Activation of Imines by Platinum(II) To Give Aminoalkyl Complexes: Scope and Limitations of the Reaction

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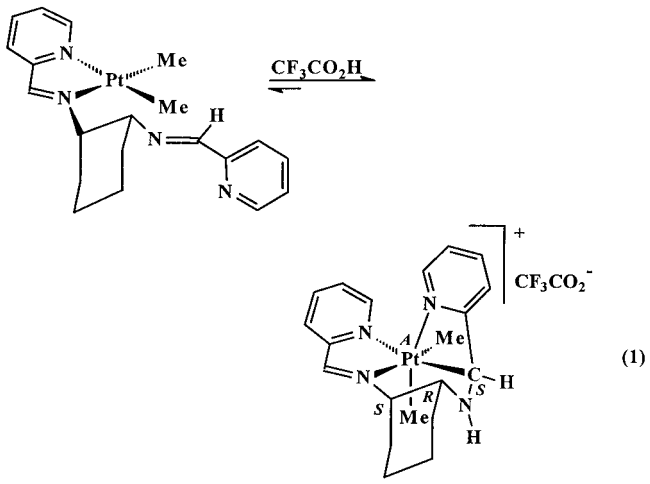
Reaction of an excess of the ligand 1,2-$C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (**1**), 1,2-$C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)_2$ (**2**), or 1,3-$C_3H_6(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (**3**) with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gives the following platinum(II) complexes that contain a free imine functional group: $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(N{=}CH\text{-}2\text{-}C_5H_4N)\}]$ (**4**), $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(N{=}CH\text{-}2\text{-}C_9H_6N)\}$ (**5**), or $[PtMe_2\{C_3H_6(N{=}CH\text{-}2\text{-}C_5H_4N)(N{=}CH\text{-}2\text{-}C_5H_4N)\}]$ (**6**) (C_5H_4N = pyridyl, C_9H_6N = quinolyl). The reaction of complexes **4**−**6** with excess CF_3CO_2H or HCl gave aminoalkylplatinum(IV) products, and it is suggested that the reactions occur by protonation of the free imine nitrogen atom followed by oxidative addition of the transient iminium group so formed. The products were formed as a mixture of isomers whose structures were deduced from their spectroscopic properties and, for the complexes $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}(O_2CCF_3)][O_2CCF_3]_2$ (**7a**) $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}Cl][Cl]_2$ (**8a**), and $[PtMe_2\{C_3H_6(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2\text{-}CH\text{-}2\text{-}C_5H_4N)Cl][Cl]$ (**14a**), by X-ray structure determinations. The reaction of **5** with an equimolar amount of CF_3CO_2H gave $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(NHCH\text{-}2\text{-}C_9H_6N)\}][CF_3CO_2]$ (**9**), which was shown by X-ray structure determination to contain a four-membered azametallacyclobutane ring. Attempts to effect the intermolecular protonation/metalation of imines by platinum(II) were unsuccessful, since reactions of $[PtMe_2(bu_2bpy)]$ (bu_2bpy = 4,4′-di-*tert*-butylbipyridine) with *N*-benzylidenemethylamine or *N*-benzylideneaniline and CF_3CO_2H led only to protonolysis of the methyl−platinum bonds.

Introduction

Interest in the activation of C=N double bonds by transition metals is growing, since the insertion of imines into metal−carbon bonds might provide a route to the polymerization of imines or to metal-mediated polypeptide synthesis[1] and asymmetric hydrogenation of imines catalyzed by chiral metal complexes has given useful agrochemicals.[2] For rhodium(I)- and iridium(I)-based catalysts, an important intermediate in catalytic hydrogenation is thought to be an amidometal complex which is formed by insertion of an imine into a metal−hydride bond.[3] When the reactions of acids with a chiral dimethylplatinum(II) complex which contains a pendant imine group were studied, the stereoselective formation of an aminoalkylplatinum(IV) complex was observed, as shown in eq 1.[4] The reaction is believed to occur by



(1)

protonation of the tethered imine, followed by oxidative addition of the resultant transient iminium ion to platinum(II).[5]

It was then considered important to determine the scope and limitations of the above reactions, and the results are reported below. It is shown that the reactions are successful with dimethylplatinum(II) complexes containing simpler achiral ligands than those used previously (eq 1), but only if the imine group is tethered

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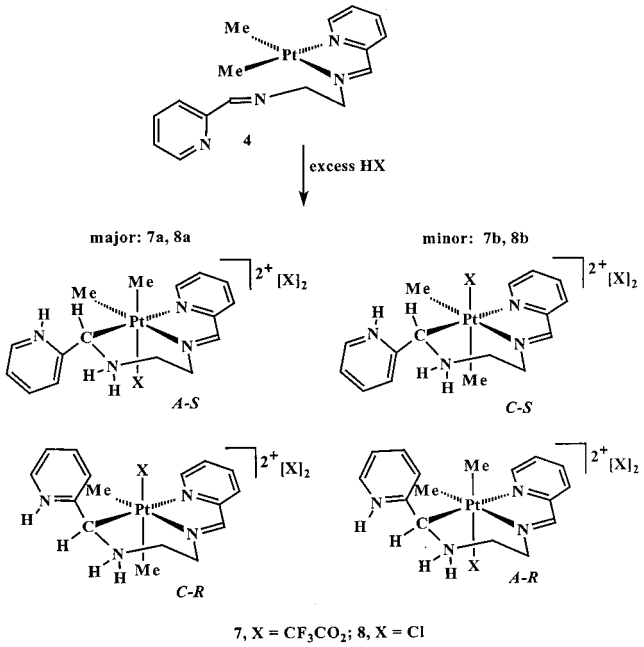
Scheme 1



to the complex. It is also shown that the reactions are diastereoselective.

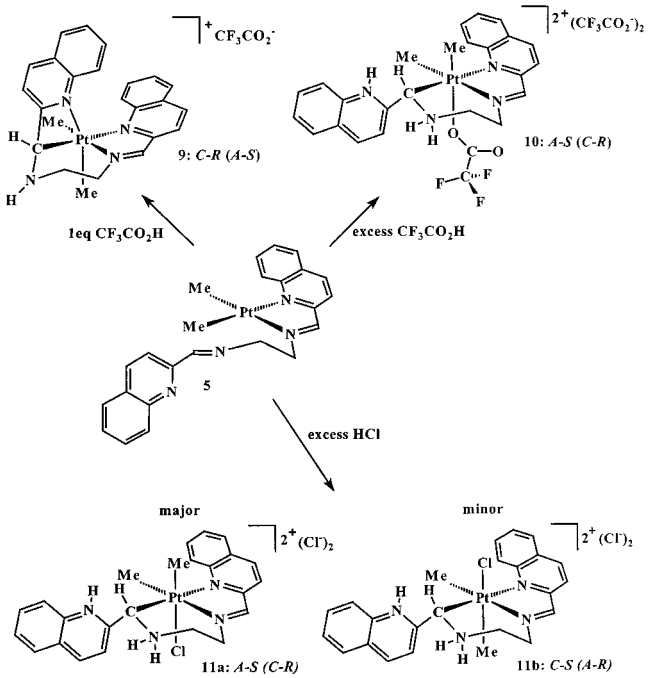
Results

Synthesis of Dimethylplatinum(II) Complexes. The bis(diimine) ligands $(CH_2)_n(N{=}CHR)_2$ (n = 2, R = 2-pyridyl, **1**; n = 2, R = 2-quinolyl, **2**; n = 3, R = 2-pyridyl, **3**) were prepared by the condensation reaction of 1,2-diaminoethane or 1,3-diaminopropane with either 2-pyridinecarboxaldehyde or 2-quinolinecarboxaldehyde. The corresponding dimethylplatinum(II) complexes $[PtMe_2\{(CH_2)_n(N{=}CHR)_2\}]$ (**4**−**6**), in which the ligand acts as a bidentate species only (Schemes 1−3) were then prepared by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with a large excess of the ligand, so as to prevent formation of the diplatinum complexes in which the ligand acts as a bis(bidentate) species. The complexes were readily characterized by their ^{1}H NMR spectra, by comparison with related complexes,[4] and by elemental analysis.

Reactions of $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(N{=}CH\text{-}2\text{-}C_5H_4N)\}]$ (4) with CF_3CO_2H and HCl. Initial attempts to carry out these reactions using a stoichiometric amount of acid were unsuccessful, since NMR analysis showed that a complex mixture of products was formed. Fortunately, the reactions with excess acid were successful in giving pure products, and the results are summarized in Scheme 1. The reaction of complex **4** with 3 molar equiv of CF_3CO_2H was monitored by ^{1}H NMR and gave $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}(O_2CCF_3)][O_2CCF_3]_2$ as a mixture of isomers **7a** and **7b** (Scheme 1), with **7a** strongly favored (**7a**:**7b** = 4:1).

