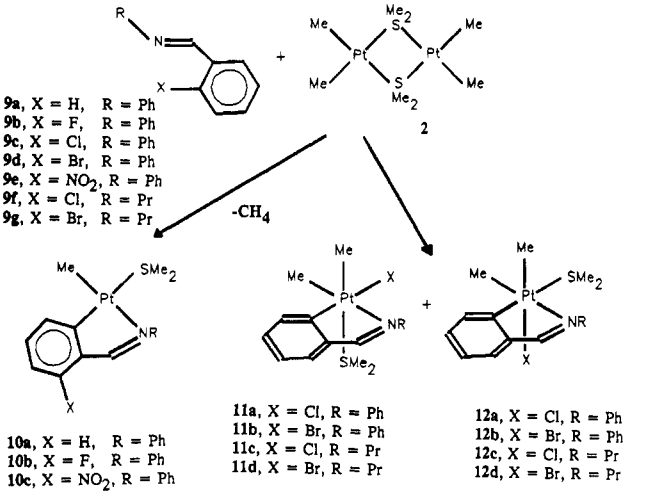
5b

13a, L = SMe_2
13b, L = PPh_3

14a, L = SMe_2
14b, L = PPh_3

When L = SMe_2, the reaction was reversible; thus, **5b** was formed on evaporation of the solutions containing **13a** or **14a**, whereas addition of SMe_2 to a solution of **5b** gave **13a** or **14a** as monitored by ^1H NMR spectroscopy. The reaction with PPh_3 to give **13b** or **14b** was irreversible, and the adduct could be isolated in pure form. The complexes **13** and **14** are analogous to **12** or **11**, respectively, and the structures could not easily be distinguished by NMR spectroscopy when L = SMe_2. In the product from reaction with PPh_3, the coupling constant $^2J(PtCH_3)$ for one methylplatinum group decreased from 74 Hz in **5b** to 60 Hz, strongly suggesting the presence of a methylplatinum group trans to phosphorus and hence structure **14b** rather than **13**. The ligand addition to platinum(IV) illustrated in eq 1 must occur by a dissociative mechanism, and so the dimethylamine group in **5b** must undergo easy reversible dissociation to give a 5-coordinate intermediate. This will be significant to the mechanism of the metalation and oxidative addition reactions.

Scheme II



9a, X = H, R = Ph
9b, X = F, R = Ph
9c, X = Cl, R = Ph
9d, X = Br, R = Ph
9e, X = NO_2, R = Ph
9f, X = Cl, R = Pr
9g, X = Br, R = Pr

2

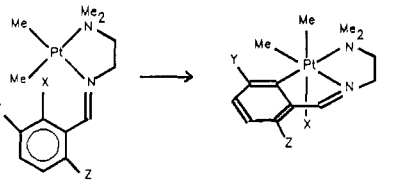
-CH_4

10a, X = H, R = Ph
10b, X = F, R = Ph
10c, X = NO_2, R = Ph

11a, X = Cl, R = Ph
11b, X = Br, R = Ph
11c, X = Cl, R = Pr
11d, X = Br, R = Pr

12a, X = Cl, R = Ph
12b, X = Br, R = Ph
12c, X = Cl, R = Pr
12d, X = Br, R = Pr

Table VIII. First-Order Rate Constants and Activation Parameters[a] for the Intramolecular Oxidative-Addition Reactions at 25.5 °C in Acetone



X	Y	Z	k_1, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
Cl	Cl	H	3.9×10^{-5}	111 ± 2	43 ± 5
Cl	H	H	4.0×10^{-5}	101 ± 5	10 ± 17
Cl	H	H	1.3×10^{-4} [b]		
Cl	H	NO_2	1.1×10^{-4}	100 ± 5	14 ± 18
Cl	H	F	2.35×10^{-4}	93 ± 8	-3 ± 28
Cl	H	Cl	5.8×10^{-4}	71 ± 7	-70 ± 25
Br	H	H		97 ± 2	11 ± 10

[a] Calculated from rate constants measured for at least three temperatures covering a temperature range of at least 20 °C. [b] Rate constant in benzene solution.

Mechanistic Studies. Kinetic studies of the reactions of the ligands $RCH{=}NCH_2CH_2NMe_2$ with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ were carried out in acetone solution, monitoring the reactions by UV-visible spectroscopy. Initially a peak grew at $\lambda \sim 390$ nm due to the formation of the intermediate **3** (Scheme I), and for the oxidative additions, this then decayed as the oxidative-addition products **5**, **7**, or **8** were formed. The band at 390 nm is assigned as due to a Pt(5d) → imine(π^*) MLCT transition, and this moves to higher energy on oxidation of platinum(II) to platinum(IV). The decay of the band at ~390 nm was then used to monitor the rate of the intramolecular oxidative-addition reaction. In each case, this reaction followed first-order kinetics, and data are given in Table VIII. Activation parameters are also given in Table VIII.

