$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$(CH_3) (**7**), and (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)-Ta(DIPP)$_2$Cl (**9**), tables of experimental details, atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles for **1**, **7**, and **9**, tables of torsion angles for **1** and **7**, and ORTEP figures for **1**, **7**, and **9** (56 pages); tables of observed and calculated structure factor amplitudes for **1**, **7**, and **9** (46 pages). Ordering information is given on any current masthead page.

Syntheses and Mechanistic Studies in the Formation of Endo- and Exo-Cyclometalated Platinum Compounds of *N*-Benzylidenebenzylamines

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The bifunctional ligands 2-$XC_6H_4CH{=}NCH_2$-2′-$X'C_6H_4$, and related ligands with more substituents on the aryl rings, react with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] to give cyclometalated complexes [$PtMe_2X(SMe_2)(C_6H_4CHNCH_2$-2′-$X'C_6H_4)$] (**4**) by oxidative addition of C–X bonds (X = Cl, Br), or complexes [$PtMe(SMe_2)(C_6H_4CHNCH_2$-2′-$X'$-$C_6H_4)$] **5** by orthometalation with loss of methane. In both types of compound the iminic functionality is endo to the cycle. Complexes **4** with an exocyclic structure are obtained only for X′ = Br, or for X′ = Cl when the ligand 2,4,6-$C_6H_2(CH_3)_3CH{=}NCH_2$-2′-ClC_6H_4 is used. Compounds **5** with an exocyclic structure are not formed. The following order of reactivity has been deduced: C–Cl endo ≈ C–Br exo > C–H endo > C–Cl exo ≫ C–H exo. Complexes **4** and **5** and the coordination compounds [$PtMe_2(SMe_2)$(2,4,6-$C_6H_2(CH_3)_3CH{=}NCH_2$-2′-XC_6H_4)] (**3**) have been characterized by NMR spectroscopy. Complexes **4** react with PPh_3 to give a displacement reaction of SMe_2 for PPh_3, and the resulting compounds have been characterized by NMR spectroscopy; the compound [$PtMe_2Cl(PPh_3)(C_6H_3ClCHNCH_2C_6H_5)$] (**6c**) has been characterized crystallographically. Complex **6c** crystallizes in the monoclinic space group $P2_1/a$, with a = 17.677 (3) Å, b = 15.495 (3) Å, c = 11.371 (2) Å, β = 104.59 (2)°, and Z = 4. The kinetics of formation of compounds **4** and **5** has been studied. It is suggested that formation of coordination compounds **3** takes place prior to the oxidative addition, which follows first-order kinetics and occurs by a concerted mechanism.

Introduction

A number of synthetic approaches to cyclometalated complexes have been investigated;[1] the earliest method involves thermal activation of a C–H bond. There has been increasing interest in the cyclometalated platinum compounds of N-donor ligands. van Koten has reported the preparation of platinum(II) complexes containing tridentate NCN ligands, which are useful substrates for the study of the oxidative addition of electrophiles to square-planar d^8 metal complexes.[2] Canty and co-workers have also studied the chemistry of cyclometalated platinum compounds with polydentate nitrogen donor ligands containing one or more pyrazol-1-yl groups.[3] The preparation of platinum(IV) cyclometalated compounds of an azobenzene derivative has been described recently by the reaction of the corresponding platinum(II) cyclometalated compound with chlorine or with *m*-chloroperbenzoic acid.[4]

Recently, platinum(II) and platinum(IV) cyclometalated complexes have been obtained by intramolecular oxidative addition of the Ar–X bonds in the compounds [$PtMe_2$(2-$XC_6H_4CHNCH_2CH_2NMe_2$)] and it has been shown that the reactivity of the Ar–X bond follows the inverse order of Ar–X bond energies.[5] The fact that the intramolecular oxidative addition is much easier than the intermolecular process could be related, among other factors, to the presence of the C=N group, which conjugates with the phenyl group in the cycles formed.

In order to evaluate the importance of this factor, we describe the reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) with different *N*-benzylidenebenzylamines in which two different five-membered metallacycles could in principle be obtained, one in which the cycle contains the C=N group (endo) and the other in which it does not (exo).

The oxidative addition of aryl–halogen bonds of *N*-benzylidenebenzylamines to palladium(0) compounds has been reported recently,[6] and for this system, there is a strong tendency to form endocyclic compounds.

Results and Discussion

Syntheses and Characterization of Products. The *N*-benzylidenebenzylamine ligands were prepared by a condensation reaction of the corresponding amine with the

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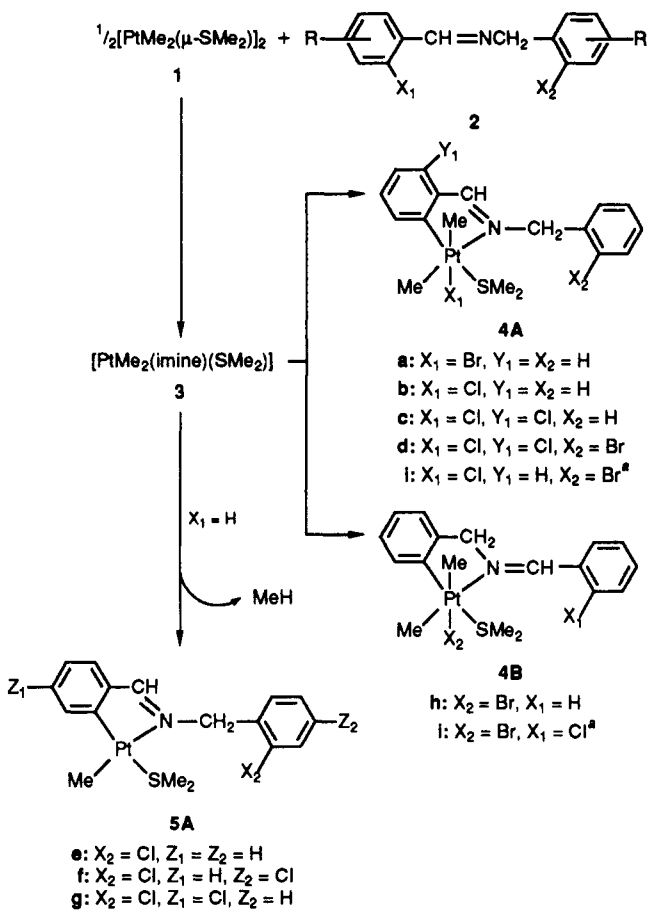
Scheme I



[a] For ligand **i**, a mixture of **4A** and **4B** is obtained.

Table I. ^{1}H NMR Spectra for Compounds [PtMe$_2$X(SMe$_2$)(C^N)] (4) in Acetone-d_6[a]

imine	δ(Me$_a$) (^2J(PtH))	δ(Me$_b$) (^2J(PtH))	δ(CH$_2$) (^2J(HH))	δ(CHN) (^3J(PtH))	δ(SMe$_2$) (^3J(PtH))
a	0.96 (71)	1.30 (69)	5.33 5.41 (14)	8.72 (47)	2.07 (10)
b	0.84 (70)	1.20 (65)	5.18 5.39 (10)	8.68 (45)	1.95 (13)
c	0.84 (70)	1.19 (68)	5.27 5.49 (12)	9.07 (50)	2.01 (13)
d	0.82 (72)	1.17 (67)	5.31 5.49 (10)	9.10 (49)	1.99 (12)
h	1.06 (71)	1.38 (68)	5.40 5.64 (12)	8.74 (45)	2.04 (13)
j	0.78 (72)	1.37 (70)	5.20 5.80 (15)	9.29 (30)	*b*
k	0.62 (76)	1.23 (70)	5.12 5.92 (14)	9.52 (32)	*b*

[a] δ in ppm and J in Hz; reference SiMe$_4$. Legend: Me$_a$, cis to N; Me$_b$, trans to N. [b] Obscured by methyl resonances of the mesityl group.

corresponding aldehyde.[7] They were formed as single isomers which are assumed to have *E* stereochemistry about the C=N bond.