The formation of the (aminoalkyl)platinum(IV) complexes **7** was demonstrated by changes in the ^{1}H NMR spectra, as the characteristic free imine N=CH proton

Scheme 2



resonance of **4** decayed on reaction with trifluoroacetic acid. Complex **7a** gave a resonance at δ 4.94, with ^2J(Pt-H) = 56 Hz, which is attributed to an aminoalkyl group bonded to platinum and two methylplatinum(IV) resonances at δ 0.68, with ^2J(PtH) = 64 Hz, and at δ 1.03, with ^2J(PtH) = 75 Hz.[6] A similar set of resonances was also observed for **7b**, but the aminoalkyl proton showed a markedly higher value of ^2J(PtH) = 128 Hz. The stereochemistries were assigned by comparison of the NMR data with those for related complexes,[4] in which a similar change in aminoalkylplatinum ^2J(PtH) value was observed, and the structure was confirmed for **7a** by an X-ray structure determination. The products contain two chiral centers, the platinum center (*C* or *A*, clockwise or anticlockwise) and the aminoalkyl carbon (*R* or *S*), and since the precursor complex is achiral, they must be produced in racemic form. In stereochemical terms then, the two diastereomers are described as *A*-*S*/*C*-*R* (**7a**) and *A*-*R*/*C*-*S* (**7b**), as illustrated in Scheme 1.[7] There was little change in the isomeric ratio with time, and recrystallization failed to separate the isomers. If the reaction was carried out using a larger excess of CF_3CO_2H (greater than 5 equiv),then the single (aminoalkyl)platinum(IV) isomer **7a** was obtained.

A view of the structure of **7a** is shown in Figure 1, and selected bond distances and angles are provided in Table 1. The structure shows a platinum(IV) center octahedrally coordinated by two methyl ligands, a trifluoroacetate ligand, and an NNC tridentate ligand

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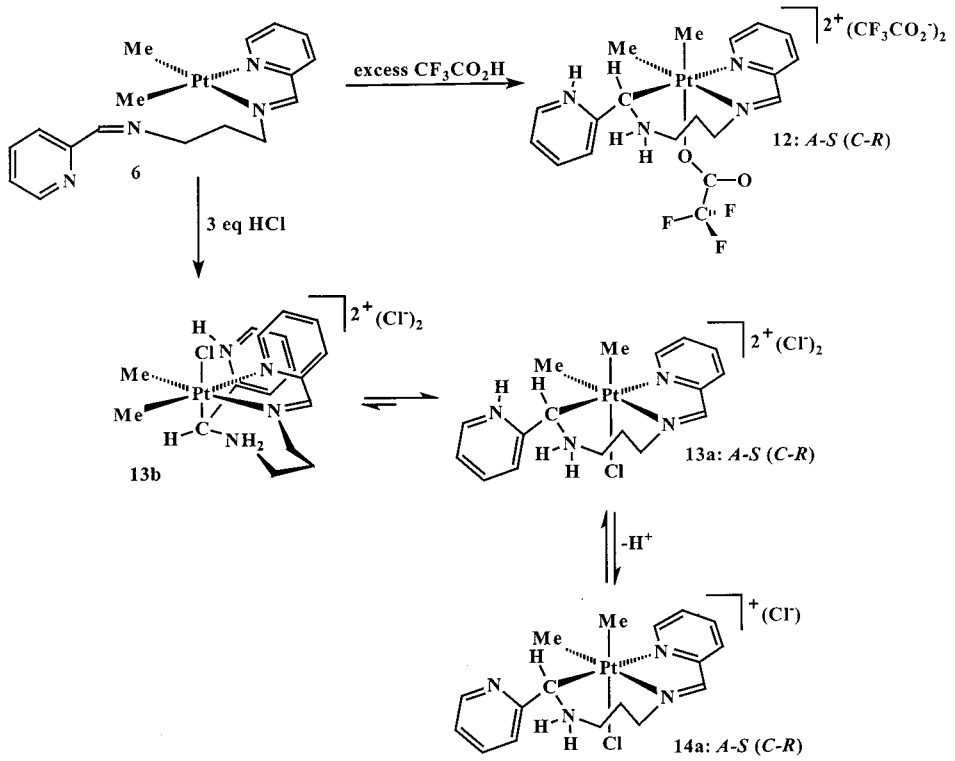
(7) In the descriptor *A*-*S*, the first letter defines the chirality at platinum and the second letter defines chirality at the aminoalkyl carbon (*A* = anticlockwise, *C* = clockwise). Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Chemical Nomenclature: Principles and Practice*; American Chemical Society: Washington, DC, 1990; Chapter 16.

Scheme 3



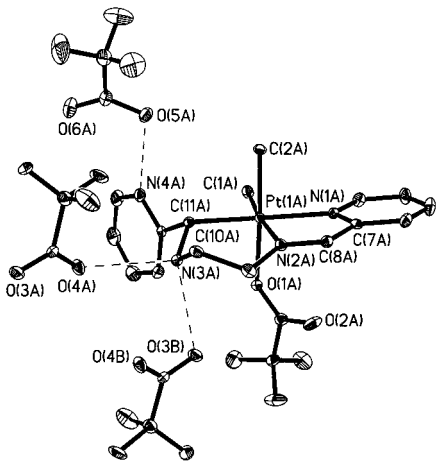


Figure 1. View of the *A-S* enantiomer of the complex $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}(O_2CCF_3)][O_2CCF_3]_2$ (**7a**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7a

(a) Bond Lengths (Å)			
Pt(1)−C(1)	2.051(6)	Pt(1)−C(2)	2.063(6)
Pt(1)−C(11)	2.076(6)	Pt(1)−N(2)	2.123(5)
Pt(1)−N(1)	2.139(5)	Pt(1)−O(1)	2.183(4)
C(8)−N(2)	1.285(8)	N(2)−C(9)	1.479(8)
C(9)−C(10)	1.510(9)	C(10)−N(3)	1.503(8)
N(3)−C(11)	1.515(7)		
(b) Bond Angles (deg)			
C(1)−Pt(1)−C(2)	87.6(3)	C(1)−Pt(1)−C(11)	90.7(2)
C(2)−Pt(1)−C(11)	89.3(3)	C(1)−Pt(1)−N(2)	174.3(2)
C(2)−Pt(1)−N(2)	91.0(2)	C(11)−Pt(1)−N(2)	94.8(2)
C(1)−Pt(1)−N(1)	96.9(2)	C(2)−Pt(1)−N(1)	87.6(2)
C(11)−Pt(1)−N(1)	171.7(2)	N(2)−Pt(1)−N(1)	77.52(19)
C(1)−Pt(1)−O(1)	87.5(2)	C(2)−Pt(1)−O(1)	174.8(2)
C(11)−Pt(1)−O(1)	89.2(2)	N(2)−Pt(1)−O(1)	94.07(19)
N(1)−Pt(1)−O(1)	94.60(19)	N(2)−C(8)−C(7)	118.3(6)
C(8)−N(2)−C(9)	119.0(5)	C(8)−N(2)−Pt(1)	114.8(4)
C(9)−N(2)−Pt(1)	126.1(4)	C(10)−N(3)−C(11)	114.2(5)
N(3)−C(11)−C(12)	108.0(5)	N(3)−C(11)−Pt(1)	110.8(4)
C(12)−C(11)−Pt(1)	115.3(4)		

which includes a new (aminoalkyl)platinum bond, C11−Pt1. The C11−N3 bond length is 1.515(7) Å, consistent with a carbon−nitrogen single bond, and both centers are sp^3-hybridized with angles C10−N3−C11 = 114.2(5)° and N3−C11−Pt = 110.8(4)° close to tetrahedral. The NNC tridentate ligand occupies a meridian of the octahedron, with the aminoalkyl carbon, C11, trans to the pyridyl group. One methyl group is trans to the trifluoroacetate ligand, and the other is trans to the imine nitrogen. The chirality of the aminoalkyl carbon shown in Figure 1 is *S* (with the free pyridyl substituent syn to the trifluoroacetate ligand and the aminoalkyl proton C11−H syn to the methyl group, C2), and the chirality at platinum is *A*. Thus, Figure 1 shows the *A-S* enantiomer of diastereomer **7a** (Scheme 1).[7] Because excess CF_3CO_2H was used to obtain crystals of **7a**, both the amino group and free pyridyl groups are protonated to give a dicationic complex. There is extensive hydrogen bonding present, since both NH protons at the dialkylammonium group (N3···O4 = 2.75(1) Å, N3···O3 = 2.76(1) Å) and the pyridinium proton (N4···O5 = 2.66(1) Å) are hydrogen-bonded to trifluoroacetate anions.