The following observations are of interest. The first-order rate constants at 25.5 °C in acetone for C–Cl oxidative additions vary by only 1 order of magnitude for the series of complexes. When Y = H, the series of rates follows the sequence Z = Cl > F > NO_2 > H, and when Z = H, the rate for Y = H > Cl. When Y = Z = H, the rate for X = Br > Cl. The dependence on Z follows no obvious electronic sequence, and the rates could be influenced both by the electronic and steric effects of Z. Steric

acceleration by bulky groups Z might be expected. For C–Cl oxidative additions, the values of $\Delta H^{\ddagger}$ fall in the range 71–111 kJ mol^{-1} and $\Delta S^{\ddagger}$ was in the range 43 to −70 J K^{-1} mol^{-1}. The values of $\Delta S^{\ddagger}$ are usually small and can be positive or negative. They do not indicate the type of highly ordered transition state found for most S_N2 oxidative additions of alkyl halides, for which large negative values of $\Delta S^{\ddagger}$ are usually observed.[1] The reaction of **3c** to give **5a** (Scheme I) occurs faster in benzene than in acetone solution (Table VIII), and this suggests a nonpolar transition state and so is also inconsistent with an S_N2 mechanism.

For comparison, the rate of reaction of **3a** to give **4a** and methane was determined. This reaction also followed first-order kinetics with $k_1 = 6 \times 10^{-6}$ s^{-1} at 25.5 °C and with $\Delta H^{\ddagger} = 81 \pm 7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -75 \pm 22$ J K^{-1} mol^{-1}. The reaction was too slow to study more systematically. The entropy of activation, for which there is a significant uncertainty, is more negative than for the oxidative additions but not by a large margin.

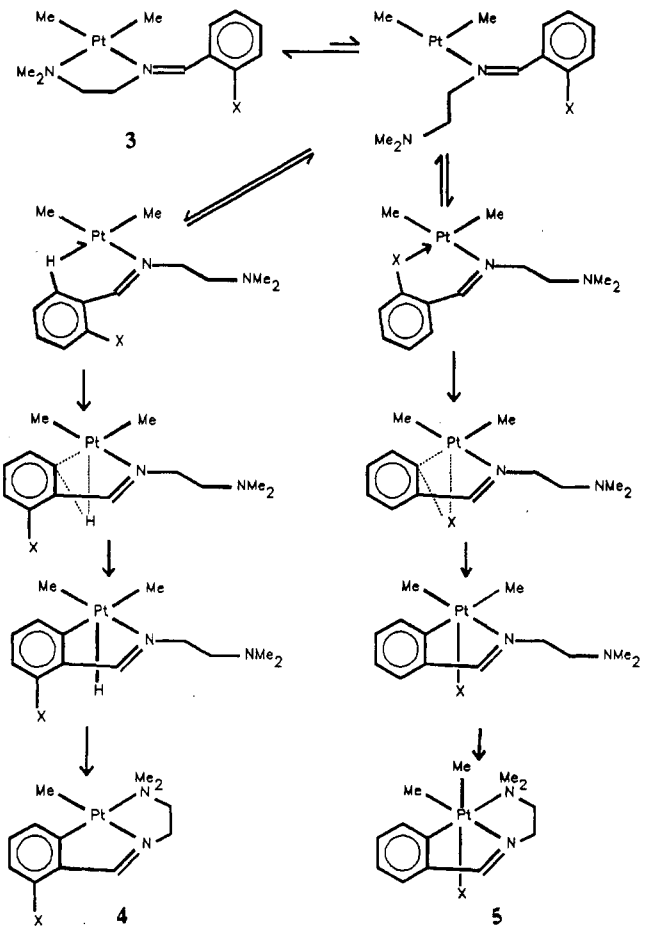
The reactivity series, established by a combination of competition and kinetic studies as described above, is C–Br > C–Cl > C–H > C–F for oxidative addition of aryl–X bonds to platinum(II). This is the inverse of the Ar–X bond energies, as might be expected.