The reaction of these ligands with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (1) in acetone at room temperature gave either platinum(IV) compounds **4** by oxidative addition of C–halogen bonds or ortho-metalated platinum(II) compounds **5** by oxidative addition of C–H bonds followed by reductive elimination of methane (see Scheme I). In each case the reaction was monitored by ^{1}H NMR spectroscopy, and except for ligand **i**, which will be discussed later on, only one final product (**4** or **5**) was formed. Compounds [PtMe$_2$(imine)(SMe$_2$)] (**3**) have not been detected. The oxidative-addition products **4A** in which the metallacycle contains the iminic functionality are obtained when the iminic phenyl ring has at least one chloro or one bromo substituent in an ortho position (ligands **a**–**d**). Selected ^{1}H NMR data for complexes **4A** are given in Table I; two methylplatinum resonances coupled with ^{195}Pt appear at δ 0.82–0.96 ppm (^2J(Pt–CH$_3$) = 70–72 Hz) and δ 1.17–1.30 ppm (^2J(Pt–CH$_3$) = 65.69 Hz). From these values, a *fac*-PtC$_3$ stereochemistry is deduced, as a smaller coupling constant with platinum is expected for a methylplatinum(IV) group trans to carbon[8] and the resonance at lower field with a smaller coupling constant is assigned to the methyl trans to N. It is not possible to distinguish between the two possible isomers with a *fac*-PtC$_3$ stereochemistry **4** and **4′** (Figure 1), as similar values are expected for ^2J(Pt–CH$_3$) trans to SMe$_2$ or trans to X. In each case only one isomer is formed and, assuming that the oxidative addition of the aryl–hydrogen bond occurs with cis stereochemistry at platinum, structure **4** is proposed.

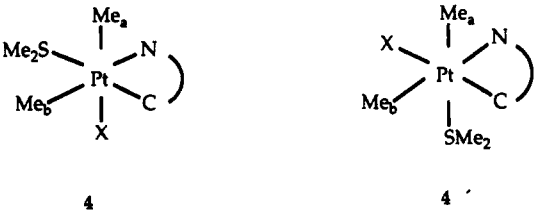


Figure 1. Two possible isomers for compounds **4**.

Table II. ^{1}H NMR Spectra for Compounds [PtMe(SMe$_2$)(C^N)] (5) in Acetone-d_6[a]

imine	δ(Me) (^2J(PtH))	δ(CH$_2$) (^3J(PtH))	δ(CHN) (^3J(PtH))	δ(SMe$_2$) (^3J(PtH))
e	0.91 (80)	5.22 (12)	8.81 (53)	2.04 (27)
f	0.94 (83)	5.15 (14)	8.79 (50)	2.07 (27)
g	0.91 (83)	5.26 (13)	8.92 (55)	2.06 (28)

[a] δ in ppm and J in Hz; reference SiMe$_4$.

For ligands **e**–**g**, the C–Cl bond in the benzylic ring was not activated, and an ortho metalation took place in the iminic phenyl ring, with elimination of methane, to give compounds **5A**. That is, activation of a C–H bond to give an endo metallacycle is easier than activation of the weaker C–Cl bond to give an exo metallacycle. Selected ^{1}H NMR data for complexes **5** are given in Table II. There is a single methylplatinum resonance at δ 0.91–0.94 ppm with ^2J(Pt–CH$_3$) = 80–83 Hz. These values are characteristic of platinum(II) complexes with the methyl group trans to N.[9]

Activation of the C–Br bond in the benzylic ring was achieved for ligand **h**, and an oxidative-addition platinum(IV) product with the exocyclic structure **4B** was obtained. Activation of a C–H bond to give a platinum(IV) hydride complex is ruled out, since no resonance appears in the hydride region in the ^{1}H NMR spectrum. ^{1}H NMR data for this compound are given in Table I and are similar to the values obtained for compounds **4A**.

When the ligand **i**, containing a Cl substituent in the iminic ring and a Br substituent in the benzylic ring, is reacted with complex **1**, an approximately equimolecular mixture of compounds **4A** and **4B** is obtained. Two sets

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Table III. ^{1}H NMR Spectra for Compounds [$PtMe_2(SMe_2)(N\frown C)$] (3) in Acetone-d_6[a]

imine	$\delta(Me_a)$ (^2J(PtH))	$\delta(Me_b)$ (^2J(PtH))	$\delta(CH_2)$ (^3J(PtH))	δ(CHN) (^3J(PtH))	$\delta(SMe_2)$ (^3J(PtH))
j	0.15 (86)	0.50 (86)	5.30 (19)	9.25 (50)	1.52 (28)
k	0.13 (86)	0.67 (83)	5.10 (*b*)	9.30 (50)	1.50 (28)
l	0.15 (86)	0.49 (83)	5.14 (22)	9.44 (50)	1.41 (28)
m	0.17 (86)	0.46 (83)	5.15 (*b*)	9.46 (50)	1.48 (25)
n	0.15 (83)	0.48 (83)	5.25 (22)	9.50 (50)	1.40 (28)
o	0.15 (83)	0.48 (80)	5.34 (*b*)	9.54 (46)	1.38 (26)

[a] δ in ppm and J in Hz; reference $SiMe_4$. Legend: Me_a, trans to N; Me_b, trans to SMe_2. [b] Not observed.

of methylplatinum resonances coupled with ^{195}Pt appear in the ^{1}H NMR spectrum at δ 1.07 (^2J = 70 Hz), 1.42 ppm (^2J = 69 Hz) and δ 1.19 (^2J = 69 Hz), 1.33 ppm (^2J = 67 Hz). These values are well within the range of values obtained for the compounds **4A** and **4B**. The possibility of a mixture of isomers **4** and **4'** is ruled out, since in all other reactions only one isomer is formed. Separation of the two products was not attempted. This result shows that activation of a C–Cl bond in the iminic phenyl ring and activation of a C–Br bond in the benzylic ring are equally favored.

For ligand **d**, with two Cl substituents in ortho positions in the iminic phenyl group and a Br substituent in the benzylic phenyl ring, compound **4A** was obtained exclusively, as mentioned earlier. The reaction of this compound with $AgBF_4$ gave only AgCl, and no AgBr was formed; thus, C–Cl was the only activated bond in this case. In comparison with ligand **i**, the presence of a second chloro substituent at the ortho position in the iminic ring drives the reaction to the exclusive formation of an endocycle. The electron-withdrawing effect of the chloro substituent might account for this result. Thus, changes in the substituents have a decisive effect on the reactivity of these ligands.

Exocyclic compounds are only obtained when the weaker C–Br bond is present in the benzylic ring.

In order to achieve activation of C–Cl and C–H bonds to give exocycles, imine ligands with the ortho positions at the iminic ring blocked with methyl groups were used.