The reactions of **4** with HCl were similar, as shown in Scheme 1. Thus, reaction of **4** with 3 molar equiv of HCl gave the isomeric (aminoalkyl)platinum(IV) products $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}Cl][Cl]_2$ (**8a**,**b**). The ^1H NMR spectrum showed an aminoalkyl resonance for **8a** at δ 5.28 with $^2J(PtH)$ = 72 Hz and for **8b** at δ 5.99 with $^2J(PtH)$ = 125 Hz. If greater than 3 equiv of acid was used, the reaction gave mostly **8a** (**8a**:**8b** = 7:1) and there was little subsequent change. However, if less than 3 equiv of acid was used and the reaction was monitored over time at ambient temperature, it was shown that **8a** and **8b** were present in nearly equal amounts after 5 min; however, **8b** quickly became dominant and after 2 days was the only complex detectable. It is clear then that **8a** is the kinetic product but that, under conditions in which there is no

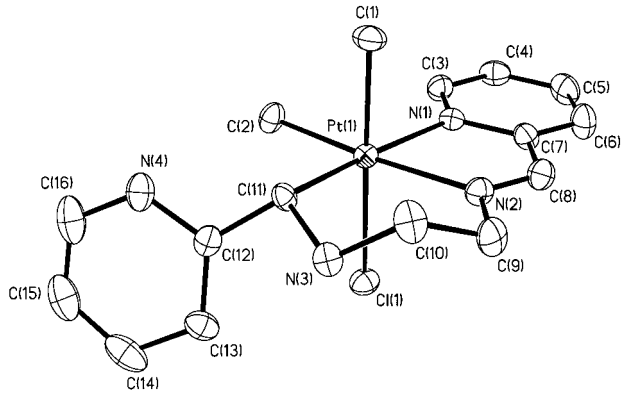


Figure 2. View of the *A*-*S* enantiomer of the complex $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)(NH_2CH\text{-}2\text{-}C_5H_4NH)\}Cl][Cl]_2$ (**8a**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8a

(a) Bond Lengths (Å)

Pt(1)−C(11)	2.072(7)	Pt(1)−C(1)	2.072(7)
Pt(1)−C(2)	2.072(7)	Pt(1)−N(1)	2.126(6)
Pt(1)−N(2)	2.135(6)	Pt(1)−Cl(1)	2.4714(18)
C(8)−N(2)	1.270(9)	N(2)−C(9)	1.471(9)
C(9)−C(10)	1.512(11)	C(10)−N(3)	1.494(9)
N(3)−C(11)	1.510(8)		

(b) Bond Angles (deg)

C(11)−Pt(1)−C(1)	89.3(3)	C(11)−Pt(1)−C(2)	90.1(3)
C(1)−Pt(1)−C(2)	87.3(3)	C(11)−Pt(1)−N(1)	172.9(2)
C(1)−Pt(1)−N(1)	88.8(3)	C(2)−Pt(1)−N(1)	96.6(3)
C(11)−Pt(1)−N(2)	95.6(2)	C(1)−Pt(1)−N(2)	91.2(3)
C(2)−Pt(1)−N(2)	174.2(3)	N(1)−Pt(1)−N(2)	77.7(2)
C(11)−Pt(1)−Cl(1)	94.3(2)	C(1)−Pt(1)−Cl(1)	176.1(2)
C(2)−Pt(1)−Cl(1)	91.1(2)	N(1)−Pt(1)−Cl(1)	87.85(16)
N(2)−Pt(1)−Cl(1)	90.03(17)	N(2)−C(8)−C(7)	119.2(7)
C(8)−N(2)−C(9)	119.7(6)	C(8)−N(2)−Pt(1)	114.1(5)
C(9)−N(2)−Pt(1)	126.2(5)	C(10)−N(3)−C(11)	114.9(6)
C(12)−C(11)−N(3)	107.0(6)	C(12)−C(11)−Pt(1)	116.5(5)
N(3)−C(11)−Pt(1)	111.8(4)		

excess acid present, it can isomerize to the thermodynamic product **8b**.[4,8]

A view of the structure of **8a** is shown in Figure 2, and selected bond distances and angles are given in Table 2. The structure is similar to that found for complex **7a**, containing an octahedral platinum(IV) center that, relative to complex **4**, has new bonds to an aminoalkyl ligand and a chloride ligand. Once again the aminoalkyl group, C11, is part of a meridional tridentate ligand and has an *S* configuration which places the aminoalkyl proton anti to the chloride ligand and syn to the axially located methyl ligand. The overall absolute configuration is *A*-*S* for the enantiomer of **8a** shown in Figure 2. As with **7a**, the complex is fully protonated and is thus dicationic, and it forms hydrogen bonds through the dialkylammonium group, N3, to two chloride ions. The protonated pyridyl substituent, N4, is also hydrogen-bonded to a chloride ion.

Reactions of $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(N{=}CH\text{-}2\text{-}C_9H_6N)\}]$ (5) with CF_3CO_2H and HCl. Reactions of the quinolyl derivative **5** are mostly similar to those of the pyridyl analogues discussed above, but there is one notable difference, as indicated in Scheme 2. The addition of only 1 equiv of CF_3CO_2H to complex **5** gave clean formation of the complex $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(NHCH\text{-}2\text{-}C_9H_6N)\}][CF_3CO_2]$ (**9**) (Scheme 2). ^{1}H NMR spectroscopy showed the quantitative formation

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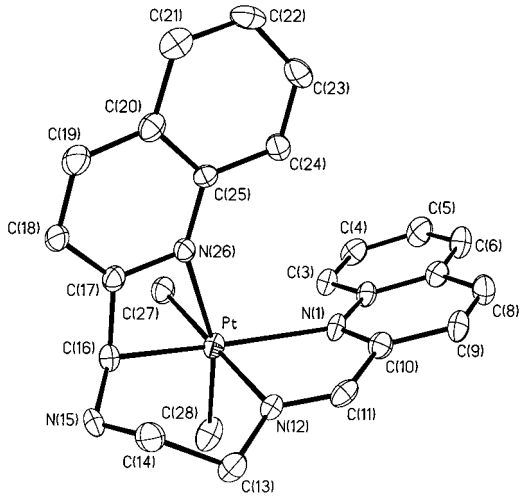

Figure 3. View of the *C*-*R* enantiomer of the complex $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(NHCH\text{-}2\text{-}C_9H_6N)\}][CF_3CO_2]$ (**9**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9

(a) Bond Lengths (Å)

Pt−C(28)	2.030(7)	Pt−C(27)	2.059(7)
Pt−C(16)	2.068(7)	Pt−N(12)	2.113(6)
Pt−N(26)	2.181(6)	Pt−N(1)	2.319(6)
Pt−C(17)	2.635(8)	C(11)−N(12)	1.267(8)
N(12)−C(13)	1.454(9)	C(13)−C(14)	1.517(9)
C(14)−N(15)	1.445(9)	N(15)−C(16)	1.414(9)

(b) Bond Angles (deg)

C(28)−Pt−C(27)	89.1(3)	C(28)−Pt−C(16)	98.8(3)
C(27)−Pt−C(16)	87.8(3)	C(28)−Pt−N(12)	92.4(3)
C(27)−Pt−N(12)	178.4(3)	C(16)−Pt−N(12)	91.6(3)
C(28)−Pt−N(26)	163.6(3)	C(27)−Pt−N(26)	86.3(3)
C(16)−Pt−N(26)	65.3(3)	N(12)−Pt−N(26)	92.1(2)
C(28)−Pt−N(1)	93.2(3)	C(27)−Pt−N(1)	105.4(3)
C(16)−Pt−N(1)	162.4(3)	N(12)−Pt−N(1)	75.0(2)
N(26)−Pt−N(1)	103.2(2)	N(12)−C(11)−C(10)	121.0(7)
C(11)−N(12)−C(13)	120.5(7)	C(11)−N(12)−Pt	116.5(5)
C(13)−N(12)−Pt	122.9(5)	C(16)−N(15)−C(14)	118.0(7)
N(15)−C(16)−C(17)	113.2(7)	N(15)−C(16)−Pt	118.9(5)
C(17)−C(16)−Pt	93.3(5)		

of only a single isomer, with a new aminoalkyl resonance appearing at δ 5.01 with ^2J(PtH) = 52 Hz and methylplatinum(IV) resonances at δ 0.88 and 1.41 with ^2J(PtH) = 75 and 72 Hz, respectively. In addition, an aromatic proton of a quinolyl group appeared at δ 6.20, and this unusual chemical shift is attributed to an edge-to-face aromatic interaction between the two quinolyl groups. The reaction of **5** with excess CF_3CO_2H gave a single dominant isomer of the complex $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(NH_2CH\text{-}2\text{-}C_9H_6NH)\}(O_2CCF_3)][CF_3CO_2]_2$ (**10**), which was characterized by its ^{1}H NMR spectrum to have the same stereochemistry as complex **7a** (Schemes 1 and 2) but which was unstable in the absence of excess acid. The reaction of **5** with excess HCl gave a mixture of the isomers $[PtMe_2\{C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)(NH_2CH\text{-}2\text{-}C_9H_6NH)\}Cl][Cl]_2$ (**11a**,**b**) with the ratio **11a**:**11b** = 8:1, and stereochemical assignments were made by comparison of the ^{1}H NMR parameters with those of **8a**,**b**.