Conclusions

The kinetic data described above clearly rule out a mechanism of oxidative addition of aryl–halogen bonds involving ionic intermediates, such as is found in the S_N2 oxidative addition of most alkyl halides to dimethylplatinum(II) complexes. Free-radical chain mechanisms are ruled out, since the reaction rate was not affected by radical initiators or scavengers and no radicals could be trapped by PhCH=N(O)*t*-Bu. This leaves a free-radical nonchain mechanism or a concerted mechanism, and we suggest that the latter is more probable. It is also likely, but not proved, that the dimethylamino group of the intermediate **3** dissociates prior to oxidative addition. Thus, it has been shown that concerted reductive elimination from octahedral platinum(IV) occurs after ligand dissociation,[13] and hence, by microscopic reversibility, concerted oxidative addition probably requires a preliminary ligand dissociation also. The ease of dissociation of the dimethylamino group has already been demonstrated. Overall then, the mechanism of Scheme III is proposed. If the oxidative-addition step is rate determining in the two competitive reactions, it is not surprising that the activation parameters for the two types of reaction are similar, and a small value of $\Delta S^{\ddagger}$ is reasonable, since the dissociative step will give a positive contribution and the oxidative addition step a negative contribution to $\Delta S^{\ddagger}$. The correlation of increasing reactivity with decreasing D(C–X) bond energy is also reasonable. A concerted mechanism of oxidative addition of aryl iodides to palladium(0) has been proposed recently.[14]

In the case of the monodentate ligands, a related mechanism is likely with a dimethyl sulfide ligand playing a similar role to the dimethylamino group in Scheme III, that is as a ligand which undergoes easy reversible dissociation.

Scheme III



Experimental Section

^{1}H and ^{19}F NMR spectra were recorded by using a Varian XL200 spectrometer, and ^{13}C, ^{31}P and ^{195}Pt NMR spectra, by using a Varian XL300 spectrometer. Kinetic studies were carried out by using a Varian Cary 2290 spectrophotometer, with a thermostated cell compartment. Mass spectra were recorded by using a Finnegan MAT 8230 spectrometer. The molecular mechanics calculations were carried out by using the MMX force field developed by K. Gilbert and J. J. Gajewski (Indiana University). The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ was prepared by the literature method.[11]

2-BrC$_6$H$_4$CH=NCH$_2$CH$_2$NMe$_2$ (1d). To a solution of *N,N*-dimethylethylenediamine (1.6 mL, 1.28 g, 1.4×10^{-2} mol) in benzene was added 2-bromobenzaldehyde (2.6 g, 1.4×10^{-2} mol), and the solution was allowed to stir for 90 min. The mixture was dried over $MgSO_4$, the solution was filtered, and the solvent was removed under vacuum to give the product. MS (*m/e*): found, 254.0421; calcd for $C_{11}H_{15}N_2Br$, 254.0419.

Similarly were prepared the following.

2-ClC$_6$H$_4$CH=NCH$_2$CH$_2$NMe$_2$ (1c). MS (*m/e*): found, 210.0854; calc for $C_{11}H_{15}N_2Cl$, 210.0924.

2-FC$_6$H$_4$CH=NCH$_2$CH$_2$NMe$_2$ (1b). ^{19}F NMR: δ = −122.7 (m). MS (*m/e*): found, 194.1217; calc for $C_{11}H_{15}N_2F$, 194.1219.

C$_6$H$_5$CH=NCH$_2$CH$_2$NMe$_2$ (1a). MS (*m/e*): found, 176.1310; calc for $C_{11}H_{16}N_2$, 176.1313.

2-NO$_2$C$_6$H$_4$CH=NCH$_2$CH$_2$N(CH$_3$)$_2$ (1e). MS (*m/e*): found, 221.1167; calc, 221.1164.

2-BrC$_6$H$_4$CH=NC$_6$H$_5$ (9d). ^{1}H NMR (acetone-d_6): δ = 8.85 (s, 1 H), 8.21 (m, 1 H), 7.67 (d, 1 H, ^3J(HH) = 7 Hz), 7.41 (m, 7 H). MS (*m/e*): found, 258.9996; calc, 258.9997.

2-ClC$_6$H$_4$CH=NC$_6$H$_5$ (9c). ^{1}H NMR (acetone-d_6): δ = 8.92 (s, 1 H), 8.23 (d, 1 H, ^3J(HH) = 7 Hz), 7.43 (m, 8 H). MS (*m/e*): found, 215.0509; calc, 215.0502.

2-FC$_6$H$_4$CH=NC$_6$H$_5$ (9b). ^{1}H NMR (acetone-d_6): δ = 8.79 (s, 1 H), 8.18 (t, 1 H, ^3J(FH) = 8 Hz), 7.2–7.4 (m, 8 H). ^{19}F NMR: δ = −121.2 (m). MS (*m/e*): found, 199.0798; calc, 199.0797.