The reactions of these ligands with **1** gave the compounds **3**, in which the imine ligand is coordinated to platinum and which were characterized by ^{1}H NMR spectroscopy. For the previous series of imines, it was not possible to detect this kind of compound, but in this case the presence of the methyl groups enhances the basic nature of the nitrogen and probably hinders further reaction. These two factors allow the detection of such coordination compounds. Selected ^{1}H NMR data for these compounds are given in Table III; two methyl resonances appear at δ 0.13–0.17 ppm and at δ 0.46–0.67 ppm, with ^2J(Pt–CH_3) = 83–86 and 80–86 Hz, respectively. These values are characteristic of platinum(II) methyl compounds. The iminic proton at δ 9.25–9.54 ppm also couples with ^{195}Pt, (^3J(Pt–H) = 46–50 Hz).

For ligands **j** and **k**, a further reaction took place to give the oxidative-addition product **4B** (see Scheme II). Thus, activation of a C–Cl bond to give exocyclic compounds was achieved. Selected ^{1}H NMR data for these compounds are given in Table I and are similar to the values obtained for compounds **4A**, except for the iminic proton, which appears at lower field (δ 9.29–9.52 ppm) with an smaller coupling constant with platinum (^3J(Pt–H) = 30–32 Hz). These data are consistent with a $E \rightarrow Z$ isomerization of the imine. Usually imines exist in the more stable E form, from which both endo- and exocycles can be formed, while only exocycles are possible for the Z form (Figure 2). In

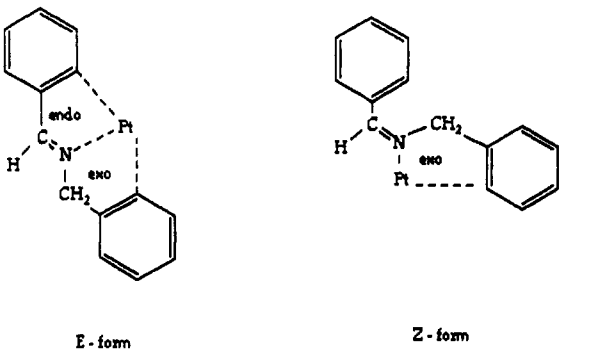
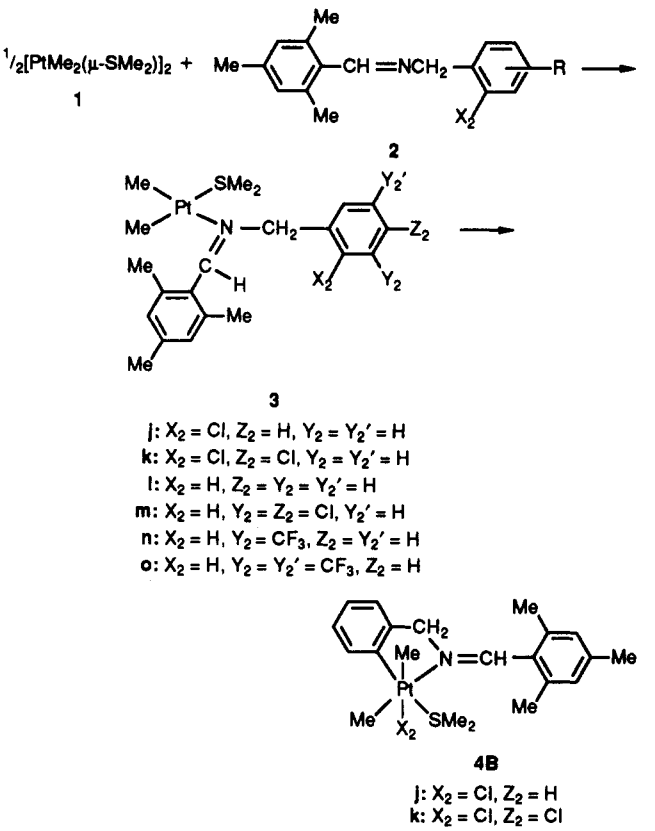


Figure 2. Two possible conformations of the iminic ligands.

Scheme II



the E form a larger coupling constant between H and Pt nuclei, mutually trans, is expected (45–50 Hz) than for the Z form (30–32 Hz). The $E \rightarrow Z$ isomerization for ligands **j** and **k** can be related with the steric crowding due to the mesityl group as the isomerization was not observed for ligand **h**, which also gave an exocyclic compound. Such isomerization was reported for cyclopalladated compounds.[10]

For ligand **l**, activation of C–H bonds in the benzylic phenyl ring was not achieved. As it has been reported that the intramolecular oxidative addition at tungsten[11] or at platinum[5] occurs by a nucleophilic pathway and is greatly accelerated by electron-withdrawing groups, ligands bearing electron-withdrawing groups in different positions were tested (ligands **m–o**). The reaction of [$Pt_2Me_4(\mu$-$SMe_2)_2$] with these ligands was monitored by ^{1}H NMR

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Table IV. ^{1}H and ^{31}P NMR Data for Compounds [$PtMe_2X(PPh_3)(C\frown N)$] (6) in Acetone-$d_6$[a]

imine	$\delta(Me_a)$ (^2J(PtH)) [J(PH)]	$\delta(Me_b)$ (^2J(PtH)) [J(PH)]	$\delta(CH_2)$ (^2J(HH))	δ(CHN) (^3J(PtH))
a	0.91 (60) [7.8]	1.43 (70) [7.8]	4.5 5.4 (16)	8.2 (50)
c	0.78 (60) [8.0]	1.31 (68) [8.0]	4.7 5.4 (16)	8.5 (52)
h	0.90 (60) [7.8]	1.42 (67) [7.8]	4.8 5.5 (17)	8.2 (50)

imine	δ(P)	J(PPt)
a	−7.64	1008
c	−6.59	998
h	−7.67	1004

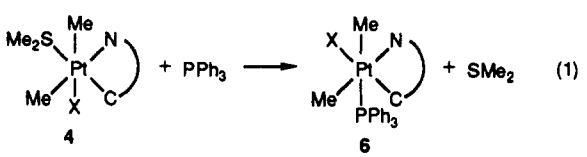
[a] δ in ppm and J in Hz; ^{1}H NMR reference $SiMe_4$ and ^{31}P NMR reference H_3PO_4 (85%). Legend: Me_a, trans to P; Me_b, trans to N.

spectroscopy, and in all cases, formation of complexes **3** took place, but they could not be isolated in a pure form due to their low stability. Activation of C–H bonds was not observed.

Activation of the methyl groups ortho to the mesityl group to give six-membered cycles was reported for palladium[12] in the reaction of similar ligands with palladium acetate in refluxing acetic acid but did not take place in these systems. This is not unexpected, since palladium reacts by an electrophilic pathway and platinum, in this system, by a nucleophilic pathway[13] and examples of C–H bond oxidative addition are much more numerous for aromatic than for aliphatic carbons.[14]

The reaction of cyclometalated compounds with phosphines has been widely studied and, depending on the nature of the cycle, cleavage of the metal–nitrogen bond may be achieved.[10]

Compounds **4a,c,h** react with triphenylphosphine according to eq 1. Even when using an excess of triphenylphosphine cleavage of the metallacycle was not observed.



4 6 (1)

Compounds **6** were characterized by ^{1}H and ^{31}P NMR spectroscopy (Table IV). Two methylplatinum resonances appear at δ 0.78–0.91 ppm (^2J(Pt–H) = 60 Hz) and δ 1.31–1.43 ppm (^2J(Pt–H) = 67–70 Hz) both coupled with the phosphorus atom. The decrease in the coupling constant of the axial methyl with platinum suggests structure **6** with the methyl group trans to PPh_3.