A view of the structure of complex **9** is shown in Figure 3, and selected bond distances and angles are provided in Table 3. In complex **9** the aminoalkyl group is part of an N,N,C,N-tetradentate ligand, because the second 2-quinolyl unit is also coordinated to platinum(IV). The tetradentate N,N,C,N coordination mode makes the (aminoalkyl)platinum bond C16−Pt part of a four-membered azametallacyclobutane ring, for which

there are some literature precedents.[9] The azametallacyclobutane ring structure causes a significant distortion of the platinum(IV) complex from octahedral geometry. The angle C16−Pt−N26 = 65.3(3)° is compressed significantly from the ideal of 90° to accommodate the four-membered ring. The structure confirms the presence of an edge-to-face aromatic interaction between the two quinolyl groups. As shown in Figure 3, the absolute configuration is *C-R* and no other diastereomer was observed by ^{1}H NMR spectroscopy.[7] The formation of the azametallacyclobutane ring, along with the constraints imposed by the N,N,C,N coordination mode, is only possible with relative chiralities *C-R* (or enantiomer *A-S*) at the aminoalkyl and platinum centers, respectively, since the 2-quinolyl substituent must be syn to the site that is occupied by the trifluoroacetate ligand in the related complex **7a**.[4]

The differences in chemistry between complexes **4** and **5** (Schemes 1 and 2) are attributed to steric effects, since there is little difference in basicities of the pyridine and quinoline substituents (pK_a values in nitromethane: $C_5H_5NH^+$, 11.95; $C_6H_9NH^+$, 11.40; $PhCHNHPh^+$, 9.43).

Reaction of [PtMe$_2${C$_3$H$_6$(*N*=CH-2-C$_5$H$_4$*N*)(N=CH-2-C$_5$H$_4$N)}] (6) with CF$_3$CO$_2$H and HCl. The reaction of complex **6** with excess CF_3CO_2H led to immediate formation of a single isomer of [PtMe$_2${C$_3$H$_6$(*N*=CH-2-C$_5$H$_4$*N*)(NH$_2$*C*H-2-C$_5$H$_4$NH)}(O$_2$CCF$_3$)][CF$_3$CO$_2$]$_2$ (**12**), as shown in Scheme 3. The presence of the aminoalkyl group was indicated by a resonance in the ^{1}H NMR spectrum at δ 5.65 with ^2J(PtH) = 89 Hz, a value intermediate between those observed for isomers **7a**,**b**. The stereochemistry was therefore uncertain at this stage but was later shown (see below) to be *A-S*/*C-R*, analogous to that in **7a** and **10** (Schemes 1 and 2) and in **13a** (Scheme 3). There is a general increase in the magnitude of the (aminoalkyl)platinum coupling constant ^2J(PtH) for complexes derived from the ligand **3** compared to the values for **1** and **2**. Complex **12** had limited thermal stability, and it decomposed in solution over a period of a few hours.

The reaction of **6** with excess HCl gives a mixture of isomers [PtMe$_2${C$_2$H$_4$(*N*=CH-2-C$_5$H$_4$*N*)(NH$_2$*C*H-2-C$_5$H$_4$NH)}Cl][Cl]$_2$ (**13a**,**b**) (Scheme 3), and recrystallization led to partial deprotonation of **13a** to give **14a**. Complex **14a** was characterized by an X-ray structure determination (see below), and its ^{1}H NMR spectrum (very similar to that of **13a**) contained an aminoalkyl resonance at δ 5.31 with ^2J(PtH) = 96 Hz which, as found for **12**, is intermediate between values for **8a** and **8b**. The stereochemistry is analogous to that of **7a**, **8a**, **10**, **11a**, and **12** (Schemes 1−3). The stereochemistry of the second isomer **13b** is less certain, since its ^{1}H NMR parameters are significantly different from those of all other complexes studied. The ^{1}H NMR of **13b** shows methylplatinum(IV) peaks at δ 1.04 with ^2J(PtH) = 66 Hz and at an unusual value of δ 1.69 with ^2J(PtH) = 67 Hz. The almost identical methylplatinum(IV) coupling constants suggest that the methyl groups are trans to a pyridyl and an imine ligand, since these groups exhibit similar trans influences.[10] The (aminoalkyl)platinum(IV) resonance for **13b** (−70 °C in CD_3OD solvent) was observed at δ 4.56 with ^2J(Pt−H) = 64 Hz. These data suggest that **13b** may contain a *facially* coordinated N,N,C(aminoalkyl) ligand, as indicated in Scheme 3. The reaction was monitored by ^{1}H NMR spectroscopy in CD_3OD solution, with the acid addition carried out at −70 °C, and it was shown that complex **13b** forms first and is the only complex present at low temperature. When it is warmed to room temperature, isomerization of **13b** to isomer **13a** occurred slowly and, after 15 h at ambient temperature, the ratio **13a**:**13b** was 2:1.

On crystallization, partial deprotonation of complex **13a** occurred to yield **14a**, with the free pyridyl group not protonated. The structure of complex **14a** is given in Figure 4, and selected bond distances and angles are given in Table 4. The structure is similar to that established for **8a** (Figure 2), having relative chiralities at platinum and carbon of *A-S*. However, the conformation is significantly different as a result of the presence of the seven-membered ring in **14a**. This conformational change allows the aminoalkyl proton to be in a staggered position with respect to the axial methylplatinum ligand (compare Figures 2 and 4), and this is probably the cause of the different NMR parameters for **8a** and **13a** discussed above. The N(12)H$_2$ hydrogen atoms were

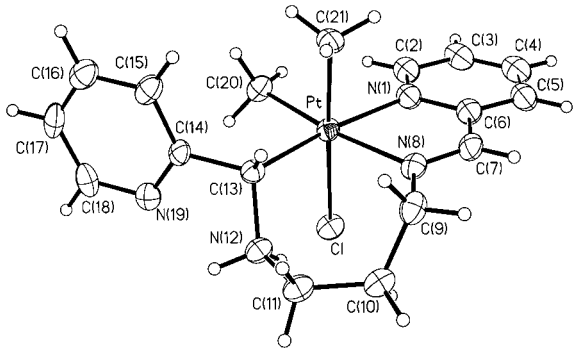

Figure 4. View of the *A-S* enantiomer of the complex [PtMe$_2${C$_3$H$_6$(*N*=CH-2-C$_5$H$_4$*N*)(NH$_2$*C*H-2-C$_5$H$_4$N)}Cl][Cl] (**14a**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 14a

(a) Bond Lengths (Å)

Pt−C(21)	2.060(5)	Pt−C(20)	2.062(6)
Pt−C(13)	2.090(5)	Pt−N(1)	2.130(5)
Pt−N(8)	2.140(5)	Pt−Cl	2.4961(13)
C(6)−C(7)	1.451(8)	C(7)−N(8)	1.276(7)
N(8)−C(9)	1.467(8)	C(9)−C(10)	1.531(9)
C(10)−C(11)	1.509(8)	C(11)−N(12)	1.505(6)
N(12)−C(13)	1.518(6)	C(13)−C(14)	1.506(7)

(b) Bond Angles (deg)

C(21)−Pt−C(20)	89.9(2)	C(21)−Pt−C(13)	89.4(2)
C(20)−Pt−C(13)	92.7(2)	C(21)−Pt−N(1)	90.5(2)
C(20)−Pt−N(1)	95.4(2)	C(13)−Pt−N(1)	171.90(19)
C(21)−Pt−N(8)	87.2(2)	C(20)−Pt−N(8)	172.7(2)
C(13)−Pt−N(8)	93.92(19)	N(1)−Pt−N(8)	77.99(19)
C(21)−Pt−Cl	177.22(17)	C(20)−Pt−Cl	90.46(18)
C(13)−Pt−Cl	93.32(15)	N(1)−Pt−Cl	86.76(13)
N(8)−Pt−Cl	92.13(12)	N(8)−C(7)−C(6)	119.6(5)
C(7)−N(8)−C(9)	119.6(5)	C(7)−N(8)−Pt	113.7(4)
C(9)−N(8)−Pt	126.5(4)	N(8)−C(9)−C(10)	112.3(5)
C(11)−C(10)−C(9)	116.3(5)	N(12)−C(11)−C(10)	115.0(5)
C(11)−N(12)−C(13)	115.8(4)	C(14)−C(13)−N(12)	107.6(4)
C(14)−C(13)−Pt	115.6(3)	N(12)−C(13)−Pt	108.9(3)

(9) Aminoalkyl complexes containing MCCN rings, M = Pd, Pt, can be prepared by reaction of an amide with a metal−alkene complex. (a) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 3806. (b) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. (d) Mitchenko, S. A.; Zamashchikov, V. V.; Slinkin, S. M. *Russ. J. Gen. Chem.* **1993**, *63*, 667. (e) Zamashchikov, V. V.; Mitchenko, S. A.; Slinkin, S. M. *Russ. Chem. Bull.* **1994**, *43*, 478.