2-NO$_2$C$_6$H$_4$CH=NC$_6$H$_5$ (9e). ^{1}H NMR (acetone-d_6): δ = 8.92 (s, 1 H), 8.28 (d, 1 H, ^3J(HH) = 7 Hz), 8.09 (d, 1 H, ^3J(HH) = 7 Hz), 7.80 (m, 2 H), 7.42 (m, 2 H), 7.29 (m, 3 H). MS (*m/e*): found, 226.0724; calc, 226.0742.

(13) Roy, R.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121.
(14) Amatore, C.; Pfluger, F. *Organometallics* **1990**, *9*, 2276.

2-$BrC_6H_4CH{=}NCH_2CH_2CH_3$ (9g). ^1H NMR (acetone-d_6): δ = 0.94 (t, 3 H, ^3J(HH) = 7 Hz), 1.68 (sextet, 2 H, ^3J(HH) = 7 Hz), 3.60 (t, 2 H, ^3J(HH) = 7 Hz), 8.63 (s, 1 H), 8.02 (d, 1 H, ^3J(HH) = 6 Hz), 7.63 (d, 1 H, ^3J(HH) = 7 Hz), 7.38 (m, 2 H). MS (*m/e*): found, 225.0153; calc, 225.0153.

2-$ClC_6H_4CH{=}NCH_2CH_2CH_3$ (9f). ^1H NMR (acetone-d_6): δ = 0.94 (t, 3 H, ^3J(HH) = 7 Hz), 1.66 (sextet, 2 H, ^3J(HH) = 7 Hz, H^b), 3.60 (t, 2 H, ^3J(HH) = 7 Hz), 8.70 (s, 1 H), 8.06 (d, 1 H, ^3J(HH) = 7 Hz), 7.40 (m, 3 H). MS (*m/e*): found, 181.0663; calc, 181.0658.

$C_6H_5CH{=}NC_6H_5$ (9a). ^1H NMR: δ = 8.57 (s, 1 H), 7.97 (m, 2 H), 7.36 (m, 8 H). MS (*m/e*): found, 181.0893; calc, 181.0891.

[$PtMe_2$(2-$NO_2C_6H_4CH{=}NCH_2CH_2NMe_2$)] (3e). To a solution of complex **2** (72.0 mg) in acetone (20 mL) was added a solution of ligand **1e** (93.4 mg) in acetone, and the resulting solution was stirred. The reaction mixture turned yellow and then dark purple. The mixture was stirred for 8 h, and the solvent was removed under vacuum to give a purple solid. This was washed with pentane (2 × 20 mL) and recrystallised from acetone/ether. Mp: 117 °C. Anal. Calc for $C_{13}H_{21}N_3O_2Pt$: C, 33.8; H, 4.55; N, 9.1. Found: C, 33.3; H, 4.6; N, 8.7.

Similarly were prepared the following.

[$PtMe_2$(2-NO_2-5-$ClC_6H_3CH{=}NCH_2CH_2NMe_2$)]. Anal. Calc for $C_{13}H_{20}ClN_3O_2Pt$: C, 32.5; H, 4.2; N, 8.7. Found: C, 32.7; H, 4.6; N, 8.6.

[$PtMe_2$(2-$MeOC_6H_4CH{=}NCH_2CH_2NMe_2$)]. Anal. Calc for $C_{14}H_{24}N_2OPt$: C, 39.0; H, 5.6; N, 6.5. Found: C, 38.4; H, 5.3; N, 6.6.

[$PtBrMe_2$($C_6H_4CH{=}NCH_2CH_2NMe_2$)] (5b). To solution of **2** (55.0 mg, 9.58 × 10^{-5} mol) in acetone (60 mL) was added 2 equiv of ligand **1d** (61.8 mg). The solution immediately turned yellow. The mixture was stirred overnight, the solvent was removed under vacuum, and pentane was added to the resulting oily product to precipitate a yellowish powder, which was washed with cold ether (2 × 20 mL) and cold pentane (1 × 15 mL) and recrystallized from CH_2Cl_2/pentane: yield 62%; mp 160 °C dec. Anal. Calc for $C_{13}H_{21}BrN_2Pt$: C, 32.5; H, 4.4; N, 5.8. Found: C, 31.9; H, 4.5; N, 5.5. ^{13}C NMR: δ = −9.5 (s, ^1J(PtC) = 697 Hz, MePt), −4.0 (s, ^1J(PtC) = 646 Hz, MePt), 41.8 (s, MeN), 45.1 (s, MeN), 46.9 (s, ^2J(PtC) = 15 Hz, CH_2), 61.9 (s, CH_2), 164.3 (s, ^2J(PtC) = 51 Hz, CH imine), 135.6 (^1J(PtC) = 943, CPt), 143.1 (C), {δ = 126.6 (J(PtC) = 55.7 Hz), 125.6 (s, J(PtC) = 42.2 Hz), 124.6 (s, J(PtC) = 34 Hz), 118.8 (aryl CH)}. Similarly were prepared the following.