Complex **6c** was also characterized crystallographically. The crystal structure is composed of discrete molecules separated by van der Waals distances. Crystallographic data are given in the Experimental Section, atomic coordinates are in Table V, and bond distances and angles are in Table VI. The structure is shown in Figure 3 and confirms the geometry predicted from the spectroscopic studies. In particular, the C=N group is endo to the cycle, and the three carbon donor ligands adopt a *fac*-PtC_3 geometry as found in related structures.[5] The coordination sphere of platinum is distorted octahedral due to the metallacycle and to the presence of the bulky PPh_3 ligand.

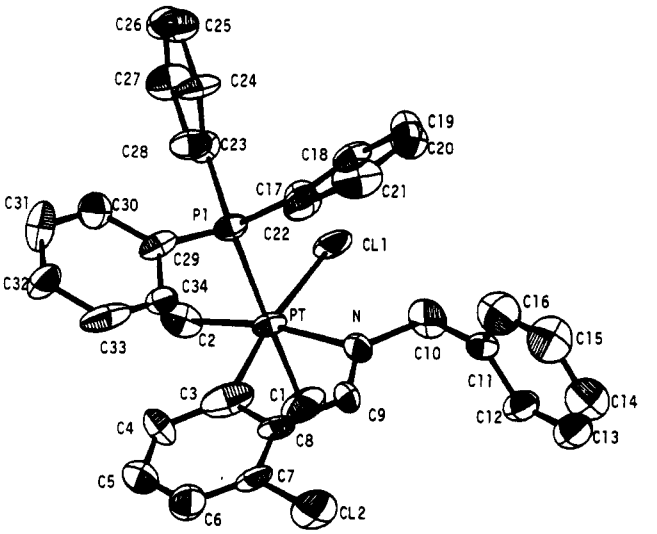


Figure 3. View of the structure of compound **6c**.

The angles between adjacent atoms in the coordination sphere of platinum lie in the range 80.4 (4)–95.9 (3)°; the smallest angle corresponds to the metallacycle, while the largest angles correspond to P(1)–Pt–C(3) = 95.9 (3)° and P(1)–Pt–N = 94.8 (2)°. The Cl(1), N, C(2), and C(3) atoms are on a plane, while the platinum atom deviates 0.107 Å from this plane. The metallacycle is planar, and the dihedral angle with the coordination plane is 4.7°. All bond distances are in the expected range. The Pt–C(3) bond length (2.027 (10) Å) is similar to the platinum–aryl carbon bond length in related structures.[2,4,5] The Pt–Me distance is slightly longer for the methyl trans to the phosphorus atom (2.097 (10) Å) than for the methyl trans to the nitrogen atom (2.048 (9) Å), in agreement with the ^{1}H NMR data.

According to the structure described for compound **6**, either an isomerization takes place during the displacement reaction of SMe_2 for PPh_3 or the actual stereochemistry of the dimethyl sulfide complexes is **4'**. In the latter case, the formation of **4** by concerted oxidative addition of C–X bonds would be followed by a fast isomerization process.

Mechanistic Studies. The reaction of [$Pt_2Me_4(\mu$-$SMe_2)_2$] with several imine ligands was studied kinetically in acetone solution by means of UV–visible spectroscopy. Only Pt(II) cyclometalated complexes (**5e–g**) show definite absorption maxima in acetone solution (λ = 390 nm (1800–1900 M^{-1} cm^{-1}) and λ = 368 nm (2100–2300 M^{-1} cm^{-1})), the rest of the compounds showing only an increasing absorbance from 370 to 330 nm, whereafter the acetone background cannot be subtracted. At the working wavelength an increase of the extinction coefficient from ca. 50 M^{-1} cm^{-1} to ca. 2000 M^{-1} cm^{-1} occurs. The observed rate was [imine]-dependent, and when pseudo-first-order conditions were used ([Pt_2]:[imine] $\ll$ 20), well-behaved first-order absorbance versus time traces were obtained and no dependence on platinum complex concentration was observed in the range of concentrations used ((5–10) $\times$ 10^{-4} M). Table i (supplementary material) collects all k_{obs} values obtained as a function of imine concentration and temperature for each ligand used. Figure 4 shows a typical k_{obs} versus [imine] plot, from which a rate law such as $k_{obs} = k[\text{imine}]/(K + [\text{imine}])$ can be associated.[15]

Small quantities of added SMe_2 produced a definite decrease in the k_{obs} values, indicating that the dissociation

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Table V. Atomic Coordinates (×10⁴; Pt ×10⁵) with Estimated Standard Deviations

	x/a	y/b	z/c		x/a	y/b	z/c
Pt	37595 (2)	15335 (2)	21553 (3)	C(31)	6859 (5)	-357 (6)	3196 (10)
Cl(1)	3873 (1)	420 (1)	3685 (2)	C(32)	6450 (6)	-1127 (7)	2931 (9)
Cl(2)	3422 (2)	5090 (2)	1617 (3)	C(33)	5652 (6)	-1134 (6)	2476 (10)
P(1)	5168 (1)	1486 (1)	2430 (2)	C(34)	5249 (5)	-342 (5)	2349 (10)
C(1)	2548 (5)	1503 (7)	1955 (12)	H(1)	2406 (5)	992 (7)	2508 (12)
C(2)	3582 (5)	654 (6)	769 (9)	H(1)′	2254 (5)	1390 (7)	1014 (12)
C(3)	3569 (5)	2542 (6)	982 (11)	H(1)″	2359 (5)	2114 (7)	2241 (12)
C(4)	3453 (6)	2529 (7)	-283 (9)	H(2)	4136 (5)	491 (6)	586 (9)
C(5)	3334 (7)	3271 (7)	-930 (11)	H(2)′	3199 (5)	928 (6)	-37 (9)
C(6)	3341 (6)	4079 (7)	-348 (11)	H(2)″	3318 (5)	79 (6)	1026 (9)
C(7)	3424 (5)	4101 (5)	867 (10)	H(4)	3462 (6)	1922 (7)	-747 (9)
C(8)	3535 (5)	3351 (5)	1568 (9)	H(5)	3229 (7)	3247 (7)	-1907 (11)
C(9)	3660 (5)	3322 (6)	2902 (9)	H(6)	3283 (6)	4669 (7)	-869 (11)
N	3791 (4)	2576 (4)	3418 (7)	H(9)	3646 (5)	3898 (6)	3431 (9)
C(10)	3829 (7)	2435 (6)	4703 (10)	H(10)	3895 (7)	1896 (6)	5322 (10)
C(11)	3782 (5)	3250 (6)	5388 (8)	H(13)	2455 (6)	4560 (6)	6209 (10)
C(12)	3063 (5)	3580 (6)	5484 (10)	H(14)	3637 (7)	5381 (6)	7154 (11)
C(13)	3018 (6)	4332 (6)	6131 (10)	H(15)	4926 (6)	4814 (8)	7048 (11)
C(14)	3676 (7)	4786 (6)	6679 (11)	H(16)	5026 (7)	3484 (8)	5948 (11)
C(15)	4401 (6)	4469 (8)	6606 (11)	H(18)	6070 (6)	870 (5)	733 (10)
C(16)	4456 (7)	3719 (8)	5983 (11)	H(19)	6547 (7)	1581 (7)	-845 (11)
C(17)	5527 (5)	1998 (5)	1239 (9)	H(20)	6130 (6)	3062 (8)	-1482 (10)
C(18)	5939 (6)	1544 (5)	542 (10)	H(21)	5421 (6)	3905 (7)	-267 (12)
C(19)	6185 (7)	1934 (7)	-376 (11)	H(22)	4985 (5)	3217 (5)	1408 (8)
C(20)	5973 (6)	2775 (8)	-711 (10)	H(24)	5445 (5)	965 (5)	4884 (10)
C(21)	5562 (6)	3237 (7)	-43 (12)	H(25)	6152 (6)	1598 (7)	6846 (9)
C(22)	5324 (5)	2852 (5)	913 (8)	H(26)	6776 (6)	3031 (7)	6911 (10)
C(23)	5679 (5)	2019 (5)	3833 (8)	H(27)	6701 (6)	3793 (7)	5001 (13)
C(24)	5722 (5)	1588 (5)	4902 (10)	H(28)	6041 (5)	3181 (6)	3047 (10)
C(25)	6121 (6)	1947 (7)	6014 (9)	H(30)	6786 (5)	1013 (6)	3273 (10)
C(26)	6474 (6)	2745 (7)	6055 (10)	H(31)	7488 (5)	-364 (6)	3518 (10)
C(27)	6425 (6)	3169 (7)	4976 (13)	H(32)	6746 (6)	-1732 (7)	3083 (9)
C(28)	6053 (5)	2833 (6)	3874 (10)	H(33)	5339 (6)	-1732 (6)	2224 (10)
C(29)	5661 (4)	435 (5)	2626 (8)	H(34)	4620 (5)	-331 (5)	2032 (10)
C(30)	6466 (5)	416 (6)	3054 (10)				