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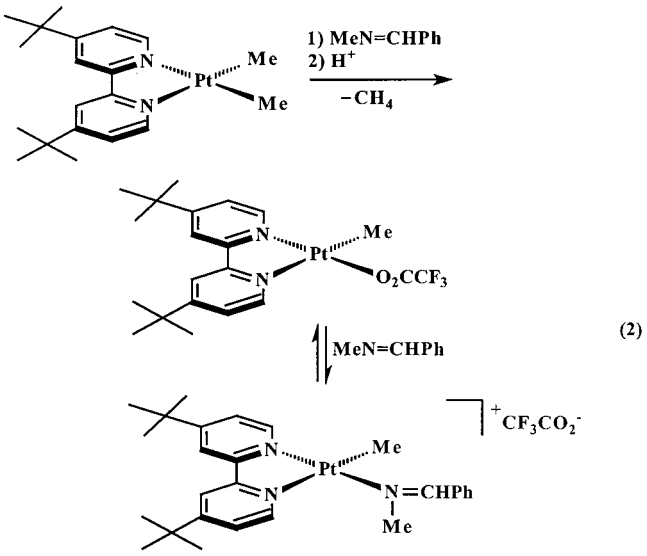
located in the X-ray structure determination, while no hydrogen was located on N(19), and this is consistent with the greater basicity of a secondary amine compared to pyridine. There was hydrogen bonding between the dialkylammonium group and a methanol solvent molecule, while the chloride counterion is not involved in H-bonding.

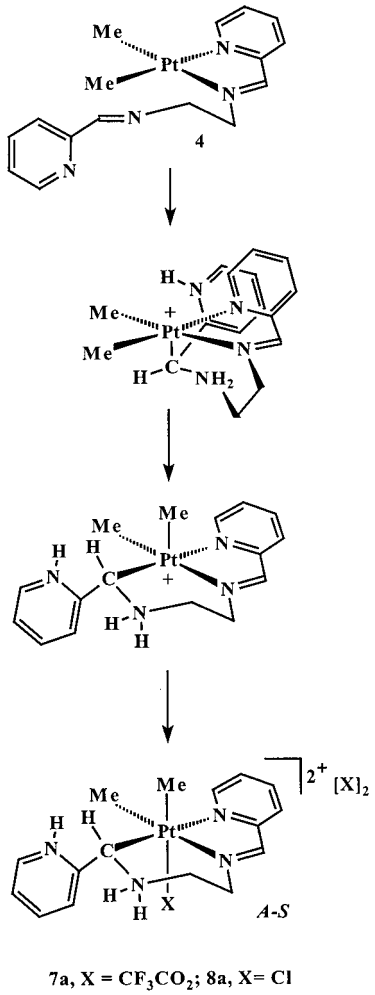
The structure of **14a** demonstrates the flexible nature of the seven-membered ring and indicates that the facial complex **13b** might not be unduly strained. It is expected that the metalation reaction occurs by initial formation of a Pt−C bond above or below the square plane of the platinum(II) substrate to give the facial stereochemistry,[4,11] but rearrangement to the meridional isomer is usually rapid. Isomerization of **13b** to **13a** can occur by loss of the chloride ligand and migration of the aminoalkyl group from an axial to an equatorial position (with migration of a methyl group), followed by recoordination of the chloride trans to a methyl group (Scheme 3).

Reactions of a a Dimethylplatinum(II) Complex with Imines and Protic Acid. Several reactions were carried out in which the simple dimethylplatinum(II) complex [$PtMe_2(bu_2bpy)$] in the presence of a free imine, MeN=CHPh or PhN=CHPh, was reacted with a protic acid, to determine if (aminoalkyl)platinum(IV) complexes might be formed by intermolecular activation of the imine. The reaction with PhN=CHPh and CF_3CO_2H gave only [$PtMe(O_2CCF_3)(bu_2bpy)$], identified by its ^1H NMR spectrum.[12] Thus, the reaction occurs by protonolysis of a methylplatinum bond and the imine plays no role. The similar reaction of [$PtMe_2(bu_2bpy)$] with MeN=CHPh and CF_3CO_2H also gave [$PtMe(O_2CCF_3)(bu_2bpy)$],[12] but as a mixture with the complex [$PtMe(MeN{=}CHPh)(bu_2bpy)][O_2CCF_3$], characterized in the ^1H NMR spectrum by a doublet resonance at δ 4.15 with $^3J(PtH)$ = 40 Hz, characteristic of the MeN group coordinated to platinum(II).[13] The overall reaction is thus similar to that with PhN=CHPh, but the stronger base MeN=CHPh is able to compete with trifluoroacetate for coordination to platinum(II) (eq 2). The reactions were carried out under varying conditions, and monitored by ^1H NMR, but there was no evidence for formation of (aminoalkyl)platinum(IV) complexes, even as short-lived intermediates.



(2)

Scheme 4

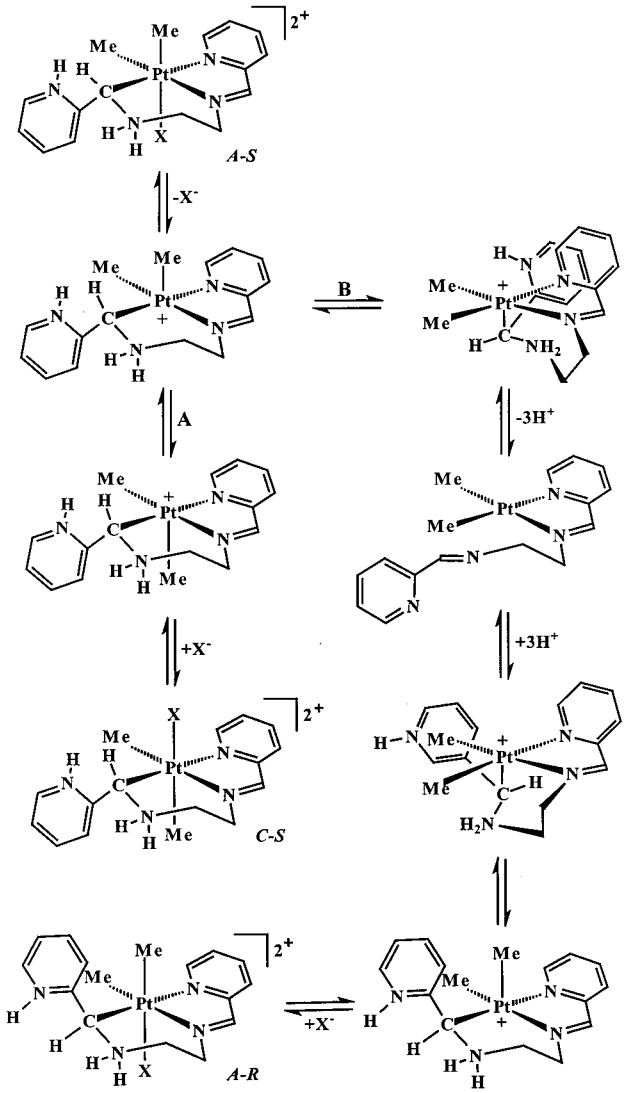


7a, X = CF_3CO_2; 8a, X= Cl

Discussion

The chemistry reported here shows that the protonation of imines tethered to dimethylplatinum(II) centers to give (aminoalkyl)platinum(IV) complexes is a general reaction.[4] With the simple ligands employed here, the reactions usually gave the products containing a meridionally bound NNC-tridentate ligand. These can be formed in two diastereomeric forms, described as *A-S/C-R* and *C-S/A-R* (Schemes 1−3). Activation of the imine bond should initially form a Pt−C bond above or below the plane of the dimethylplatinum(II) complex precursor to give a five-coordinate intermediate, and because the ligands are achiral, addition above or below the plane is equally probable. It is likely that the Pt−C bond forms in such a way as to maximize the $\pi-\pi$ overlap between the two aromatic pyridyl (or quinolyl) groups, as shown in Scheme 4, and rapid isomerization of the initially formed facially coordinated NNC ligand to the preferred *mer*- tridentate form will then give the *A-S/C-R* diastereomer as the kinetic product. This stereoselectivity is supported by X-ray structure determinations on the complexes **7a**, **8a**, **9**, and **13a**.

Scheme 5



7, X = CF_3CO_2; 8, X = Cl

The minor diastereomers **7b**, **8b**, and **11b**, which have the absolute configuration *A-R*/*C-S* can be formed in one of two ways, involving overall change in stereochemistry at carbon or platinum. This can be illustrated by the isomerization of complex **8a** to **8b**. Stereochemical change at platinum would convert the *A-S* to the *C-S* enantiomer. It might occur by dissociation of chloride followed by methyl group migration and recoordination of chloride (Scheme 5, path A), and there are precedents for this mechanism in several other organoplatinum(IV) complexes.[4,8] Alternatively, stereochemical change at carbon would convert the *A-S* to the *A-R* enantiomer. This might occur by deprotonation of the aminoalkyl group to regenerate the imine group, followed by reprotonation and metalation at the opposite face (Scheme 5, path B). Of course, it is possible that both mechanisms might contribute to the observed changes.

If a large excess of CF_3CO_2H was added to an isomeric mixture of **7a** and **7b** (formed by the addition of 2 molar equiv of CF_3CO_2H to **4**), a rapid change to give exclusively **7a** was observed. A similar but less dramatic change was observed when excess HCl was added to a mixture of isomers **8a**,**b**, causing a slower increase in the ratio **8a**:**8b**. These results suggest that the isomerization occurs by path A (Scheme 5) under these conditions, since epimerization at the aminoalkyl carbon by reversible deprotonation is expected to be slow in the presence of excess acid. The position of equilibrium between **8a** and **8b** also appears to be affected by the presence of excess acid. However, in the absence of excess acid, it is likely that path B is preferred for the rearrangement, on the basis that the isomerization of **8a** to **8b** is retarded in the presence of acid.