[$PtClMe_2$($C_6H_4CH{=}NCH_2CH_2NMe_2$)] (5a). Anal. Calc for $C_{13}H_{21}ClN_2Pt$: C, 35.8; H, 4.9; N, 6.4. Found: C, 35.4; H, 4.6; N, 6.4.

[$PtClMe_2$(2-$FC_6H_3CH{=}NCH_2CH_2NMe_2$)] (7a). Anal. Calc for $C_{13}H_{20}ClFN_2Pt$: C, 34.4; H, 4.4; N, 6.2. Found: C, 34.0; H, 4.3; N, 5.9.

[$PtClMe_2$(2-$ClC_6H_3CH{=}NCH_2CH_2NMe_2$)] (7b). Anal. Calc for $C_{13}H_{20}Cl_2N_2Pt$: C, 33.2; H, 4.3; N, 6.0. Found: C, 33.1; H, 4.2; N, 5.8.

[$PtClMe_2$(2-$NO_2C_6H_3CH{=}NCH_2CH_2NMe_2$)] (7c). Anal. Calc for $C_{13}H_{20}ClN_3O_2Pt$: C, 32.5; H, 4.2; N, 8.7. Found: C, 32.5; H, 3.9; N, 8.5.

[$PtClMe_2$(3-$ClC_6H_3CH{=}NCH_2CH_2NMe_2$)] (8). Anal. Calc for $C_{13}H_{20}Cl_2N_2Pt$: C, 33.2; H, 4.3; N, 6.0. Found: C, 33.0, H, 4.1; N, 6.0.

[$PtBrMe_2(PPh_3)$($C_6H_4CH{=}NCH_2CH_2NMe_2$)]. To a solution of **5b** (53.2 mg) in acetone-d_6 (0.5 mL) was added 1 equiv of PPh_3 (29.1 mg), and the solution was allowed to stir for 30 min. ^1H and ^{31}P NMR spectra were then recorded. The solvent was removed under vacuum, and a white solid remained, which was recrystallized from CH_2Cl_2/pentane. Mp: 157 °C. Anal. Calc for $C_{31}H_{36}BrN_2PPt$: C, 50.1; H, 4.85; N, 3.8. Found: C, 50.3; H, 5.0; N, 3.5. ^1H NMR (acetone-d_6): δ = 1.01 (d, 3 H, ^2J(PtH) = 60 Hz, ^3J(PH) = 8 Hz, Me^aPt), 1.38 (d, 3 H, ^2J(PtH) = 68 Hz, ^3J(PH) = 8 Hz, Me^bPt), 2.12 (s, 6 H, Me), 8.34 (s, 1 H, ^3J(PtH) = 50 Hz, CH=N], 4.1, 3.4 (m, 2 H), 2.7, 2.3 (m, 2 H), 6.8 (m, 4 H), 7.3 (m, phenyl protons). ^{31}P NMR: δ = −9.32 (s, ^1J(PPt) = 1007 Hz).

[$PtBrMe(CD_3)$($C_6H_4CH{=}NCH_2CH_2NMe_2$)]. Excess CD_3Br (0.3 mL) was added to a solution of **4a** (49.4 mg) in an NMR tube, all reagents at −80 °C. The solution immediately turned from bright red to a pale yellow. ^1H NMR spectra were recorded at −80, −40, and −10 °C as the solution was warmed.

[$PtIMe_2$($C_6H_4CH{=}NCH_2CH_2NMe_2$)] (5c). To a solution of **4a** (39.2 mg) in acetone was added excess methyl iodide (0.5 mL). The solution immediately turned pale yellow and was allowed to stir for 1 h. The solvent volume was reduced, and ether (10 mL) was added to give a white solid, which was washed with ether (2 × 10 mL) and dried under vacuum. Mp: 152 °C dec. Anal. Calc for $C_{13}H_{21}IN_2Pt$: C, 30.3; H, 4.08; N, 5.14. Found: C, 30.6; H, 4.07; N, 5.14. ^1H NMR (acetone-d_6): δ = 0.75 (s, 3 H, ^2J(PtH) = 72 Hz, Me^aPt), 1.14 (s, 3 H, ^3J(PtH) = 64 Hz, Me^bPt), 2.63 (t, 3 H, ^3J(PtH) = 16 Hz), 3.16 (t, 3 H, ^3J(PtH) = 12 Hz), 8.6 (s, 1 H, ^3J(PtH) = 48 Hz, CH=N), 7.4 (d, 1 H, ^3J(HH) = 8 Hz), 7.17 (d, 1 H, ^3J(HH) = 4 Hz, ^3J(PtH) = 40 Hz), 6.95 (m, 2 H), 4.2 (b), 3.4 (b). ^{13}C NMR: δ = 9.0 (Me^a or Me^bPt), −3.2 (Me^a or Me^bPt), 47.1 (MeN), 53.1 (MeN), 52.4 (CH_2), 68.4 (CH_2), 170 (^2J(PtC) = 48 Hz, CH imine), 148 (C), 140 (C), 132 (J(PtC) = 42 Hz, CH), 131 (J(PtC) = 62 Hz, CH), 130 (J(PtC) = 33 Hz, CH), 124 (J(PtC) = 6 Hz, CH).