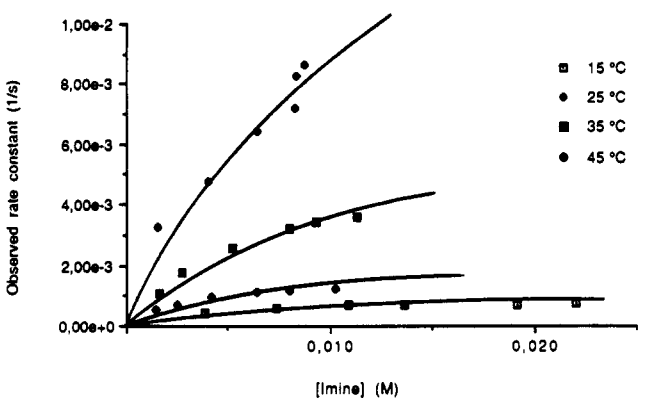


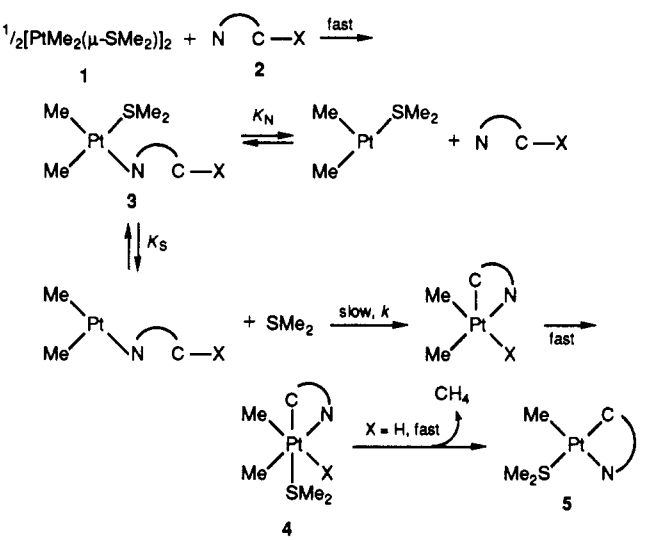
Figure 4. k_{obs} versus [imine] plot for reaction of 1 with imine e.

of SMe_2 plays an important role in the metalation process. On the other hand, the well-behaved absorbance versus time first-order traces are indicative of the absence of a dimer ⇄ monomer slow reaction.

Scheme III is proposed for the overall process, in agreement with the experimental data obtained.

Coordination of the iminic nitrogen to platinum in compound 1 to yield a monomeric species is fast;[16] such compounds have been detected by ^1H NMR spectroscopy for some of the reactions studied. This monomeric tetracoordinate complex must be in equilibrium with two tricoordinate species in order to explain the data obtained. In one, the imine ligand has been lost, and in the other, the SMe_2 stabilizing ligand has dissociated. Such equilibria to form $[PtMe_2(SMe_2)]$ and $[PtMe_2(imine)]$ account for

Scheme III



the [imine] dependence and the $[SMe_2]$ retardation, respectively. These monomeric tricoordinate species have already been postulated in some reaction mechanisms of the dimer 1,[17] and they also explain the decomposition of compound 1 in solution when no further reaction takes place as for ligands l–o.

From Scheme III rate law I can be obtained where $K_S = [[PtMe_2(imine)]][SMe_2]/[[PtMe_2SMe_2(imine)]]$ and $K_N = [[PtMe_2SMe_2]][imine]/[[PtMe_2SMe_2(imine)]]$.

In the absence of added SMe_2 the $[SMe_2]$ term becomes negligible when compared with K_S and expression I be-

(16) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1991**, *406*, 261.

(17) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

$$k_{obs} = \frac{\dfrac{kK_S}{K_S + [SMe_2]}[\text{imine}]}{\dfrac{K_N[SMe_2]}{K_S + [SMe_2]} + [\text{imine}]} \qquad (I)$$

comes $k_{obs} = k[\text{imine}]/((K_N[SMe_2]/K_S) + [\text{imine}])$, where $K_N[SMe_2]/K_S = [[PtMe_2SMe_2]][\text{imine}]/[[PtMe_2(\text{imine})]]$ now represents the relative amount of tricoordinate $[PtMe_2SMe_2]$ with respect to $[PtMe_2(\text{imine})]$ under the conditions of our study. Table VII collects all k and $K_N[SMe_2]/K_S$ values obtained for the systems studied at different temperatures, as well as the thermal activation parameters derived from Eyring plots. When SMe_2 is added, the $[SMe_2]$ term is no longer negligible and a decrease in k_{obs} is observed (Table i, supplementary material).

From the values of Table VII, it is clear that the relative ratio from equilibria N and S favors the dissociation of the imine versus that of the SMe_2 for all complexes to approximately the same extent ([imine] = ca. 5×10^{-3} M), as would be expected from the stronger soft–soft bond of the latter. Furthermore, Table VII shows that when the reaction was carried out in toluene solution, the reaction first-order rate constant was the same as that obtained for acetone solution, indicating the "true" nature of the tricoordinate species. Nevertheless, for this solvent the ratio $K_N[SMe_2]/K_S$ is somewhat larger (giving lower k_{obs} values; see Table i, supplementary material) indicating that, in toluene solution and at this imine concentration range, the $[[PtMe_2SMe_2]]/[[PtMe_2(\text{imine})]]$ ratio becomes larger than in acetone. The activation enthalpy and entropy values are in the same range for all the systems studied, indicating a common mechanism for all reactions.[18] On average, activation enthalpy values follow the trend of the C–X bond energies (C–H > C–Cl > C–Br)[19] for both exo- and endocycles, although they are smaller for the exocycles, probably indicating a better "space distribution" for the reaction to take place. Interestingly, reaction with ligands **c**, **f**, and **g** shows that the presence of chloro substituents at the 2- and 4-positions of the benzylic ring, or the 4- and 6-positions of the iminic ring, does not affect the kinetic parameters for benzylic or iminic metalation reactions.