The reaction of **6** with HCl also supports a reaction pathway in which diastereomeric discrimination occurs in an initially formed facial intermediate. The absolute configuration of the final product **13a** is *A-S* and so is expected to arise from a facial intermediate that has π-stacking between the pyridyl unit of a newly formed (aminoalkyl)platinum group and the pyridyl ligand bound to platinum(IV) (Scheme 4). The intermediate **13b** detected in this reaction is suggested to contain the *fac*-NNC ligand, but attempts to grow single crystals to confirm the stereochemistry have been unsuccessful.

Overall, good stereoselectivity has been demonstrated for formation of (aminoalkyl)platinum(IV) complexes derived from precursor complexes with achiral ligands and the generality of formation of (aminoalkyl)platinum(IV) complexes from platinum(II) complexes having a tethered imine substituent and acid has been established. However, the more desirable activation of untethered imines has not yet been accomplished, since cleavage of methylplatinum groups occurs preferentially.

Experimental Section

General Procedures. All reactions were carried out using standard Schlenk techniques unless otherwise noted. NMR spectra were recorded using a Varian Gemini spectrometer (^{1}H at 300 MHz, ^{19}F at 282 MHz). Chemical shifts are reported relative to TMS (^{1}H) or $CFCl_3$ (^{19}F). The ^{19}F chemical shifts are referenced to $CFCl_3$ contained in a coaxial insert. The complexes $[PtMe_2(\mu\text{-}SMe_2)]_2$[14] and $[PtMe_2(bu_2bpy)]$[15] were prepared by the literature methods.

Synthesis of Ligands. $C_2H_4(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (1). To a solution of 1,2-diaminoethane (1 mL) in diethyl ether (30 mL) was added 2-pyridinecarboxaldehyde (2.85 mL). A large excess of $MgSO_4$ was added to the reaction mixture to remove product water. The solution was stirred for 15 h and then filtered to give a pale yellow filtrate. The filtrate was concentrated under reduced pressure until a white precipitate separated. The off-white solid was isolated by filtration and washed with cold diethyl ether (3 × 8 mL). The ligand was stored under an inert atmosphere. Yield: 81%. MS: calcd *m/e* for $C_{14}H_{14}N_4$, 238.122; found, 238.122. ^{1}H NMR (CD_2Cl_2): δ 4.01 [s, 4H, CH_2]; 7.28 [m, 2H]; 7.70 [t d, 2H]; 7.99 [d t, 2H]; 8.39 [s, 2H, N=CH]; 8.58 [m, 2H].

$C_2H_4(N{=}CH\text{-}2\text{-}C_9H_6N)_2$ (2) was similarly prepared from 1,2-diaminoethane and 2-quinolinecarboxaldehyde. Yield: 84%. MS: calcd *m/e* for $C_{22}H_{18}N_4$, 338.153; found, 338.152. ^{1}H NMR

(11) A facial intermediate is expected if an S_N2 mechanism is operating.[8]

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(CD_3Cl): δ 4.13 [s, 4H, CH_2]; 7.51 [m, 2H]; 7.68 [m, 2H]; 7.77 [d d, 2H]; 8.07 [d, 2H]; 8.12 [s, 4H]; 8.58 [s, 2H, N=CH].

$C_3H_6(N{=}CH\text{-}2\text{-}C_5H_4N)_2$ (3) was similarly prepared from 1,2-diaminopropane and 2-pyridinecarboxaldehyde. Evaporation of the solvent gave a pale yellow oil which was dried extensively under reduced pressure. MS: calcd *m/e* for $C_{15}H_{16}N_4$, 252.137; found, 252.137. ^{1}H NMR (CD_2Cl_2): δ 2.11 [quin, 2H, CH_2]; 3.13 [t d, 4H, CH_2]; 7.30 [m, 2H]; 7.73 [m, 2H]; 8.02 [d t, 2H]; 8.39 [s, 2H, NCH]; 8.61 [d, 2H].

[$PtMe_2${C_2H_4(*N*=CH-2-C_5H_4N)(N=CH-2-C_5H_4N)}] (4). A solution of [$PtMe_2(\mu$-$SMe_2)]_2$ (0.12 g, 0.21 mmol) in CH_2Cl_2 (10 mL) was treated with Me_2S (30 μL) to convert it into [$PtMe_2$-$(SMe_2)_2$]. This solution was then added to a large excess of ligand **1** (0.74 g, 3.11 mmol) in CH_2Cl_2 (10 mL), producing a deep red color. After 30 min the solvent was removed to give a red oil. The oil was dissolved in the minimum amount of CH_2Cl_2, and the product was crystallized by adding ether (3 × 2 mL) and then pentane (3 × 8 mL), followed by stirring for 1 h. The red powder was washed well with ether (2 mL) and then pentane (8 mL). The product was recrystallized two more times from CH_2Cl_2 and ether/pentane and then dried under reduced pressure. Yield: 0.15 g (77%). Anal. Calcd for $C_{16}H_{20}N_4$-Pt·0.1CH_2Cl_2: C, 41.0; H, 4.3; N, 11.9. Found: C, 40.9; H, 4.6; N, 11.7 (solvent confirmed by NMR). ^{1}H NMR (CD_2Cl_2): δ 1.11 [s, 3H, ^2J(PtH) = 87 Hz, Pt−Me]; 1.14 [s, 3H, ^2J(PtH) = 84 Hz, Pt−Me]; 4.13 [m, 2H, N−CH_2]; 4.48 [m, 2H, N−CH_2]; 7.30 [m, 1H]; 7.58 [m, 1H]; 7.72 [m, 2H]; 7.93 [d d, 1H]; 8.06 [m, 1H]; 8.33 [s, 1H, N=CH], 8.58 [m, 1H]; 9.14 [s, 1H, ^3J(PtH) = 36 Hz]; 9.17 [d, 1H].

[$PtMe_2${C_2H_4(*N*=CH-2-C_9H_6N)(N=CH-2-C_9H_6N)}] (5). To a solution of excess ligand **3** (0.29 g, 0.86 mmol) in diethyl ether (40 mL) was added [$PtMe_2(\mu$-$SMe_2)]_2$ (0.041 g, 0.07 mmol), turning the solution blue. The solution was stirred for 15 h, and the blue color darkened while a deep purple precipitate separated. The purple product was isolated and washed with small amounts of diethyl ether (5 × 2 mL). Yield: 0.34 g (43%). Anal. Calcd for $C_{24}H_{24}N_4Pt$: C, 51.2; H, 4.3; N, 9.9. Found: C, 51.2; H, 4.4; N, 9.6. ^{1}H NMR (CD_2Cl_2): δ 1.38 [s, 3H, ^2J(PtH) = 90 Hz, Pt−Me]; 1.56 [s, 3H, ^2J(PtH) = 84 Hz, Pt−Me]; 4.22 [t, 2H, N−CH_2]; 4.58 [m, 2H, N−CH_2]; 7.56 [m, 1H]; 7.60 [d d, 1H]; 7.71 [m, 2H]; 7.80−7.94 [m, 3H]; 8.01 [d, 1H]; 8.06 [d, 1H]; 8.18 [d, 1H]; 8.51 [s, 1H, N=CH]; 8.56 [d, 1H]; 9.07 [d, 1H]; 9.60 [s, 1H, ^3J(PtH) = 34 Hz, N=CH].

[$PtMe_2${C_3H_6(*N*=CH-2-C_5H_4N)(N=CH-2-C_5H_4N)}] (6) was prepared similarly to complex **4**. Yield: 91%. Anal. Calcd for $C_{17}H_{22}N_4Pt$: C, 42.8; H, 4.6; N, 11.7. Found: C, 42.9; H, 4.9; N, 11.6. ^{1}H NMR (CD_2Cl_2): δ 1.08 [s, 3H, ^2J(PtH) = 88 Hz, Pt−Me]; 1.11 [s, 3H, ^2J(PtH) = 84 Hz, Pt−Me]; 2.27 [quin, 2H]; 3.72 [m, 2H]; 4.27 [m, 2H]; 7.33 [m, 1H]; 7.59 [m, 1H]; 7.68 [m, 1H]; 7.75 [m, 1H]; 8.02 [m, 1H]; 8.09 [m, 1H]; 8.38 [s, 1H, N=CH]; 8.62 [m, 1H]; 9.17 [d, 1H]; 9.20 [s, 1H, ^3J(PtH) = 35 Hz, N=CH].

