Easy Making and Breaking of Metal−Metal Donor−Acceptor Bonds in the Chemistry of Binuclear Methylplatinum(II) Complexes

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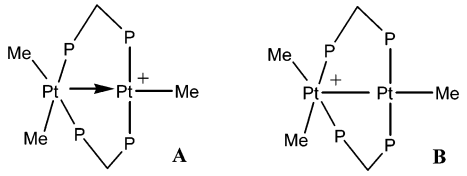
Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with PN = 2-$Ph_2PC_5H_4N$ gave *cis,cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)(\mu\text{-}PN)]$, which reacts regioselectively with CF_3CO_2H at low temperature to give $[Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-}PN)PtMe(O_2CCF_3)]$, which then isomerizes to give $[Me(CF_3CO_2)Pt(\mu\text{-}PN)PtMe_2(SMe_2)]$, which contains a PtPt donor−acceptor bond. This bond is broken on addition at low temperature of more ligand PN to give $[Me(NP)Pt(\mu\text{-}SMe_2)(\mu\text{-}PN)PtMe_2](CF_3CO_2)$, which loses dimethyl sulfide easily to form the unusual head-to-head bis(PN)-bridged complex $[MePt(\mu\text{-}PN)_2PtMe_2](CF_3CO_2)$, and this complex then isomerizes to the head-to-tail isomer $[MePt(\mu\text{-}PN)(\mu\text{-}NP)PtMe_2](CF_3CO_2)$. These isomers both contain donor−acceptor PtPt bonds. The complexes are characterized by multinulear NMR methods, and the structures of *cis,cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)(\mu\text{-}PN)]$ and $[MePt(\mu\text{-}PN)_2PtMe_2](CF_3CO_2)$ have been determined crystallographically. The complexes with PtPt bonds give couplings ^1J(PtPt) in the range 2721−3812 Hz, while those without such bonds give couplings ^2J(PtPt) in the range 0−275 Hz in the ^{195}Pt NMR spectra.

Introduction

The complex $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, dppm = $Ph_2PCH_2PPh_2$, was one of the first organometallic compounds to be formulated with a donor−acceptor metal−metal bond, **A**, with both platinum atoms present as Pt(II), rather than the alternate structure **B**, containing both Pt(I) and Pt(III).[2] Since that time, such donor−acceptor



bonds have been proposed in several other dppm-bridged binuclear complexes,[3] and even unbridged donor−acceptor bonds have been established.[4] There has also been much interest in the use of other binucleating ligands to extend the early dppm chemistry,[5] and P,N donors such as 2-diphenylphosphinopyridine, PN, have proved to be especially useful in forming reactive binuclear complexes.[6−9] In particular, the ligand PN tends to favor short metal−metal separations in its bridged complexes.[8] It was of interest to study methylplatinum complexes with the ligand PN, and this article describes how the reversible formation of PtPt donor−acceptor bonds can play a key role in the reactions. An unusual example of characterization of both head-to-head and head-to-tail isomers in doubly PN-bridged complexes is also established.[6,8]

Results

Synthesis of the Bis(dimethylplatinum) Complex *cis,cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)(\mu\text{-}PN)]$ Dimethylplatinum(II) complexes with PN ligands were prepared

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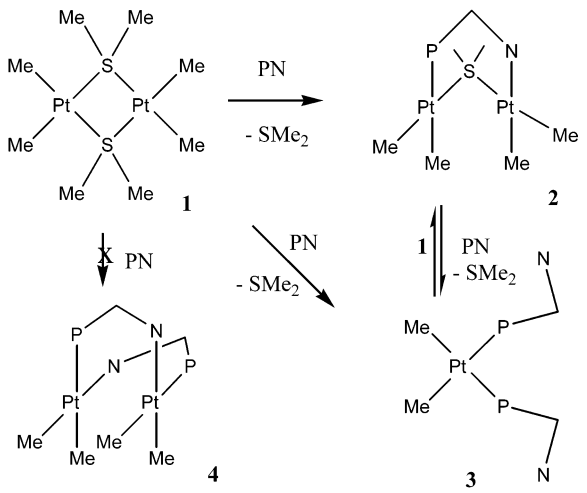
Scheme 1[a]



[a] PN = 2-$Ph_2PC_5H_4N$.

Table 1. Selected NMR Data for the Complexes

complex	δ(P)	^1J(PtP)	*trans*[a]	δ(Pt)	^1J(PtPt)	M−M bond
2	26.9	1855	C	−940	130	no
				−300		
5	35.2	1840	C	−917	275	no
				−160		
6	25.0	5040	O	−896	3200	yes
				−48		
9	24.8	3160	P	−1397	*b*	no
	25.2	3060	P	−241		
10	42.5	3200	P	−1270	3810	yes
				510		
11	23.8	4260	N	−747	2720	yes
	21.5	1085	C	−61		

[a] Atom *trans* to phosphorus; where there are two nonequivalent P or Pt atoms in a complex, the atom labeled *a* in Chart 1 is given first. [b] Not resolved, so presumed to be less than 100 Hz.

according to Scheme 1. Thus reaction of [Pt_2Me_4(μ-SMe_2)$_2$], **1**,[10] with 1 equiv of PN led to displacement of SMe_2 and formation of *cis*,*cis*-[Pt_2Me_4(μ-SMe_2)(μ-PN)], **2**. Reaction of **1** with 2 equiv of PN did not give the expected complex *cis*,*cis*-[Pt_2Me_4(μ-PN)$_2$], analogous to [Pt_2Me_4(μ-dppm)$_2$],[11] but instead gave a mixture of **2** and the known complex *cis*-[$PtMe_2$(PN-κ^1P)$_2$], **3**.[12] Complex **3** could be prepared in pure form by reaction of **1** with 4 equiv of PN or by reaction of **2** with 3 equiv of PN. Similarly complex **3** reacted with **1** to give **2**, but did not form *cis*,*cis*-[Pt_2Me_4(μ-PN)$_2$], **4**. The failure to form **4** is presumed to be associated with strain when two PN ligands span a long metal···metal distance.[6,8]