[$PtMe(C_6H_4CH{=}NCH_2CH_2NMe_2$)] (4a). To a solution of **2** (46 mg) in acetone (20 mL) was added ligand **1a** (28.1 mg) in acetone (5 mL), and the solution was allowed to stir for 14 days. The solution turned red. The solvent was removed under vacuum, and the resulting oily product was triturated with acetone (0.25 mL) and pentane (2 mL) to give a red powder, which was filtered and dried under vacuum. Mp: 148 °C. Anal. Calc for $C_{12}H_{18}N_2Pt$: C, 37.4; H, 4.7; N, 7.3. Found: C, 37.2; H, 4.5; N, 7.1. ^1H NMR: δ = 0.79 (s, 3 H, ^2J(PtH) = 80 Hz, MePt), 2.7 (s, 6 H, ^3J(PtH) = 20 Hz, MeN), 3.1 (t, 2 H, ^3J(HH) = 12 Hz), 4.0 (t, 3 H, ^3J(HH) = 12 Hz), 8.56 (s, 1 H, ^3J(PtH) = 62 Hz, CH=N), 7.44 (d, 1 H, ^3J(HH) = 7 Hz, ^3J(PtH) = 64 Hz), 7.22 (d, 1 H, ^3J(HH) = 7 Hz), 7.04 (t, 1 H, J(HH) = 7 Hz), 6.84 (t, 1 H, J(HH) = 7 Hz). ^{13}C NMR: δ = −11.6 (^1J(PtC) = 810, MePt), 48.8 (MeN), 52.7 (^2J(PtC) = 30 Hz, CH_2), 68.4 (CH_2), 168 (^2J(PtC) = 97 Hz, CH imine), 153 (C), 147 (^1J(PtC) = 1200 Hz, CPt), 122 (CH), 134 (J(PtC) = 94 Hz, CH), 131 (J(PtC) = 71 Hz, CH), 128 (J(PtC) = 41 Hz, CH).

Similarly prepared were the following.

[$PtMe$(2-$FC_6H_3CH{=}NCH_2CH_2NMe_2$)] (4b). Anal. Calc for $C_{12}H_{17}FN_2Pt$: C, 35.7; H, 4.2; N, 6.95. Found: C, 35.6; H, 4.6; N, 6.5. ^1H NMR: δ = 0.84 (s, 3 H, ^2J(PtH) = 80 Hz, MePt), 2.76 (s, 6 H, ^3J(PtH) = 22 Hz, MeN), 3.2 [t, 2 H, ^3J(HH) = 12 Hz), 4.16 (t, 2 H, ^3J(HH) = 12 Hz, ^3J(PtH) = 20 Hz), 8.96 (s, 1 H, ^3J(PtH) = 62 Hz, CH=N), 6.55 (m, 1 H), 7.2 (d, 1 H, ^3J(HH) = 8 Hz, ^3J(PtH) = 26 Hz), 7.1 (m, 2 H). ^{13}C NMR: δ = −11.3 (^1J(PtC) = 810 Hz, MePt), 49 (MeN), 53 (^3J(PtC) = 31 Hz, CH_2), 69 (CH_2), 108 (d, J(CF) = 20 Hz, J(PtC) = 20 Hz, C), 129.4 (d, J(CF) = 3.5 Hz, J(PtC) = 90 Hz, CH), 133 (d, J(CF) = 8 Hz, J(PtC) = 86 Hz, CH), 139 (C), 150 (^1J(PtC) = 1205 Hz, CPt), 162 (^2J(PtC) = 102 Hz, CH). ^{19}F NMR: δ = −117 (dd, J(PtF) = 70 Hz, J(FH) = 6 Hz, J(FH) = 10 Hz).