[$PtMe_2${C_2H_4(*N*=CH-2-C_5H_4N)(NH_2*C*H-2-C_5H_4NH)}-(O_2CCF_3)][O_2CCF_3]$_2$ (7a,b). To a red solution of complex **4** (0.036 g, 0.078 mmol) in CH_2Cl_2 (8 mL) was added CF_3CO_2H (18.0 μL, 0.23 mmol) to give a yellow solution. The solution was stirred for 15 h, and then it was placed in a freezer to precipitate the pale yellow product, as a mixture of isomers **7a** and **7b**. Yield: 0.034 g (54%). Anal. Calcd for $C_{22}H_{23}N_4$-PtO_6F_9: C, 32.8; H, 2.9; N, 7.0. Found: C, 32.7; H, 2.5; N, 6.9. ^{1}H NMR (CD_3CN): **7a**, δ 0.68 [s, 3H, ^2J(PtH) = 64 Hz, Pt−Me], 1.03 [s, 3H, ^2J(PtH) = 75 Hz, Pt−Me], 3.30 [t d, 1H], 3.88 [m, 1H], 4.46 [m, 1H], 4.88 [m, 1H], 4.94 [s, 1H, ^2J(PtH) = 56 Hz, PtCHR−NH], 7.25 [m, 2H], 7.76 [t d, 1H], 7.86 [m, 1H], 8.15 [d, 1H], 8.29 [m, 1H], 8.42 [d, 1H], 8.76 [d, 1H, ^3J(PtH) = 15 Hz], 9.15 [s, 1H, ^3J(PtH) = 34 Hz, N=CH]; **7b**, δ 0.45 [s, 3H, ^2J(PtH) = 77 Hz, Pt−Me], 1.08 [s, 3H, ^2J(PtH) = 64 Hz, Pt−Me], 5.72 [s, 1H, ^2J(PtH) = 128 Hz, PtCHR−NH], 9.25 [s, 1H, ^3J(PtH) = 36 Hz, N=CH]. A similar reaction of complex **4** in CD_2Cl_2 with 5 equiv of CF_3CO_2H in an NMR tube gave pure **7a**. ^{1}H NMR (CD_2Cl_2): **7a**, δ 0.75 [s, 3H, ^2J(PtH) = 61 Hz, Pt−Me]; 1.22 [s, 3H, ^2J(PtH) = 72 Hz, Pt−Me]; 3.54 [m, 1H]; 4.15 [br d, 1H]; 4.58 [br d, 1H]; 4.94 [m, 1H]; 5.53 [s, 1H, ^2J(PtH) = 62 Hz, PtCHR−NH]; 7.89−8.06 [m, 3H]; 8.21 [d, 1H]; 8.35 [m, 1H]; 8.54 [m, 1H]; 8.68 [m, 1H]; 8.77 [d, 1H, ^3J(PtH) = 18 Hz]; 9.25 [s, 1H, ^3J(PtH) = 34 Hz, N=CH]. ^{19}F NMR (CD_2Cl_2): δ −76.2 (s); −76.6 (s).

[$PtMe_2${C_2H_4(*N*=CH-2-C_5H_4N)(NH_2*C*H-2-C_5H_4NH)}Cl]-[Cl]$_2$ (8a,b). To a solution of **4** (0.028 g, 0.060 mmol) in CH_2-Cl_2 (10 mL) was added 5 molar equiv of HCl, generated in situ from H_2O (5.4 μL, 0.30 mmol) and Me_3SiCl (38.3 μL, 0.30 mmol). The red solution turned yellow, and a pale yellow precipitate began to separate. The solution was stirred for 15 h, and the supernatant was removed via cannula, leaving a pale yellow solid. The product, a mixture of isomers **8a** and **8b**, was washed with CH_2Cl_2 (3 × 8 mL) and dried under reduced pressure. Yield: 0.021 g (59%). Anal. Calcd for $C_{16}H_{23}N_4PtCl_3$·H_2O: C, 32.5; H, 4.3; N, 9.5. Found: C, 32.4; H, 4.0; N, 9.1. ^{1}H NMR (CD_3OD): **8a**, δ 0.66 [s, 3H, ^2J(Pt−H) = 64 Hz, Pt−Me], 1.11 [s, 3H, ^2J(Pt−H) = 69 Hz, Pt−Me], 3.52 [m, 1H], 3.98 [m, 1H], 4.66 [m, 2H], 5.28 [s, 1H, ^2J(Pt−H) = 72 Hz, PtCHR−NH], 7.95 [m, 1H], 8.04 [m, 1H], 8.39 [m, 2H], 8.66 [m, 2H], 8.87 [m, 2H], 9.47 [s, 1H, ^3J(Pt−H) = 34 Hz, N=CH]; **8b**, δ 0.70 [s, 3H, ^2J(Pt−H) = 73 Hz, Pt−Me], 0.87 [s, 3H, ^2J(Pt−H) = 65 Hz, Pt−Me], 5.99 [s, 1H, ^2J(Pt−H) = 125 Hz, PtCHR−NH], 9.44 [s, 1H, N=CH]. The presence of water was confirmed by the proton NMR spectrum.

[$PtMe_2${C_2H_4(*N*=CH-2-C_9H_6N)(NH*C*H-2-C_9H_6N)}][CF_3CO_2] (9). To a blue suspension of **5** (0.025 g, 0.054 mmol) in diethyl ether (10 mL) was added CF_3CO_2H (3.4 μL, 0.054 mmol), turning the solution a dark orange. The solution was stirred for 15 h, and a peach-colored solid precipitated, which was isolated by filtration. The product was then washed with ether (3 × 10 mL). Yield: 0.02 g (55%). Anal. Calcd for $C_{26}H_{25}N_4PtO_2F_3$: C, 46.1; H, 3.7; N, 8.3. Found. C, 45.7, H, 3.3; N, 7.8. ^{1}H NMR (CD_2Cl_2): δ 0.88 [s, 3H, ^2J(PtH) = 75 Hz, Pt−Me]; 1.41 [s, 3H, ^2J(PtH) = 72 Hz, Pt−Me]; 2.41 [t, 1H]; 3.48 [m, 1H]; 3.98 [t, 1H]; 4.16 [m, 1H]; 5.01 [s, 1H, ^2J(PtH) = 52 Hz, PtCHR−NH]; 6.20 [d, 1H]; 7.20 [m, 1H]; 7.47 [m, 1H]; 7.53 [d, 1H]; 7.87 [m, 2H]; 8.00 [m, 1H]; 8.20 [d, 1H]; 8.31 [d, 1H]; 8.50 [d, 1H]; 8.79 [m, 2H]; 10.18 [s, 1H, ^3J(PtH) = 39 Hz, N=CH]. ^{19}F NMR (CD_2Cl_2): δ −75.4 (s). ^{13}C NMR (CD_2Cl_2): δ −10.6 [^1J(Pt−C) = 747 Hz, PtMe]; −2.1 [^1J(Pt−C) = 734 Hz, PtMe]; 42.2 [^1J(Pt−C) = 521 Hz, PtCHR−NH]; 44.8 [^2J(Pt−C) = 36 Hz, NCH_2]; 56.4 [^3J(Pt−C) = 11 Hz, NCH_2]; 120.1 [^3J(Pt−C) = 49 Hz, CH]; 123.8 [^3J(Pt−C) = 9 Hz, CH]; 125.2 [CH]; 128.0 [CH]; 128.2 [CH]; 128.6 [C]; 129.2 [CH]; 129.4 [CH]; 130.1 [CH]; 130.8 [C]; 131.9 [CH]; 133.3 [CH]; 138.9 [CH]; 141.6 [CH]; 143.9 [C]; 148.3 [C]; 153.0 [^2J(Pt−C) = 18 Hz, C]; 170.5 [^2J(Pt−C) = 16 Hz, N=CH]; 171.8 [^2J(Pt−C) = 88 Hz, C].

[$PtMe_2${C_2H_4(*N*=CH-2-C_9H_6N)(NH_2*C*H-2-C_9H_6NH)}-(O_2CCF_3)][CF_3CO_2]$_2$ (10). The complex was prepared in situ by addition of an excess (5 equiv) of CF_3CO_2H to an NMR tube charged with a CD_2Cl_2 solution of **5**. The ^{1}H NMR spectrum was recorded after 5 min. ^{1}H NMR (CD_2Cl_2): δ 1.0 [s, 3H, ^2J(PtH) = 62 Hz, Pt−Me]; 1.16 [s, 3H, ^2J(PtH) = 69 Hz, Pt−Me]; 3.61 [m, 1H]; 4.28 [m, 1H]; 4.76 [m, 1H]; 5.10 [m, 1H]; 5.66 [s, 1H, ^2J(PtH) = 66 Hz, Pt−Me]; 7.87 [m, 2H]; 7.98−8.09 [m, 2H]; 8.10−8.31 [br m, 6H]; 8.81 [d, 1H]; 9.04 [d, 1H]; 9.52 [d, 1H, ^3J(PtH) = 35 Hz, N=CH]. ^{19}F NMR (CD_2Cl_2): δ −75.9 (s); −76.6 (s).