Complex **2** is unsymmetrical, and this is reflected in the ^{1}H NMR spectrum, which contains four methylplatinum resonances and two methylsulfur resonances, and in the ^{195}Pt NMR spectrum, which contains two platinum resonances at δ(Pt) = −940 [^1J(PtP) = 1860 Hz] and −300 [^3J(PtP) = 90 Hz] and with ^2J(PtPt) = 130 Hz (Table 1). The structure of **2** was confirmed crystallographically, with the structure illustrated in

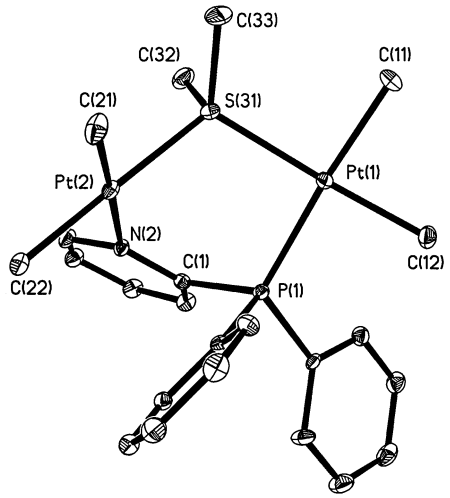
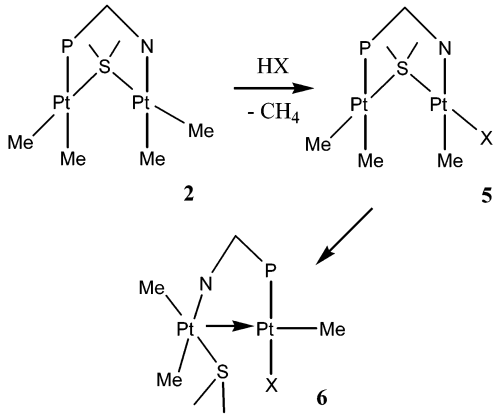


Figure 1. View of the structure of [Me_2Pt(μ-SMe_2)(μ-PN)-$PtMe_2$], **2**, showing 25% probability ellipsoids.

Table 2. Bond Lengths [Å] and Angles [deg] for [Pt_2Me_4(μ-SMe_2)(μ-2-$Ph_2PC_5H_4N$)], 2

Pt(1)−C(12)	2.059(6)	Pt(1)−C(11)	2.079(5)
Pt(1)−P(1)	2.302(1)	Pt(1)−S(31)	2.345(1)
Pt(2)−C(22)	2.038(6)	Pt(2)−C(21)	2.036(6)
Pt(2)−N(2)	2.125(4)	Pt(2)−S(31)	2.319(1)
C(12)−Pt(1)−C(11)	84.2(3)	C(12)−Pt(1)−P(1)	91.7(2)
C(11)−Pt(1)−S(31)	92.7(2)	P(1)−Pt(1)−S(31)	91.57(5)
C(22)−Pt(2)−C(21)	87.6(3)	C(22)−Pt(2)−N(2)	91.1(2)
C(21)−Pt(2)−S(31)	93.1(2)	C(22)−Pt(2)−S(31)	88.2(1)

Scheme 2[a]



[a] PN = 2$Ph_2PC_5H_4N$, X = CF_3CO_2.

Figure 1 and with selected bond parameters in Table 2. There are two square-planar platinum(II) centers with PtC_2SN and Pt_2C_2SP coordination, respectively, with platinum atoms separated by 3.85 Å. The two square planes are mutually twisted to accommodate the one- and three-atom bridging groups SMe_2 and PN, respectively.

Reactions with Acids. The reaction of complex **2** with trifluoroacetic acid occurred according to Scheme 2, yielding methane and complex **6**. Complex **6** contains a donor−acceptor PtPt bond, and the selectivity of its formation suggests that cleavage of a methylplatinum bond occurs at the $PtMe_2PS$ rather than the $PtMe_2NS$ center, but this is not actually the case. Thus, reaction of complex **2** with trifluoroacetic acid at −75 °C gave the complex **5** (Scheme 2), which is formed by selective cleavage of the PtMe bond *trans* to sulfur at the $PtMe_2$-

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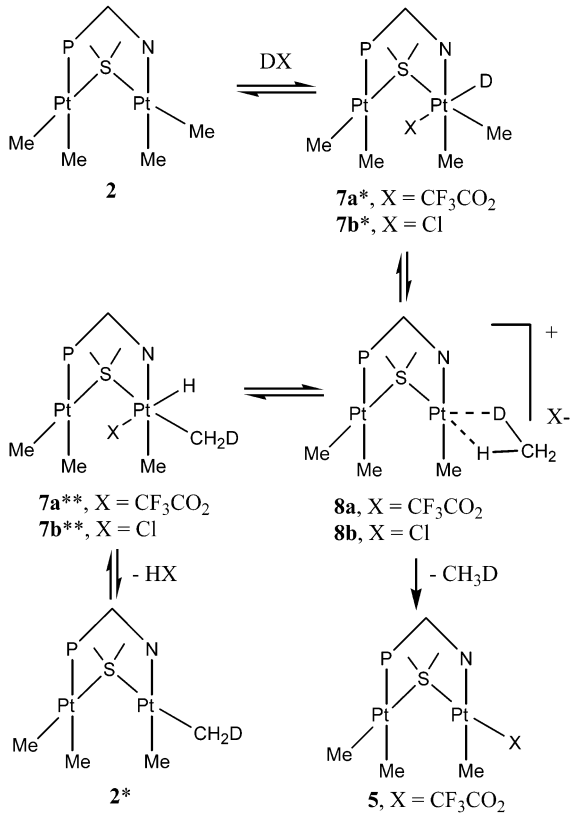
NS center. The conversion of complex **5** to **6** involves formation of a PtPt donor−acceptor bond, rearrangement of the dimethyl sulfide ligand from a bridging to a terminal position, and one more step that is less well defined. It could involve reorientation of the PN ligand,[6−8] or it could involve methyl for trifluoroacetate exchange between platinum centers;[13] the cited references show that either mechanism can occur easily. The conversion of **5** to **6** was complete at −10 °C.