All the activation entropy values are clearly negative, in agreement with a concerted mechanism with a highly ordered transition state, allowing a tricentered C–Pt–X interaction.[13] In this respect, activation entropy values are more negative for the exocycles, as the more flexible benzylic ring should adopt an ordered conformation that allows lower activation enthalpy values (Table VII). As a result, it seems that the entropic factor could be responsible for the favorable formation of endo- versus exocycles, given the fact that the enthalpic changes would favor the contrary. On the other hand, the absence of solvent dependence for the cyclometalation step confirms the concerted nature of the intimate mechanism for the reaction.

Conclusions

The imine functionality appears to be quite important in directing the regiochemistry of the C–X bond activation. Thus, the formation of endocycles is more favored than formation of exocycles. This results in activation of a C–H bond (112 kcal/mol) to give an endocycle in preference to activation of a weaker C–Cl bond (86 kcal/mol) to give an exocycle, as for ligands e–g. For the imines with the ortho positions at the iminic ring blocked with methyl groups, activation of C–Cl bonds in the benzylic ring was achieved while activation of a C–H bond was not successful. The following order of reactivity is deduced:

C–Cl endo ≈ C–Br exo > C–H endo > C–Cl exo ≫ C–H exo

The effect of electron-withdrawing substituents on the imine ligand is not decisive in directing the reaction.

From the kinetic studies a concerted mechanism is proposed for the intramolecular oxidative addition of both C–halogen and C–H bonds. Entropic factors favor the intramolecular versus the intermolecular process and might be responsible for the different reactivities of the C–X bonds in the saturated or the unsaturated arm of the imine. However, thermodynamic aspects related with endo nature

Table VI. Bond Lengths (Å) and Angles (deg) for 6c

Cl(1)–Pt	2.422 (2)	C(31)–C(30)	1.372 (13)
P(1)–Pt	2.431 (2)	C(32)–C(31)	1.388 (14)
C(3)–Pt	2.027 (10)	C(33)–C(32)	1.376 (14)
N–Pt	2.152 (7)	C(34)–C(33)	1.409 (12)
C(1)–Pt	2.097 (10)	C(8)–C(3)	1.429 (13)
C(2)–Pt	2.048 (9)	C(4)–C(3)	1.401 (16)
C(17)–P(1)	1.816 (11)	C(7)–C(8)	1.394 (12)
C(23)–P(1)	1.821 (8)	C(9)–C(8)	1.478 (15)
C(29)–P(1)	1.836 (8)	Cl(2)–C(7)	1.754 (9)
C(18)–C(17)	1.393 (15)	C(6)–C(7)	1.353 (17)
C(22)–C(17)	1.397 (12)	C(5)–C(6)	1.414 (16)
C(19)–C(18)	1.369 (17)	C(4)–C(5)	1.353 (15)
C(20)–C(19)	1.382 (16)	C(10)–N	1.462 (14)
C(21)–C(20)	1.378 (18)	C(9)–N	1.291 (11)
C(22)–C(21)	1.394 (17)	C(11)–C(10)	1.497 (13)
C(24)–C(23)	1.372 (14)	C(12)–C(11)	1.400 (14)
C(28)–C(23)	1.419 (12)	C(16)–C(11)	1.413 (14)
C(25)–C(24)	1.398 (14)	C(13)–C(12)	1.391 (14)
C(26)–C(25)	1.381 (14)	C(14)–C(13)	1.367 (14)
C(27)–C(26)	1.375 (18)	C(15)–C(14)	1.394 (17)
C(28)–C(27)	1.363 (16)	C(16)–C(15)	1.377 (18)
C(30)–C(29)	1.383 (11)		

P(1)–Pt–Cl(1)	89.4 (1)	C(28)–C(27)–C(26)	123.0 (10)
C(3)–Pt–Cl(1)	172.6 (3)	C(27)–C(28)–C(23)	118.9 (10)
C(3)–Pt–P(1)	95.9 (3)	C(30)–C(29)–P(1)	118.5 (6)
N–Pt–Cl(1)	94.1 (2)	C(34)–C(29)–P(1)	122.0 (6)
N–Pt–P(1)	94.8 (2)	C(34)–C(29)–C(30)	119.5 (8)
N–Pt–C(3)	80.4 (4)	C(31)–C(30)–C(29)	120.3 (8)
C(1)–Pt–Cl(1)	87.7 (3)	C(32)–C(31)–C(30)	120.3 (8)
C(1)–Pt–P(1)	176.8 (3)	C(33)–C(32)–C(31)	121.1 (9)
C(1)–Pt–C(3)	87.1 (4)	C(34)–C(33)–C(32)	118.4 (8)
C(1)–Pt–N	86.7 (4)	C(33)–C(34)–C(29)	120.3 (8)
C(2)–Pt–Cl(1)	92.7 (3)	C(8)–C(3)–Pt	112.9 (8)
C(2)–Pt–P(1)	91.8 (3)	C(4)–C(3)–Pt	128.5 (7)
C(2)–Pt–C(3)	92.2 (4)	C(4)–C(3)–C(8)	118.6 (9)
C(2)–Pt–N	170.5 (3)	C(7)–C(8)–C(3)	118.8 (10)
C(2)–Pt–C(1)	87.0 (4)	C(9)–C(8)–C(3)	116.0 (8)
C(17)–P(1)–Pt	115.5 (3)	C(9)–C(8)–C(7)	125.2 (8)
C(23)–P(1)–Pt	111.4 (3)	Cl(2)–C(7)–C(8)	117.9 (8)
C(23)–P(1)–C(17)	105.5 (4)	C(6)–C(7)–C(8)	121.7 (9)
C(29)–P(1)–Pt	118.8 (3)	C(6)–C(7)–Cl(2)	120.4 (7)
C(29)–P(1)–C(17)	103.5 (4)	C(5)–C(6)–C(7)	119.1 (10)
C(29)–P(1)–C(23)	100.4 (4)	C(4)–C(5)–C(6)	121.1 (11)
C(18)–C(17)–P(1)	122.4 (7)	C(5)–C(4)–C(3)	120.6 (10)
C(22)–C(17)–P(1)	119.8 (7)	C(10)–N–Pt	122.8 (5)
C(22)–C(17)–C(18)	117.6 (9)	C(9)–N–Pt	113.4 (6)
C(19)–C(18)–C(17)	121.5 (9)	C(9)–N–C(10)	123.0 (8)
C(20)–C(19)–C(18)	120.7 (11)	C(11)–C(10)–N	113.6 (7)
C(21)–C(20)–C(19)	118.8 (12)	C(12)–C(11)–C(10)	121.2 (8)
C(22)–C(21)–C(20)	120.8 (10)	C(16)–C(11)–C(10)	122.1 (9)
C(21)–C(22)–C(17)	120.3 (9)	C(16)–C(11)–C(12)	116.6 (9)
C(24)–C(23)–P(1)	117.4 (6)	C(13)–C(12)–C(11)	121.4 (8)
C(28)–C(23)–P(1)	123.8 (7)	C(14)–C(13)–C(12)	121.1 (10)
C(28)–C(23)–C(24)	118.8 (8)	C(15)–C(14)–C(13)	118.7 (10)
C(25)–C(24)–C(23)	120.6 (8)	C(16)–C(15)–C(14)	120.9 (10)
C(26)–C(25)–C(24)	120.6 (10)	C(15)–C(16)–C(11)	121.2 (11)
C(27)–C(26)–C(25)	118.1 (10)	N–C(9)–C(8)	117.2 (8)