[$PtMe_2${C_2H_4(*N*=CH-2-C_9H_6N)(NH_2*C*H-2-C_9H_6NH)}Cl]-[Cl]$_2$ (11a,b). To a solution of **5** (0.014 g, 0.025 mmol) in CH_2-Cl_2 (6 mL) was added 5 equiv of HCl, generated in situ by the addition of Me_3SiCl (16 μL, 0.076 mmol) to CH_3OH (4.3 μL, 0.076 mmol). The purple solution lightened to pale peach. After the mixture was stirred for 15 h, a peach-colored precipitate was isolated and washed with CH_2Cl_2 (3 × 2 mL). The product, a mixture of **11a** and **11b**, was then dried under reduced pressure. Yield: 0.005 g (25%). Anal. Calcd for $C_{24}H_{27}N_4Cl_3$-Pt·2.5CH_3OH: C, 38.3; H, 3.6; N, 7.4. Found: C, 38.3; H, 4.1;

Table 5. Crystallographic Details for Complexes 7a, 8a, 9, and 14a

	7a	8a	9	14a
formula	$C_{22}H_{23}F_9N_4O_6Pt$	$C_{17}H_{25}Cl_3N_4OPt$	$C_{26}H_{25}F_3N_4O_2Pt$	$C_{18}H_{28}Cl_2N_4OPt$
fw	805.53	602.85	677.59	582.43
temp, K	193(2)	293(2)	200(2)	150(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*1	$P2_1/c$	*C*2/*c*	$P2_1/c$
a, Å	9.2707(2)	9.3415(2)	21.7762(18)	9.0613(3)
b, Å	12.8180(2)	10.5506(2)	12.9791(8)	21.6400(10)
c, Å	13.9085(1)	22.3484(2)	19.4521(15)	11.0531(5)
α, deg	112.734(1)			
β, deg	94.479(1)	97.890(1)	115.272(3)	98.409(3)
γ, deg	110.266(1)			
V, Å^3; Z	1386.43(4); 2	2181.77(7); 4	4971.7(6); 8	2144.06(16); 4
d(calcd), Mg/m^3	1.930	1.835	1.811	1.804
abs coeff, mm^{-1}	5.165	6.812	5.698	6.808
F(000)	780	1168	2640	1136
no. of rflns collected	7788	11 813	10 811	19 522
no. of indep rflns	5369 (*R*(int) = 0.0313)	4391 (*R*(int) = 0.0427)	3156 (*R*(int) = 0.075)	4903 (*R*(int) = 0.0790)
abs cor	Sadabs	Sadabs	integration	integration
max and min transmissn	0.6946 and 0.5568	0.6123 and 0.4791	0.7795 and 0.4269	0.4088 and 0.2919
no. of data/restraints/params	5369/201/392	4391/4/245	3156/12/321	4903/0/235
GOF on F^2	1.043	1.108	0.964	1.072
R ($I > 2\sigma(I)$)	R1 = 0.0385, wR2 = 0.0841	R1 = 0.0422, wR2 = 0.0759	R1 = 0.0337, wR2 = 0.0612	R1 = 0.0380, wR2 = 0.0930
R (all data)	R1 = 0.0511, wR2 = 0.0880	R1 = 0.0663, wR2 = 0.0831	R1 = 0.0662, wR2 = 0.0678	R1 = 0.0505, wR2 = 0.1012
peak, hole, e Å^{-3}	1.141, −1.332	0.985, −0.643	0.747, −0.678	1.654, −2.371

N, 7.4. ^{1}H NMR (CD_3OD): **11a**, δ 0.90 [s, 3H, ^2J(PtH) = 65 Hz, Pt−Me], 1.04 [s, 3H, ^2J(PtH) = 67 Hz, Pt−Me], 3.60 [m, 1H], 4.08 [m, 1H], 4.78 [m, 2H], 5.49 [s, 1H, ^2J(PtH) = 71 Hz, PtCHR−NH], 7.86 [m, 2H]; 8.02 [m, 1H], 8.13−8.48 [br m, 6H], 8.73 [d, 1H], 8.95 [d, 1H], 9.20 [d, 1H], 9.76 [s, 1H, ^3J(PtH) = 35 Hz, Pt−Me]; **11b**, δ 0.91 [s, 3H, ^2J(PtH) = 65 Hz, Pt−Me], 0.97 [s, 3H, ^2J(PtH) = 74 Hz, Pt−Me], 6.08 [s, 1H, ^2J(PtH) = 126 Hz, PtCHR−NH]. The presence of methanol was confirmed by the proton NMR spectrum.

[PtMe$_2${C$_3$H$_6$(*N*=CH-2-C$_5$H$_4$*N*)(NH$_2$*C*H-2-C$_5$H$_4$NH)}(O$_2$CCF$_3$)][CF$_3$CO$_2$]$_2$ (12). An NMR tube was charged with a red solution of complex **6** in CD_2Cl_2, and to this was added 5 equiv of CF_3CO_2H, changing the color to yellow. The ^{1}H NMR spectrum was recorded after 5 min. ^{1}H NMR (CD_2Cl_2): δ 0.69 [s, 3H, ^2J(PtH) = 62 Hz, Pt−Me]; 1.09 [s, 3H, ^2J(PtH) = 73 Hz, Pt−Me]; 2.40 [m, 2H]; 3.78 [m, 2H]; 4.58 [m, 2H]; 5.65 [s, 1H, ^2J(PtH) = 89 Hz, PtCHR−NH]; 7.85 [m, 3H]; 8.16 [d d, 1H]; 8.33 [d t, 1H]; 8.52 [d t, 1H]; 8.68 [d, 1H]; 8.81 [d, 1H, ^3J(PtH) = 19 Hz]; 9.05 [s, 1H, ^3J(PtH) = 31 Hz, Pt−Me]. ^{19}F NMR (CD_2Cl_2): δ −75.0 (s); −76.5 (s).

[PtMe$_2${C$_3$H$_6$(*N*=CH-2-C$_5$H$_4$*N*)(NH$_2$*C*H-2-C$_5$H$_4$NH)}Cl][Cl]$_2$ (13a,b) were prepared similarly to complexes **8**. Yield: 58%. Anal. Calcd for $C_{17}H_{25}N_4PtCl_3$: C, 34.8; H, 4.3; N, 9.6. Found: C, 34.8; H, 4.6; N, 9.7. ^{1}H NMR (CD_3OD): **13b**, δ 1.04 [s, 3H, ^2J(Pt−H) = 66 Hz, Pt−Me], 1.69 [s, 3H, ^2J(Pt−H) = 67 Hz, Pt−Me], 2.39 [m, 2H], 3.45 [m, 2H], 4.3 [m, 1H], 4.56 [s, 1H, ^2J(Pt−H) = 64 Hz, PtCHR−NH], 4.63 [m, 1H], 7.32 [m, 1H], 7.40 [m, 1H], 7.52 [m, 1H], 7.66 [m, 1H], 7.81 [m, 1H], 7.86−7.94 [m, 1H], 8.23 [m, 2H], 9.46 [s, 1H, ^3J(Pt−H) = 31 Hz, N=CH]; **13a**, δ 0.58 [s, 3H, ^2J(Pt−H) = 64 Hz, Pt−Me], 0.96 [s, 3H, ^2J(Pt−H) = 71 Hz, Pt−Me], 2.45 [m, 2H], 3.53 [m, 1H], 3.78 [m, 1H], 4.60 [m, 2H], 5.31 [s, 1H, ^2J(Pt−H) = 96 Hz, PtCHR−NH], 7.86−7.94 [m, 1H], 7.94−8.08 [m, 2H], 8.28−8.50 [m, 3H], 8.77 [d, 1H], 8.85 [d, 1H, ^3J(Pt−H) = 10 Hz], 9.25 [s, 1H, ^3J(Pt−H) = 30 Hz, N=CH].

X-ray Structure Determinations. Crystallographic details for all structure determinations are provided in Table 5. Crystals of **7a** were grown from CH_2Cl_2 solution at −5 °C. A yellow block was selected and mounted in a capillary tube. The fluorine atoms attached to C20 were disordered. Two models were resolved with occupancies 0.08/0.02. Common isotropic thermal parameters were refined for the minor component.

Crystals of **8a** were grown from a CH_3OH/CH_2Cl_2 solution that was layered with pentane. Residual electron density in the Fourier difference map was modeled as disordered MeOH. Four such MeOH non-hydrogen atoms were included in the least-squares cycles with occupancies 0.3, 0.3, 0.2, and 0.2. A common isotropic thermal parameter was refined. N−H···Cl hydrogen bonding confirmed the location of the nitrogen atom in the pyridine ring.

Crystals of complex **9** were grown by slow diffusion of pentane into a dichloromethane solution. A red-orange needle was cut and mounted on a glass fiber. The cation was well-behaved, but the anion showed some positional disorder and was modeled as two isotropic half-occupancy groups. The C−O distance was fixed (1.22 Å), the C−C distance was fixed (1.53 Å), and the C−F distances were refined to a value of 1.34 Å. All other non-hydrogen atoms were refined with anisotropic thermal parameters.

Crystals of **14a** were grown from a CH_3OH/CH_2Cl_2 solution that was layered with pentane and then placed in the freezer. An orange crystal was mounted in a capillary for data collection. There was one solvent molecule found in the asymmetric unit, a methanol. It was refined anisotropically complete with hydrogen atoms. An examination of the final difference map generated without hydrogens on N12 or N19 revealed two peaks. They were within 0.9(±0.1) Å from N12; therefore, an AFIX instruction was used to calculate them geometrically. H12A was found to be 1.97 Å from O32.

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Supporting Information Available: Tables of X-ray data for **7a**, **8a**, **9**, and **14a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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