The ^{195}Pt NMR spectrum of complex **6** contained two resonances at δ(Pt) = −896 [d, ^1J(PtP) = 5040 Hz] and −48 [s, ^3J(PtP) not resolved], and the presence of a PtPt bond is indicated by the observation of a large coupling ^1J(PtPt) = 3200 Hz (Table 1). Complex **5**, with phosphorus *trans* to methyl, has a much smaller coupling, ^1J(PtP) = 1840 Hz, compared to **6**, in which phosphorus is *trans* to oxygen. The absence of a PtPt bond in **5** is indicated by the much smaller platinum−platinum coupling ^2J(PtPt) = 275 Hz. The magnitude of J(PtPt) is thus a good criterion of the presence or absence of a PtPt bond in these closely related compounds (Table 1). Complex **5** gives two methylsulfur resonances in either the ^{1}H or ^{13}C NMR spectra for the bridging dimethyl sulfide ligand, but complex **6** gives only one resonance for the terminal dimethyl sulfide. The structure of **6** is, at first glance, surprising since it appears that a bridging dimethyl sulfide could be formed by displacement of trifluoroacetate (Scheme 2). However formation of a μ-SMe_2 group would require twisting about the PtPt axis that is rather rigidly oriented as a result of the five-membered PtPtPCN ring formed by the PN ligand and PtPt bond, and the resulting ring strain does not allow closure. The stereochemistry of **5**, in which the PtMeX center has the methyl group *trans* to nitrogen rather than sulfur, is indicated by the low value of the coupling constant ^3J(PtNCH) *trans* to methyl and also by the higher value of ^2J(PtPt) in **5** compared to **2**.

In the reaction of complex **2** with CF_3CO_2D in a mixed CD_3OD/CD_2Cl_2 solvent mixture, the methane was formed as CH_3D with CH_2D_2 as minor product. The formation of CH_2D_2 indicates that the mechanism of methylplatinum bond protonolysis involves reversible formation of a methane complex and also reversible protonation of the platinum(II) center, as indicated in Scheme 3. According to Scheme 3, the proposed CH_3D complex intermediate can either lose CH_3D to give **5** or go back to the deuteride/hydride **7a*/7a****. Deprotonation of **7a**** gives **2***, and this can then react with more CF_3CO_2D to give CH_2D_2.[14] It was not possible to observe either proposed intermediate **7a** or **8a** in this reaction, but the reaction of **2** with HCl did give a transient intermediate identified by the ^{1}H NMR spectrum at −75 °C as a hydride with δ(PtH) = −17.8 [^1J(PtH) = 1506 Hz]. The coupling constant is consistent with a platinum(IV) hydride with the hydride *trans* to chloride, and the absence of coupling to phosphorus shows that the hydride is present at the pyridylplatinum center, consistent with structure **7b**.[14]

Scheme 3[a]



[a] PN = 2-$Ph_2PC_5H_4$.

Breaking and Making Metal−Metal Donor−Acceptor Bonds by Ligand Addition and Loss. Complex **6** reacted easily with a second equivalent of the ligand PN at −78 °C to give [Pt_2Me_3(μ-SMe_2)(μ-PN)(PN-κ^1P)](CF_3CO_2), complex **9**. This reaction involves displacement of the weakly bound trifluoroacetate ligand by the phosphorus donor of the PN ligand and cleavage of the PtPt bond by re-forming the dimethyl sulfide bridge. On warming to −10 °C, the free nitrogen center in complex **9** displaces the bridging dimethyl sulfide ligand to form [Pt_2Me_3(μ-PN)$_2$](CF_3CO_2), complex **10**, and the PtPt donor−acceptor bond is formed again. Complex **10** is a rare example of a compound with the head-to-head arrangement of two bridging PN ligands.[6−8] This complex could be isolated in pure form, but in solution, it rearranged over a period of 10 days at room temperature to form the head-to-tail isomer **11**. This represents a rare case in which both the head-to-head and head-to-tail isomers of complexes containing the M_2(μ-PN)$_2$ unit can be isolated.[6−8] The isomerization was readily monitored by NMR spectroscopy, as illustrated by the ^{31}P NMR spectra in Figure 2.

Complex **9** contains two nonequivalent PN ligands, and the phosphorus atoms are bound *trans* to each other at the same platinum atom, so that the two ^{31}P resonances appear with similar couplings ^1J(PtP) (Table 1). This platinum atom with PtP_2SC coordination thus appears as an apparent triplet in the ^{195}Pt NMR spectrum due to ^1J(PtP) coupling, whereas the other platinum atom with $PtSNC_2$ coordination gives a singlet resonance. The presence of a bridging dimethyl sulfide ligand in **9** was shown by the presence of two methylsulfur resonances in the ^{1}H NMR spectrum, and the lack

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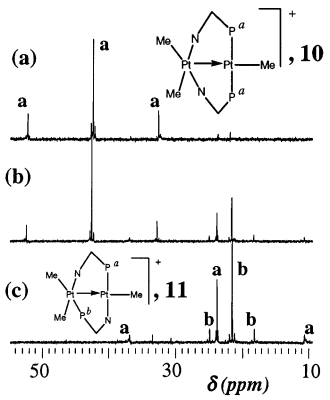


Figure 2. ^{31}P NMR spectra for the head-to-head and head-to-tail isomers of $[Pt_2Me_3(\mu\text{-}PN)_2]^+$: (a) the head-to-head isomer **10**; (b) about midway through the isomerization; (c) the head-to-tail isomer **11**. The center peak and satellites due to ^1J(PtP) coupling are labeled in (a) and (c).

of PtPt coupling indicates the absence of a PtPt bond.