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(19) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

Table VII. First-Order Rate Constants (k), Equilibrium Ratios ($K_N[SMe_2]/K_S$), and Thermal Activation Parameters for the Reactions Studied in Acetone Solution at Various Temperatures

ligand (activated bond)	$K_N[SMe_2]/K_s$, M[a]	T, °C	10^3k, s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, kJ K^{-1} mol^{-1}
a (C–Br endo)		25	5.9 ± 1.6		
		35	14 ± 2		
	0.025	45	23 ± 2	48 ± 7	−125 ± 23
b (C–Cl endo)		25	2.1 ± 0.1		
		35	5.8 ± 0.8		
	0.007	45	10 ± 1	60 ± 9	−93 ± 28
c (C–Cl endo)[b]		25	5.4 ● 0.6		
		35	16 ± 4		
	0.024	45	34 ± 7	68 ± 9	−68 ± 30
e (C–H endo)[b]		15	0.81 ± 0.11		
		25	1.6 ± 0.1		
		35	5.4 ± 0.2		
	0.007	45	12 ± 2	68 ± 5	−75 ± 18
f (C–H endo)[b]		25	2.5 ± 0.3		
		35	5.5 ± 0.8		
	0.012	45	17 ± 3	75 ± 1	−48 ± 16
g (C–H endo)[b]		15	1.7 ± 0.2		
		25	3.3 ± 0.1		
		35	10 ± 1		
	0.018	45	23 ± 6	63 ± 5	−87 ± 16
	0.035[c]	35[c]	9.9 ± 0.8[c]		
h (C–Br exo)		15	1.9 ± 0.2		
		25	2.6 ± 0.8		
	0.014	35	3.7 ± 0.4	23 ± 1	−218 ± 2
j (C–Cl exo)		25	3.6 ± 1.6		
		35	5.9 ± 0.1		
	0.013	45	9.6 ± 0.6	34 ± 2	−179 ± 7

[a] Average value at the temperatures studied. [b] A statistical factor of $^1/_2$ applies to the first-order rate constants, accounting for the two positions available for the reaction at the ligand. [c] Toluene solution.

of the metallacycle cannot be disregarded and both restricted rotation about the C=N bond and conjugation of the C=N bond with the phenyl ring promote the reaction at the iminic moiety.

Experimental Section

^1H, ^{31}P, and ^{13}C NMR spectra were recorded by using Varian Gemini 200, Bruker WP 80 SY, and Varian XL 200 FT spectrometers, respectively. IR spectra were recorded as KBr disks on a Perkin-Elmer 1330 spectrometer.

Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

Kinetics. All spectra were recorded on an HP 8452A instrument equipped with a multicell holder thermostated (±0.2 °C) by an external circulator. All kinetic runs were followed at 340 nm in acetone or toluene solutions, where the difference in absorbance between the initial and final species were large enough, and no interference from the solvent was important. Pseudo-first-order conditions were used for all runs, and absorbance versus time traces were fitted to exponential form by the Marquardt algorithm. All the k_{obs} errors were in the range of 3–5% of the actual value obtained, indicating a very good fit up to 4–5 half lives. The platinum concentration was within the (5–10) × 10^{-4} M range and was achieved by the addition of small quantities (0.1–0.2 mL) of a concentrated stock solution (kept at −10 °C) to a previously thermostated solution of the ligand.

The k_{obs} versus [imine] plots were fitted by unweighted least-squares by the standard kinetic software of an HP 8452A instrument. Thermal activation parameters were derived from standard Eyring plots by the same method.

The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1) was prepared by the literature method.[17]

Imines were prepared from the corresponding benzaldehydes and the appropriate benzylamines in refluxing ethanol.[4] δ(H) data in ppm for the iminic proton in $CDCl_3$ are given for each ligand: **a**, δ 8.70; **b**, δ 8.83; **c**, δ 8.53; **d**, δ 8.59; **e**, δ 8.55; **f**, δ 8.50; **g**, δ 8.40; **h**, δ 8.43; **i**, 8.90; **j**, δ 8.69; **k**, δ 8.72; **l**, δ 8.85; **m**, δ 8.72; **n**, δ 8.73; **o**, δ 8.78.

Compounds 3. A 20.0-mg (0.035-mmol) amount of complex 1 and 0.07 mmol of the corresponding imine were dissolved in 0.5 mL of acetone-d_6, and the ^1H NMR spectrum was recorded.

Compounds 4. To a solution of complex 1 (100 mg) in acetone (10 mL) was added a solution of the corresponding imine. The mixture was stirred for 16 h, and the solvent was removed under vacuum. The residue was washed with hexane, and white or light yellow compounds were obtained and recrystallized from acetone–hexane.

$[PtMe_2Br(SMe_2)(C_6H_4CHNCH_2C_6H_5)]$ (4a): yield 141 mg (72%); mp 118 °C dec; ν(CH=N) 1610 cm^{-1}. Anal. Calcd for $C_{18}H_{24}BrNSPt$: C, 38.51; H, 4.31; N, 2.49. Found: C, 37.27; H, 4.19; N, 2.37.

$[PtMe_2Cl(SMe_2)(C_6H_4CHNCH_2C_6H_5)]$ (4b): yield 117 mg (65); mp 80 °C dec; ν(CH=N) 1610 cm^{-1}. Anal. Calcd for $C_{18}H_{24}ClNSPt$: C, 41.82; H, 4.68; N, 2.71. Found: C, 42.50; H, 4.46; N, 2.86.

$[PtMe_2Cl(SMe_2)(C_6H_3ClCHNCH_2C_6H_5)]$ (4c): yield 138 mg (72%); mp 87 °C dec; ν(CH=N) 1600 cm^{-1}. Anal. Calcd for $C_{18}H_{23}Cl_2NSPt$: C, 39.21; H, 4.20; N, 2.54. Found: C, 38.56; H, 3.81; N, 2.54.

$[PtMe_2Cl(SMe_2)(C_6H_3ClCHNCH_2C_6H_4Br)]$ (4d): yield 153 mg (70%); mp 85 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{18}H_{22}BrCl_2NSPt$: C, 34.30; H, 3.52; N, 2.22. Found: C, 34.96; H, 3.52; N, 2.22.

$[PtMe_2Br(SMe_2)(C_6H_5CHNCH_2C_6H_4)]$ (4h): yield 133 mg (68%); mp 72 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{18}H_{24}BrNSPt$: C, 38.51; H, 4.31; N, 2.49. Found: C, 4.17; N, 2.49.

$[PtMe_2Cl(SMe_2)(C_6H_2Me_3CHNCH_2C_6H_4)]$ (4j): yield 117 mg (60%); mp 135 °C dec; ν(CH=N) 1605 cm^{-1}. Anal. Calcd for $C_{21}H_{30}ClNSPt$: C, 45.11; H, 5.41; N, 2.50. Found: C, 45.11; H, 5.01; N, 2.37.

$[PtMe_2Cl(SMe_2)(C_6H_2Me_3CHNCH_2C_6H_3Cl)]$ (4k): yield 128 mg (62%); mp 145 °C dec; ν(CH=N) 1600 cm^{-1}. Anal. Calcd for $C_{21}H_{29}Cl_2NSPt$: C, 42.50; H, 4.92; N, 2.36. Found: C, 42.14; H, 4.70; N, 2.34.

^{13}C NMR data (acetone-d_6, referenced to $SiMe_4$) are as follows.