[$PtBrMe_2(SMe_2)${$C_6H_4CHN{=}NC_6H_5$}] (11b). The compound is a yellow solid; mp 120 °C. Anal. Calc for $C_{17}H_{22}BrNPtS$: C, 37.3; H, 4.0, N, 2.6. Found: C, 36.7; H, 3.8; N, 2.6. ^1H NMR acetone-d_6): major isomer, δ = 1.18 (s, ^2J(PtH) = 70 Hz, 3 H, Me^aPt), 1.47 (s, ^2J(PtH) = 72 Hz, 3 H, Me^bPt), 2.02 (s, ^3J(PtH) = 14 Hz, 6 H, MeS), 8.83 (s, ^3J(PtH) = 44 Hz, 1 H, CH=N), 7.4 (m, 9 H, aryl protons); minor isomer, δ = 0.73 (s, ^2J(PtH) = 71 Hz, 3 H, Me^aPt), 1.37 (s, ^2J(PtH) = 70 Hz, 3 H, Me^bPt), 2.16 (s, ^3J(PtH) = 14 Hz, 6 H, MeS), 8.61 (s, ^3J(PtH) = 44 Hz, 1 H, CH=N), 7.4 (m, 9 H, aryl protons).

[$PtClMe_2(SMe_2)${$C_6H_4CH{=}NC_6H_5$}] (11a). The compound is a yellow solid; mp 170 °C dec. Anal. Calc for $PtC_{17}H_{22}NSCl$: C, 40.6; H, 4.4; N, 2.8. Found: C, 41.8; H, 3.9; N, 3.1. ^1H NMR (acetone-d_6): δ = 1.09 (s, ^2J(PtH) = 70 Hz, 3 H, Me^aPt), 1.39 (s, ^2J(PtH) = 72 Hz, Me^bPt), 1.97 (s, ^3J(PtH) = 13 Hz, 6 H, MeS), 8.85 (s, ^3J(PtH) = 42 Hz, 1 H, CH=N), 7.4 (m, 9 H). ^{13}C NMR: δ = 0.7 (^1J(PtC) = 660 Hz, Me^aPt), 18.7 (^1J(PtC) = 606 Hz, Me^bPt), 29.0 (MeS), 175 (J(PtC) = 40 Hz, CH=N), {125, 126, 128, 129, 145, 130 (J(PtC) = 37 Hz), 133 [J(PtC) = 25 Hz], 134 (J(PtC) = 60 Hz), aryl carbons}.

[$PtBrMe_2(SMe_2)$($C_6H_4CH{=}NPr$)] (11d). ^1H NMR (acetone-d_6): δ = 1.01 (s, 3 H, ^2J(PtH) = 71 Hz, Me^aPt), 1.25 (s, 3 H, ^2J(PtH) = 68 Hz, Me^bPt), 2.08 (s, 6 H, ^3J(PtH) = 14 Hz, MeS), 8.7 (s, 1 H, ^3J(PtH) = 47 Hz, CH=N), 7.4 (m, 4 H, aryl protons), 0.93 (t, ^3J(HH) = 10 Hz, H), 4.0, 4.2 (m, 2 H), 1.9 (m, 2 H). ^{13}C NMR: δ = −4.4 (^1J(PtC) = 660 Hz, Me^aPt), 0.4 (s, ^1J(PtC) = 625 Hz, Me^bPt), 11.5, 19.0, 24.1, 61.4, 174 (^2J(PtC) = 48 Hz), 147

(^1JPtC) = 960 Hz, CPt), 145 (CH=N), 132 (J(PtC) = 59 Hz), 131 (J(PtC) = 33 Hz), 129 (J(PtC) = 48 Hz), 125 (J(PtC) = 7 Hz).

[PtClMe$_2$(SMe$_2$){C$_6$H$_4$CH=NPr^i}] (11c). ^{1}H NMR (acetone-d_6): 0.91 (s, 3 H, ^2J(PtH) = 71 Hz, Me^{a}Pt), 1.16 (s, 3 H, ^2J(PtH) = 68 Hz, Me^{b}Pt), 2.1 (s, 6 H, MeS), 0.93 (t, 3 H, ^3J(HH) = 7 Hz), 2.9 (m, 2 H), 3.95, 4.10 (m, 2 H), 7.2 (m, 4 H).

[PtMe(SMe$_2$){C$_6$H$_3$FCH=NC$_6$H$_5$}] (10b). The compound crystallizes as red crystals; mp 125 °C dec. ^{1}H NMR: δ = 1.04 (s, 3 H, ^2J(PtH) = 84 Hz, Me^{a}Pt), 2.10 (s, 6 H, ^3J(PtH) = 26 Hz, MeS), 8.92 (s, 1 H, ^3J(PtH) = 52 Hz, CH=N), 6.75 (m, 1 H), 7.5 (m, 3 H), 7.3 (m, 4 H). ^{19}F NMR: δ = −116 (dd, J(PtF) = 56 Hz, J(FH) = 6 Hz, J(FH) = 10 Hz).