The head-to-head isomer of $[Pt_2Me_3(\mu\text{-}PN)_2](CF_3CO_2)$, **10**, gave two methylplatinum resonances in a 1:2 ratio, and only a single ^{31}P resonance (Figure 2). There were two ^{195}Pt resonances, with the $PtCP_2Pt$ center appearing as a triplet as a result of ^1J(PtP) coupling and the PtC_2N_2Pt center appearing as a singlet. The magnitude of ^1J(PtPt) = 3812 Hz is a clear indication of the presence of a PtPt bond. In contrast, the less symmetrical head-to-tail isomer of $[Pt_2Me_3(\mu\text{-}PN)_2](CF_3CO_2)$, **11**, gave three methylplatinum resonances in a 1:1:1 ratio and two ^{31}P resonances (Figure 3). There were two ^{195}Pt resonances, and each appeared as a doublet of doublets as a result of ^1J(PtP) and ^2J(PtP) couplings (Figure 3). The magnitude of ^1J(PtPt) = 2720 Hz is again a clear indication of the presence of a PtPt bond. The differences in the ^{31}P NMR spectra between complexes **10** and **11** are clearly illustrated in Figure 2.

The structure of the head-to-head isomer of $[Pt_2Me_3(\mu\text{-}PN)_2](CF_3CO_2)$, **10**, was determined crystallographically. The structure of the diplatinum cation is shown in Figure 4, and selected bond distances and angles are in Table 3. The atom Pt(1) has distorted square-planar stereochemistry with *trans*-PtP_2CPt coordination, while Pt(2) is square-pyramidal with *cis*-PtN_2C_2Pt coordination. The Pt−Pt bond distance of 2.6491(4) Å is in the normal range for a single bond. It is shorter than the PtPt distance in the dppm analogue $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, which has PtPt = 2.769(1) Å.[2] A comparison can also be made with the similar head-to-tail complex $[MeCOPt(\mu\text{-}Ph_2PC_5H_4N)_2PtClMe]^+$, which has Pt−Pt = 2.728(3) Å and ^1J(PtPt) = 2440 Hz.[9] All of these complexes have been formulated as containing a donor−acceptor PtPt bond, but the PtPt distance for **10** is significantly shorter than for the other two examples.

Discussion

This work has illustrated very distinctive properties of binuclear methylplatinum complexes with PN ligands. Most noteworthy is the demonstration that donor−acceptor platinum−platinum bonds can play an important role in the reaction chemistry. In the isomerization of complex **5** to **6** (Scheme 2), the net effect is to break a Pt−S bond to the bridging dimethyl sulfide ligand of

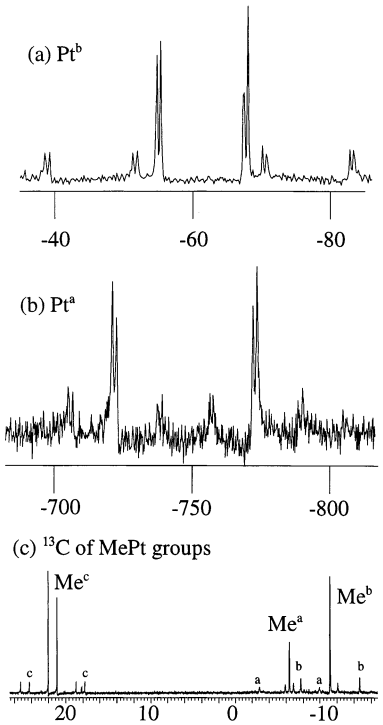


Figure 3. Selected NMR spectra for complex **11**: (a and b) the ^{195}Pt resonances, showing the doublet of doublet pattern arising from ^1J(PtP) and ^2J(PtP) couplings, with satellite spectra arising from ^1J(PtPt) in the $^{195}Pt_2$ isotopomer; and (c) the ^{13}C NMR spectrum in the methylplatinum region, showing resonances of the three inequivalent methylplatinum groups (see Chart 1 for the NMR labeling scheme).

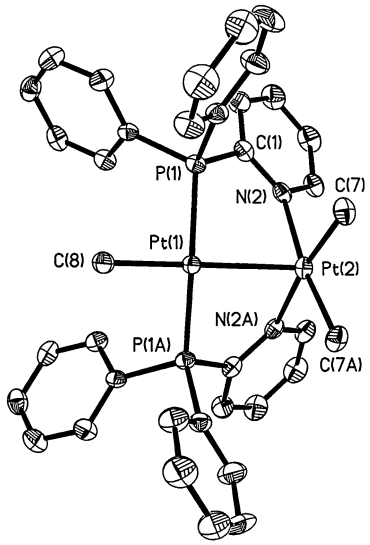


Figure 4. View of the structure of the head-to-head isomer of the cationic complex $[Pt_2Me_3(\mu\text{-}PN)_2]^+$, showing 25% probability ellipsoids.