$[PtMe_2Cl(SMe_2)(C_6H_3ClCHNCH_2C_6H_5)]$ (4c): δ −3.18 (J(PtC) = 648 Hz, MePt), −1.30 (J(PtC) = 595 Hz, MePt], 18.50 (SMe_2), 60.41 (J(PtC) = 11 Hz, CH_2), 171.50 (J(PtC) = 48 Hz, CH=N), 125.60, 128.83, 128.88, 129.50, 130.98, 134.55 ppm (J(PtC) = 65 Hz, aryl carbons).

$[PtMe_2Br(SMe_2)(C_6H_4CHNCH_2C_6H_5)]$ (4a): δ −5.53 (J(PtC) = 652 Hz, MePt), −1.13 (J(PtC) = 600 Hz, MePt), 18.23 (SMe_2), 59.94 (CH_2), 173.72 (J(PtC) = 58 Hz, CH=N), 124.24, 127.64, 127.82, 128.13, 128.54, 130.00, 130.11 (J(PtC) = 32 Hz), 132.03 (J(PtC) = 58 Hz), 136.94, 146.59 ppm (aryl carbons).

Compounds 5. The same procedure as for compounds 4 gave orange-yellow compounds.

$[PtMe(SMe_2)(C_6H_4CHNCH_2C_6H_4Cl)]$ (5e): yield 143 mg (82%); mp 123 °C dec; ν(CH=N) 1605 cm^{-1}. Anal. Calcd for $C_{17}H_{20}ClNSPt$: C, 40.76; H, 4.02; N, 2.79. Found: C, 40.80; H, 3.97; N, 2.69.

$[PtMe(SMe_2)(C_6H_4CHNCH_2C_6H_3Cl_2)]$ (5f): yield 153 mg (82%); mp 127 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{17}H_{19}Cl_2NSPt$: C, 38.14; H, 3.58; N, 2.61. Found: C, 38.46; H, 3.63; N, 2.59.

$[PtMe(SMe_2)(C_6H_3ClCHNCH_2C_6H_4Cl)]$ (5g): yield 156 mg (84%); mp 135 °C dec; ν(CH=N) 1625 cm^{-1}. Anal. Calcd for $C_{17}H_{19}Cl_2NSPt$: C, 38.14; H, 3.58; N, 2.61. Found: C, 38.04; H, 3.75; N, 2.68.

^{13}C NMR data (acetone-d_6, referenced to $SiMe_4$) are as follows.

$[PtMe(SMe_2)(C_6H_4CHNCH_2C_6H_4Cl)]$ (5e): δ −13.61 (J(PtC) = 810 Hz, MePt), 19.56 (SMe_2), 59.87 (J(PtC) = 19 Hz, CH_2), 178.15 (J(PtC) = 81 Hz, CH=N), 123.60, 127.64, 128.88, 129.40 (J(PtC) = 90 Hz), 129.01 (J(PtC) = 90 Hz), 130.02, 131.43, 132.05, 132.48, 132.80, 134.64 ppm.

Compounds 6. A 20-mg amount of compound 4 and the stoichiometric amount of PPh_3 were stirred in 20 mL of acetone over 2 h. On addition of hexane, a yellow precipitate of 6 formed, which was filtered and washed with hexane and ether.

$[PtMe_2Br(PPh_3)(C_6H_4CHNCH_2C_6H_5)]$ (6a): yield 24 mg (88%); mp 162 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{34}H_{33}BrNPPt$: C, 53.62; H, 4.37; N, 1.84. Found: C, 53.64; H, 4.32; N, 1.67.

$[PtMe_2Cl(PPh_3)(C_6H_3ClCHNCH_2C_6H_5)]$ (6c): yield 24 mg (88%); mp 185 °C dec; ν(CH=N) 1610 cm^{-1}. Anal. Calcd for

Table VIII. Summary of Crystallographic Data

formula	$C_{34}H_{32}NPCl_2Pt$
fw	751.62
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	17.677 (3)
b, Å	15.495 (3)
c, Å	11.371 (2)
β, deg	104.59 (2)
V, Å^3	3014 (2)
D_{exptl}, g cm^{-3}	1.656
Z	4
$F(000)$	1480.0
cryst size, mm^3	0.1 × 0.1 × 0.2
μ(Mo Kα), cm^{-1}	51.50
λ(Mo Kα), Å	0.71069
T, K	298
no. of rflns collected	4733
R	0.045
R_w	0.052

$C_{34}H_{32}Cl_2NPPt$: C, 54.33; H, 4.29; N, 1.86. Found: C, 54.29; H, 4.31; N, 2.10.

[$PtMe_2Br(PPh_3)(C_6H_5CHNCH_2C_6H_4)$] (6h): yield 23 mg (85%); mp 118 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{34}H_{33}BrNPPt$: C, 53.62; H, 4.37; N, 1.84. Found: C, 53.98; H, 4.49; N, 1.69.

X-ray Structure Analysis. Data Collection. Crystals of [$PtMe_2Cl(PPh_3)(C_6H_3ClCHNCH_2C_6H_5)$] (**6c**) were grown from acetone–hexane. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Phillips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 < \theta < 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, using ω-scan technique. A total of 4733 reflections were measured in the range $2 \ll \theta \ll 25°$, 3760 of which were assumed as observed by applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz–polarization and absorption corrections were made.

Structure Solution and Refinement. The structure was solved by a Patterson synthesis, using the SHELXS computer program,[20] and refined by the full-matrix least-squares method, with the SHELX76 computer program.[21] The function minimized $\sum w[|F_o| - |F_c|]^2$, where $w = (\sigma^2(F_o) + 0.0095|F_o|^2)^{-1}$. f, f', and f'' were taken from ref 22. The positions of 30 hydrogen atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final R factor was 0.045 (R_w = 0.052) for all observed reflections. The number of refined parameters was 355. The maximum shift/esd was 0.1; maximum and minimum peaks in the final difference synthesis were 0.4 and −0.4 e Å^{-3}, respectively.

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Supplementary Material Available: Tables of observed rate constants and anisotropic thermal parameters (5 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Stereoselective Stepwise Reduction of Coordinated Acetonitrile with Chiral Tp′(CO)(RC≡CR′)W$^+$ Templates

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Stepwise reduction of the acetonitrile ligand in [Tp′(CO)(RC≡CR′)W(N≡CMe)][BF_4] has been accomplished with sequential addition of nucleophiles and electrophiles to the carbon–nitrogen triple bond. Intermediate metal complexes containing coordinated azavinylidene, imine, amide, and amine nitrogen donor ligands have been isolated and characterized. Nucleophilic addition to the imine complexes is highly stereoselective. Acidification of the amine complex in acetonitrile forms the free ammonium salt, and solvent coordination regenerates the acetonitrile adduct.

Introduction

The work reported here combines the stereochemical control accessible through use of the chiral Tp′W(CO)(PhC≡CMe) fragment (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with the stepwise reduction of coordinated acetonitrile communicated previously.[1] Representative examples of stereoselective reactions of chiral transition-metal reagents, including specific instances utilizing group 6 Tp′ moieties, are referenced first. Reduction reactions of coordinated nitriles are then reviewed briefly before other reactions of coordinated nitriles are catalogued to complete the introduction.

Chiral transition-metal complexes can dictate the stereochemistry of ligand elaboration reactions. The Liebeskind[2] and Davies[3] groups have enantioselectively elaborated η^1-acyl groups in an iron system. Brookhart has used electrophilic carbene complexes, [Cp(CO)(PR_3)Fe=CHR]$^+$, to effect enantioselective formation of cyclo-

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