[PtMe(SMe$_2$){C$_6$H$_4$CH=NC$_6$H$_5$}] (10a). The compound crystallizes as orange crystals; mp 158 °C dec. Anal. Calc for C$_{16}$H$_{19}$NPtS: C, 42.5; H, 4.23; N, 3.10. Found: C, 42.7; H, 4.36; N, 3.29. ^{1}H NMR: δ = 1.0 (s, 3 H, ^2J(PtH) = 83 Hz, Me^{a}Pt), 2.2 (s, 6 H, ^3J(PtH) = 26 Hz, MeS), 7.65 (d, ^3J(H^{m}H^n) = 8 Hz, 1 H, ^3J(PtH) = 60 Hz, H^m), {7.5 (m, 3 H), 7.3 (m, 4 H), 7.1 (t, 1 H, J(HH) = 8 Hz), other aryl protons}.

[PtMe(SMe$_2$){C$_6$H$_3$NO$_2$CH=NC$_6$H$_5$}] (10c). The compound is an orange solid; mp 128 °C dec. Anal. Calc for C$_{16}$H$_{18}$N$_2$O$_2$SPt: C, 38.6; H, 3.6; N, 5.6. Found: C, 38.4; H, 3.4; N, 5.3. ^{1}H NMR: 1.06 (s, 3 H, ^2J(PtH) = 83 Hz, Me^{a}Pt), 2.13 (s, 6 H, ^3J(PtH) = 28 Hz, MeS), 9.40 (s, 1 H, ^3J(PtH) = 56 Hz, CH=N), 8.05 (d, 1 H, ^3J(HH) = 8 Hz, ^{3}(*PtH*) = 60 Hz), 7.7 (d, 1 H, ^3J(HH) = 8 Hz), 7.5 (m, 3 H), 7.3 (m, 3 H).

X-ray Structure Analysis. Crystals of [PtClMe$_2$(ClC$_6$H$_3$CH=NCH$_2$CH$_2$NMe$_2$)] (**7b**) were grown from CH$_2$Cl$_2$/pentane. A poor quality yellow block (dimensions 0.42 × 0.34 × 0.61 mm) was chosen and mounted on a glass fiber.

Cell constants and the orientation matrix for data collection were determined by using a CAD4 diffractometer, using 22 reflections in the range $12 < \theta < 15°$. From the systematic absences of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ and from subsequent least-squares refinement, the space group was determined unambiguously to be $P2_12_12_1$ (No. 19). Further details are in Table V.

Data were collected to a maximum of 54° in 2θ. Of 1985 reflections collected, 1898 were unique. Lorentz and polarization corrections were applied. During data collection, the intensities of three standard reflections remained constant (±0.7%), and hence, no decay correction was applied. An empirical absorption correction (DIFABS) was applied.

A total of 1348 reflections with $I > 3\sigma(I)$ were used in the solution and refinement. The structure was solved by using the Patterson method and subsequent difference Fourier syntheses using SDP Plus.[15] In the refinement, hydrogen atoms were included (C–H = 0.95 Å) but restrained to ride on the atom to which they are bonded. The refinement converged to $\Delta/\sigma = 0.02$ with $R = 0.033$. Scattering factors were taken from ref 16; anomalous dispersion effects were included in F_c. The space group is polar, and calculations with each hand led to a slightly lower R factor and better esd's with the model corresponding to the coordinates in Table VI.

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Supplementary Material Available: Tables of general temperature factor expressions, calculated hydrogen atom coordinates, torsion angles, and least-squares planes (5 pages); a table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Electronic Structures of Simplified Polymeric Organosilicon Systems Containing π-Conjugated Moieties

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The electronic structures of several kinds of simplified polymeric organosilicon systems containing a disilanylene (–Si–Si–) or disilenylene (–Si=Si–) unit in the π-conjugated linear organic chain are studied in detail with respect to their optimized geometries on the basis of the one-dimensional tight-binding self-consistent crystal orbital method. The results strongly suggest that in the polymers with the disilanylene unit the electrical conduction mechanism throughout the polymer skeleton should utilize the σ-type crystal orbital as the conduction path and that a special π-type bonding between the Si atom and the attaching substituents could be expected. The fundamental difference between the π-bonding behavior of the silicon-containing polymers and the ordinary organic π-conjugated polymers is also pointed out.

Introduction

Recently, polymeric organosilicon systems have been attracting much attention from both theoretical and experimental points of view,[1] due to their intriguing properties such as semiconducting behavior,[2-4] enhancement of electrical conduction with doping,[5] photoconduction,[6-9]

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