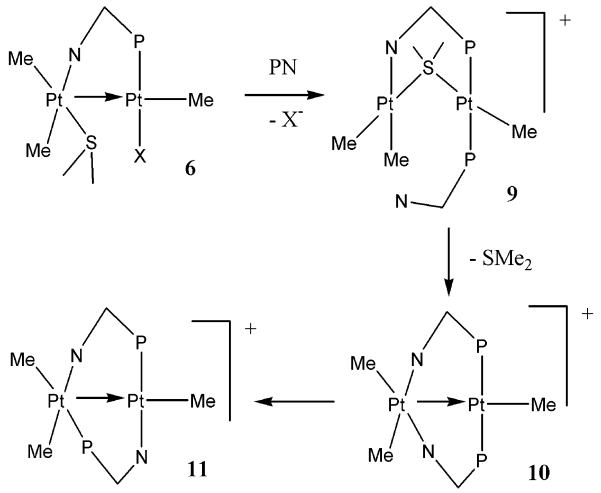
5 and to make a Pt−Pt bond in **6**. There are other, presumably favorable, changes in the rearrangement from **5** to **6**, but the result suggests that the Pt−Pt and Pt−S bonds are comparable in energy. A similar argument can be based on the rearrangement of complex **9** to **10** (Scheme 4). The strong PtPt bond in complex **10** is confirmed by the structure determination that shows the shortest PtPt donor−acceptor bond yet established.[2,9] Complex **10** also has the highest value of the

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Complex 10[CF_3CO_2]·2CH_2Cl_2[a]

Pt(1)−C(8)	2.046(7)	Pt(2)−C(7)	2.049(5)
Pt(1)−P(1)	2.259(1)	Pt(2)−N(2)	2.163(4)
Pt(1)−Pt(2)	2.6491(4)		
C(8)−Pt(1)−P(1)	92.24(5)	C(7A)−Pt(2)−C(7)	87.1(3)
P(1)−Pt(1)−P(1A)	161.29(7)	C(7A)−Pt(2)−N(2)	172.5(2)
C(8)−Pt(1)−Pt(2)	176.8(2)	C(7)−Pt(2)−N(2)	88.0(2)
P(1)−Pt(1)−Pt(2)	88.27(3)	N(2)−Pt(2)−N(2A)	96.4(2)
C(7)−Pt(2)−Pt(1)	100.7(2)	N(2)−Pt(2)−Pt(1)	85.7(1)
N(2)−C(1)−P(1)	116.5(4)		

[a] Symmetry for equivalent atoms: A, x, $-y+1/2$, z.

Scheme 4[a]



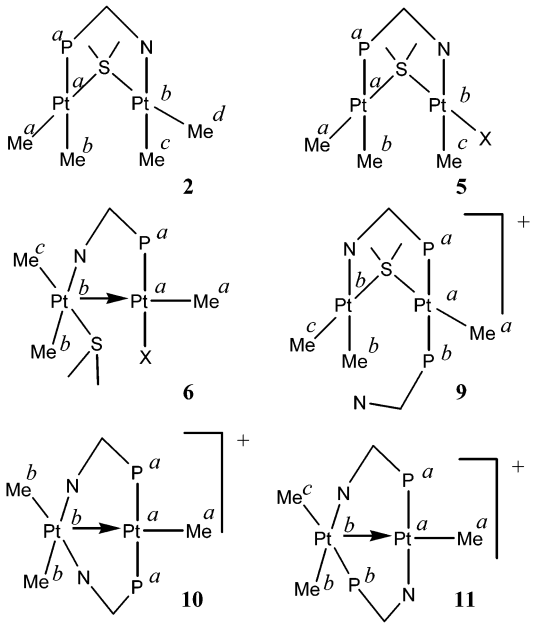
[a] PN = 2-$Ph_2PC_5H_4N$, X = CF_3CO_2.

coupling constant ^1J(PtPt) for any of the complexes studied here. It is interesting to note that the rearrangement of the head-to-head complex **10** to its head-to-tail isomer **11** (Scheme 4) occurs with a reduction of the value of ^1J(PtPt) from 3812 to 2721 Hz. Although there is no general correlation of values of ^1J(PtPt) and PtPt bond distance,[15] within these closely related compounds it is likely that this significant change does reflect a decrease in PtPt bond energy. The difference is readily explained in terms of electronic effects. Thus in **10** the donor center has $PtMe_2N_2$ coordination and so will be more electron rich, and hence a better donor, than the $PtMe_2NP$ center in **11**.[16] In addition, the acceptor center in **10** has $PtMeP_2^+$ coordination and so will be more electron poor, and so a stronger acceptor, than the $PtMeNP^+$ center in **11**. Why then does the rearrangement occur? We suggest that there is a reduction in steric effects in **11** along with minor electronic stabilization of other bonds and that this combination outweighs the effect of weakening the PtPt bond. The slow rearrangement of **10** to **11** allows both isomers to be obtained in pure form and to be fully characterized by multinuclear NMR spectroscopy. This is unusual despite the popularity of the PN ligand in coordination chemistry and catalysis, as is the structure determination of the relatively scarce head-to-head bis(PN)-bridged complex **10**.[6−8]

(15) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 1601.

(16) There is considerable independent evidence that nitrogen is a stronger net donor than phosphorus in platinum(II) complexes.[14] Independent confirmation comes from the observation that complex **2** undergoes protonation at the $PtMe_2NS$ rather than the $PtMe_2PS$ center.

Chart 1. NMR Labeling Scheme



Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded as solutions in CD_2Cl_2 by using Varian Mercury 400 or Inova 400 spectrometers, while ^{195}Pt NMR spectra were recorded using Varian Inova 400 or 600 MHz spectrometers. The spectra are referenced with respect to TMS (^{1}H, ^{13}C), H_3PO_4 (^{31}P), or [$PtCl_2(SMe_2)_2$] (^{195}Pt). In the aryl region of the ^{1}H and ^{13}C NMR spectra, many resonances overlapped and data are given only for the *ortho*-pyridyl proton (H^6) and carbon atoms (C^2 and C^6), which were resolved in all cases. The atom labeling used in describing the NMR data is defined in Chart 1. The complex [$Pt_2Me_4(\mu$-$SMe_2)_2$] was prepared by the literature method.[10]

***cis,cis*-[$Pt_2Me_4(\mu$-$SMe_2)(\mu$-PN)], 2.** To a solution of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (1.72 g, 3.0 mmol) in C_6H_6 (100 mL) was added 2-$Ph_2PC_5H_4N$ (0.789 g, 3.0 mmol). After 5 min, the solvent was removed and the product was washed with ether and dried under vacuum. It was recrystallized from CH_2Cl_2/hexane. Yield: 2.15 g (93%), mp135−138 °C. Anal. Calcd for $C_{23}H_{32}NPPt_2S$: C, 35.6; H, 4.1; N, 1.8. Found: C, 35.2; H, 4.2; N, 1.5. NMR in CD_2Cl_2: δ(^{1}H) 0.36 [d, 3H, ^2J(PtH) = 84 Hz, ^3J(PH) = 9 Hz, Me[a]]; 0.66 [d, 3H, ^2J(PtH) = 71 Hz, ^3J(PH) = 7 Hz, Me[b]]; −0.19 [s, 3H, ^2J(PtH) = 86 Hz, Me[c]]; 0.31 [s, 3H, ^2J(PtH) = 86 Hz, Me[d]]; 2.23, 2.76 [s, each 3H, SMe_2]; 9.05 [m, 1H, ^3J(HH) = 5 Hz, ^3J(PtH) = 25 Hz, H^6]; δ(^{13}C) −17.5 [s, ^1J(PtC) = 788 Hz, Me[d]]; −1.2 [s, ^1J(PtC) = 833 Hz, Me[c]]; 0.0 [d, ^1J(PtC) = 738 Hz, ^2J(PC) = 5 Hz, Me[a]]; 9.5 [d, ^1J(PtC) = 670 Hz, ^2J(PC) = 103 Hz, Me[b]]; 22.6, 31.6 [s, MeS]; 158.9 [d, ^3J(PC) = 10 Hz, ^2J(PtC) = 25 Hz, C^6]; 162.6 [d, ^1J(PC) = 48 Hz, C^2]; δ(^{31}P) 26.9 [s, ^1J(PtP) = 1860 Hz, ^3J(PtP) = 90 Hz]; δ(^{195}Pt) −940 [d, ^1J(PtP) = 1860 Hz, ^2J(PtPt) = 130 Hz, Pt[a]]; −300 [d, ^3J(PtP) = 90 Hz, ^2J(PtPt) = 130 Hz, Pt[b]].

***cis*-[$PtMe_2$(PN-κ^1P)$_2$], 3.** A solution of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (300 mg, 0.52 mmol) and 2-$Ph_2PC_5H_4N$ (549 mg, 2.09 mmol) in C_6H_6 (30 mL) was stirred for 1 h. The solvent was removed under vacuum, and the product was washed with hexane (2 × 4 mL) and dried under vacuum. Yield: 675 mg, 86%. The NMR data were identical to the literature values.[12]

[$Pt_2Me_3(O_2CCF_3)(\mu$-$SMe_2)(\mu$-PN)], 5. To a solution of CF_3CO_2H (6.2 μL, 0.08 mmol) in CD_2Cl_2 (0.2 mL) at −78 °C in an NMR tube was added a solution of *cis,cis*-[$Pt_2Me_4(\mu$-$SMe_2)(\mu$-PN)] (62 mg, 0.08 mmol) in CD_2Cl_2 (0.2 mL). Reaction occurred cleanly to give **5** and CH_4 in equimolar amounts at −75 °C, as

confirmed by integration of the NMR spectrum, but **5** rearranged to **6** above −30 °C, so it was characterized spectroscopically at low temperature. NMR in CD_2Cl_2 at −75 °C: $\delta(^1H)$ 0.46 [d, 3H, ^2J(PtH) obscured, ^3J(PH) = 9 Hz, Me[a]]; 0.55 [d, 3H, ^2J(PtH) = 71 Hz, ^3J(PH) = 7 Hz, Me[b]]; 0.33 [s, 3H, ^2J(PtH) = 82 Hz, Me[c]]; 2.22, 2.81 [s, each 3H, SMe_2]; 9.23 [m, 1H, ^3J(HH) = 4 Hz, H[6]]; $\delta(^{31}P)$ 35.2 [s, ^1J(PtP) = 1840 Hz, ^3J(PtP) = 120 Hz]; $\delta(^{195}Pt)$ −917 [d, ^1J(PtP) = 1840 Hz, ^2J(PtPt) = 275 Hz, Pt[a]]; −160 [d, ^3J(PtP) = 120 Hz, ^2J(PtPt) = 275 Hz, Pt[b]].

[$Pt_2Me_3(O_2CCF_3)(SMe_2)(\mu$-PN)], 6. To a solution of *cis*,-*cis*-[$Pt_2Me_4(\mu$-$SMe_2)(\mu$-PN)] (372 mg, 0.49 mmol) in CH_2Cl_2 (10 mL) was added a solution of CF_3CO_2H (37.2 μL, 0.49 mmol) in CH_2Cl_2 (10 mL). The solvent was evaporated immediately under vacuum, and the product was washed with hexane (2 × 4 mL) and dried under vacuum. Yield: 370 mg (91%), mp110−114 °C. Anal. Calcd for $C_{24}H_{29}F_3NO_2PPt_2S$: C, 33.0; H, 3.3; N, 1.6. Found: C, 32.6; H, 3.0; N, 1.5. NMR in CD_2Cl_2: $\delta(^1H)$ 0.79 [d, 3H, ^2J(PtH) = 84 Hz, ^3J(PtH) = 6 Hz, ^3J(PH) = 2 Hz, Me[a]]; 0.86 [s, 3H, ^2J(PtH) = 80 Hz, Me[b]]; 0.54 [s, 3H, ^2J(PtH) = 80 Hz, Me[c]]; 2.26 [s, 6H, ^3J(PtH) = 18 Hz, SMe_2]; 8.90 [m, 1H, ^3J(HH) = 4 Hz, ^3J(PtH) = 20 Hz, H[6]]; $\delta(^{13}C)$ −13.6 [s, ^1J(PtC) = 742 Hz, Me[b]]; −10.0 [d, ^2J(PC) = 4 Hz, Me[a]]; −1.5 [s, ^1J(PtC) = 723 Hz, Me[c]]; 20.2 [s, Me_2S]; 152.3 [d, ^3J(PC) = 12 Hz, C[2]]; 154.9 [d, ^1J(PC) = 80 Hz, C[2]]; $\delta(^{31}P)$ 25.0 [s, ^1J(PtP) = 5040 Hz, ^2J(PtP) = 53 Hz]; $\delta(^{195}Pt)$ −896 [d, ^1J(PtP) = 5040 Hz, ^1J(PtPt) = 3200 Hz, Pt[a]]; −48 [d, ^2J(PtP) = 53 Hz, ^1J(PtPt) = 3200 Hz, Pt[b]].

[$Pt_2Me_3(\mu$-$SMe_2)(\mu$-PN)(PN-κ^1*P*)](CF_3CO_2), 9. To a solution of [$Pt_2Me_3(O_2CCF_3)(SMe_2)(\mu$-PN)], **6** (66 mg, 0.08 mmol), in CD_2Cl_2 (0.4 mL) at −78 °C in an NMR tube was added a solution of PN (20 mg, 0.08 mmol) in CD_2Cl_2 (0.3 mL). Reaction occurred cleanly to give **9** at −70 °C, but **9** reacted further to give **10** above −20 °C, so **9** was characterized spectroscopically at low temperature. NMR in CD_2Cl_2 at −70 °C: $\delta(^1H)$ −0.05 [d, 3H, ^2J(PtH) = 80 Hz, ^3J(PH) = 9 Hz, Me[a]]; 0.33 [s, 3H, ^2J(PtH) = 80 Hz, Me[b]]; 0.32 [s, 3H, ^2J(PtH) obscured, Me[c]]; 1.88, 2.06 [s, each 3H, SMe_2]; 8.84 [m, 1H, free py H[6]]; 8.97 [m, 1H, ^3J(PtH) = 30 Hz, coord py H[6]]; $\delta(^{31}P)$ 24.8 [d, ^1J(PtP) = 3160 Hz, ^2J(PP) = 400 Hz, P[a]]; 25.2 [d, ^1J(PtP) = 3058 Hz, ^2J(PP) = 400 Hz, P[b]]; $\delta(^{195}Pt)$ −1397 [t, ^1J(PtP) ca.. 3120 Hz, Pt[a]]; −241 [s, Pt[b]].

***hh*-[$Pt_2Me_3(\mu$-PN)$_2$](CF_3CO_2), 10.** To a solution of [$Pt_2Me_3(O_2CCF_3)(SMe_2)(\mu$-PN)], **6** (210 mg, 0.24 mmol), in CH_2Cl_2 (10 mL) was added a solution of PN (63 mg, 0.24 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 min, then the solvent was evaporated under vacuum and the product was washed with hexane (2 × 3 mL) and dried under vacuum. Yield: 228 mg (88%), mp165−168 °C. Anal. Calcd for $C_{39}H_{37}F_3N_2O_2P_2Pt_2$: C, 43.6; H, 3.4; N, 2.6. Found: C, 43.1; H, 3.3; N, 2.5. NMR in CD_2Cl_2: $\delta(^1H)$ 0.95 [t, 3H, ^2J(PtH) = 75 Hz, ^3J(PH) = 6 Hz, Me[a]]; 0.41 [s, 6H, ^2J(PtH) = 73 Hz, Me[b]]; 9.80 [m, 1H, ^3J(HH) = 5 Hz, ^3J(PtH) = 12 Hz, H[6]]; $\delta(^{31}P)$ 42.5 [s, ^1J(PtP) = 3200 Hz, ^2J(PtP) = 89 Hz, P[a]]; $\delta(^{195}Pt)$ −1270 [t, ^1J(PtP) = 3200 Hz, ^1J(PtPt) = 3812 Hz, Pt[a]]; 510 [d, ^2J(PtP) = 96 Hz, ^1J(PtPt) = 3812 Hz, Pt[b]].

***ht*-[$Pt_2Me_3(\mu$-PN)$_2$](CF_3CO_2), 11**. A solution of *hh*-[$Pt_2Me_3(\mu$-PN)$_2$](CF_3CO_2), **10** (228 mg), in CH_2Cl_2 (20 mL) was allowed to stand for10 days at room temperature. The solvent was evaporated, and the product was crystallized from CH_2Cl_2/hexane. Yield: 198 mg (89%), mp 155−160 °C. Anal. Calcd for $C_{39}H_{37}F_3N_2O_2P_2Pt_2 \cdot 0.5CH_2Cl_2$: C, 42.5; H, 3.4; N, 2.5. Found: C, 42.7; H, 3.4; N, 2.4 (presence of dichloromethane solvate confirmed by NMR). NMR in CD_2Cl_2: $\delta(^1H)$ 0.99 [d, 3H, ^2J(PtH) = 79 Hz, ^3J(PtH) = 12 Hz ^3J(PH) = 3 Hz, Me[a]]; 0.63 [d, 3H, ^2J(PtH) = 79 Hz, ^3J(PtH) = 8 Hz ^3J(PH) = 8 Hz, Me[b]]; 0.41 [d, 3H, ^2J(PtH) = 66 Hz, ^3J(PtH) = 8 Hz ^3J(PH) = 8 Hz, Me[c]]; 9.04 [m, 1H, ^3J(HH) = 4 Hz, ^3J(PtH) = 37 Hz, H[6]]; 9.06 [m, 1H, ^3J(HH) = 5 Hz, ^3J(PtH) = 17 Hz, H[6]]; $\delta(^{13}C)$ −11.2 [d, ^1J(PtC) = 693 Hz, ^2J(PC) = 3 Hz, Me[b]]; −6.4 [t, ^1J(PtC) = 713 Hz, ^2J(PtC) = 98 Hz, ^2J(PC) = 4 Hz, Me[a]]; 21.5 [d, ^1J(PtC) = 650 Hz, ^2J(PC) = 103 Hz, Me[c]]; 150.2 [d, ^2J(PtC) = 36 Hz, ^3J(PC) = 13 Hz, C[6] of pyPt[a]]; 152.9 [d, ^2J(PtC) = 26 Hz, ^3J(PC) = 12 Hz, C[6] of pyPt[b]]; 156.6 [d, ^2J(PtC) = 44 Hz, ^1J(PC) = 83 Hz, C[2] of pyPt[a]]; 159.8 [d, ^2J(PtC) = 39 Hz, ^1J(PC) = 70 Hz, C[2] of pyPt[b]]; $\delta(^{31}P)$ 23.8 [d, ^1J(PtP) = 4260 Hz, ^2J(PtP) = 60 Hz, ^3J(PP) = 2 Hz, P[a]]; 21.5 [d, ^1J(PtP) = 1085 Hz, ^2J(PtP) = 123 Hz, ^3J(PP) = 2 Hz, P[b]]; $\delta(^{195}Pt)$ −747 [dd, ^1J(PtP) = 4260 Hz, ^2J(PtPt) = 123 Hz, ^1J(PtPt) = 2720 Hz Pt[a]]; −61 [dd, ^1J(PtP) = 1085 Hz, ^2J(PtP) = 60 Hz, ^1J(PtPt) = 2720 Hz, Pt[b]].

***ht*-[$Pt_2Me_3(\mu$-PN)$_2$]Cl, 11a.** To a solution of [$Pt_2Me_4(\mu$-$SMe_2)(\mu$-PN)], **2** (62 mg, 0.08 mmol), in CD_2Cl_2 (0.5 mL) at −78 °C in an NMR tube was added HCl (0.08 mmol, generated by reaction of Me_3SiCl with H_2O). The NMR recorded immediately at −78 °C showed the presence of a hydride resonance at $\delta(^1H)$ = −17.8 [s, ^1J(PtH) = 1506 Hz, PtH], but this complex was short-lived even at −78 °C giving methane, identified by its ^1H NMR spectrum. On warming the solution, a complex series of reactions occurred, finally giving *ht*-[$Pt_2Me_3(\mu$-PN)$_2$]-Cl, **11a**, as major product. The ^1H, ^{31}P, and ^{195}Pt NMR spectra were as reported above for the trifluoroacetate salt.

The same product was formed, along with [$(PtMe_3Cl)_4$] and minor unidentified compounds,[17,18] by the slow decomposition (over 10 days at room temperature) of complex **2** in $CHCl_3$.

Xray Structure Determinations. Crystals were mounted on glass fibers. Data were collected at 200 K using a Nonius Kappa-CCD diffractometer with COLLECT software (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The SHELXTL-NT V5.1 (Sheldrick, G. M.) suite of programs was used to solve the structure by direct methods and to refine by using difference Fouriers. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Crystal data are listed in Table 4.

For complex **2** all of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom

Table 4. Crystal Data and Structure Refinement for the Complexes

	2	**10**·CF_3CO_2.2CH_2Cl_2
formula	$C_{23}H_{32}NPPt_2S$	$C_{41}H_{41}Cl_4F_3N_2O_2P_2Pt_2$
fw	775.71	1244.68
temperature/K	200(2)	200(2)
wavelength/Å	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	*Pnma*
a/Å	9.7900(1)	31.6474(3)
b/Å	15.2304(3)	14.9179(1)
c/Å	15.8954(3)	9.4778(1)
β/deg	94.018(1)	90
vol/Å^3	2364.27(7)	4474.59(7)
Z	4	4
d(calc)/Mg m^{-3}	2.179	1.848
abs coeff /mm^{-1}	11.986	6.605
F(000)	1456	2392
no. of reflns	29 746	52 009
no. of ind reflns	6934 [*R*(int) = 0.059]	5980 [*R*(int) = 0.066]
abs corr	integration	integration
Goof (F^2)	0.981	1.029
R1, wR2 [$I>2\sigma(I)$]	0.0354, 0.0777	0.0376, 0.0874
R1, wR2 (all data)	0.0568, 0.0849	0.0677, 0.0970

(17) Kite, K.; Smith, J. A. S.; Wilkins, E. J. *J. Chem. Soc. A* **1966**, 1744.
(18) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1991**, *406*, 261.

positions were calculated geometrically and were included as riding on their respective carbon atoms.

For complex **10**·CF_3CO_2·$2CH_2Cl_2$ the cation was located on a mirror plane. The anion was also located on a mirror plane, but the fluorine atoms were disordered. They were modeled as a 60/40 mixture. The C−F bond lengths were constrained to be equal (SADI). The two methylene chlorides of solvation were located on mirror planes and so were modeled at half-occupancy.

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Supporting Information Available: Tables of X-ray data for the complexes are available free of charge via the Internet at http://pubs.acs.org.

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