Oxidative Addition of S−S Bonds to Dimethylplatinum(II) Complexes: Evidence for a Binuclear Mechanism

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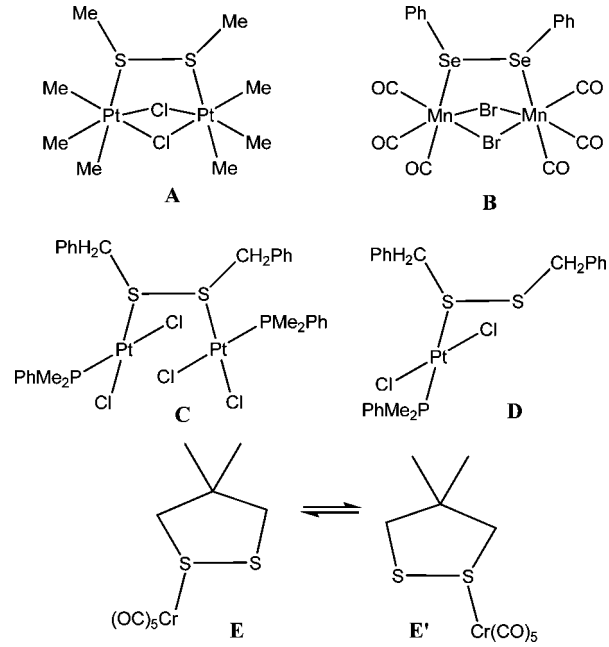
Oxidative addition of the S−S bond of S_2py_2 (py = 2-pyridyl) to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ occurs with displacement of Me_2S to give $[PtMe_2(\kappa^2\text{-}S,N\text{-}Spy)_2]$, **1**. Oxidative addition of S_2Ar_2 (Ar = 2-pyridyl or Ph) to $[PtMe_2(NN)]$, NN = 2,2′-bipyridine or 1,10-phenanthroline, gives initially the binuclear Pt(III) complexes $[\{PtMe_2(\kappa^1\text{-}S\text{-}SAr)(NN)\}_2]$, which react further with S_2Ar_2 to give $[PtMe_2(\kappa^1\text{-}S\text{-}SAr)_2(NN)]$ and then, when Ar = 2-pyridyl, to give an equilibrium with free NN and complex **1**. Evidence is presented that the S−S oxidative addition to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ occurs by a concerted mechanism whereas the reactions with $[PtMe_2(NN)]$ to give the binuclear complexes $[\{PtMe_2(\kappa^1\text{-}S\text{-}SAr)(NN)\}_2]$ occur by a polar nonconcerted mechanism, involving a loosely bonded dimer $[PtMe_2(NN)]_2$.

Introduction

The reversible cleavage of the S−S bond of a disulfide R_2S_2 by reaction with a transition metal complex or surface may be important in catalysis,[1] in medicinal chemistry involving *cis*-platin,[2] or in self-assembled monolayers and tribology.[3] It is therefore important to understand how these reactions occur. In organic chemistry, disulfides can be activated by photolysis to give thiyl radicals RS˙ or by electron transfer to give the radical anion $[R_2S_2]^{\cdot -}$, which may then react as the equivalent of a thiyl radical and a thiolate anion, RS˙ + RS^-.[4] The bond dissociation energy of Ph_2S_2 has been estimated both experimentally and theoretically.[4,5]

Disulfide and diselenide ligands usually act as bridging ligands as illustrated by **A**−**C** in Chart 1, but they can also act as terminal ligands as illustrated by **D** and **E** in Chart 1.[6] These complexes exhibit a particularly rich fluxionality, including migration of metals between chalcogen centers (e.g., **E** and **E**′ in Chart 1), inversion at the pyramidal chalcogen center (found in all complexes) and switching of the ligand between metal centers (e.g., in complex **A**).

Chart 1. Selected Disulfide Complexes



Disulfides can also take part in redox reactions at metal centers with reversible formation of thiolate ligands as illustrated in Scheme 1. Oxidation of thiolate complexes can lead to formation of free or complexed disulfide.[4,6,7]

The ligand di-2-pyridyldisulfide can act as an *N*,*N*-donor or *N*,*S*-donor chelate (forming 7- or 5-membered rings respectively) as in complexes **F** and **G** (Chart 2), as a bridging ligand, or it may undergo S−S bond cleavage to give 2-pyridylthiolate complexes such as **H**.[8]

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Scheme 1

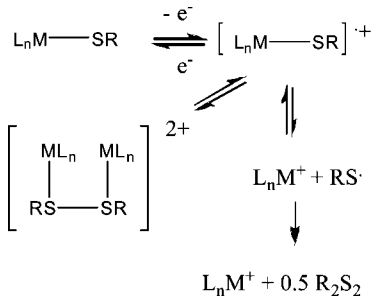


Chart 2

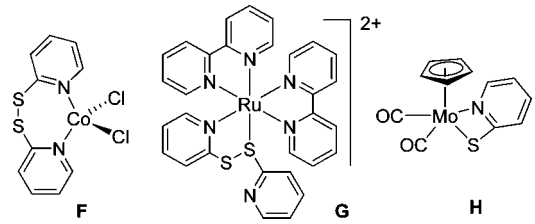
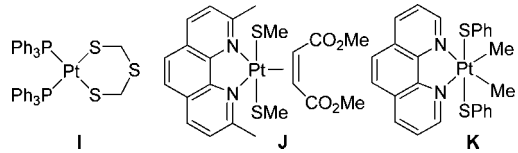


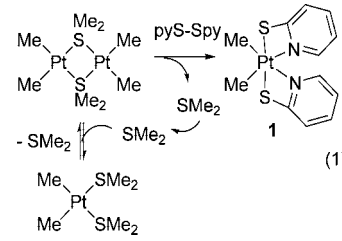
Chart 3



The oxidative addition reactions of disulfides and diselenides to platinum(0) or platinum(II) have been studied previously.[9−11] Cyclic disulfides can give *cis*-dithiolate complexes, but the formation of *trans*-dithiolates is more common, as illustrated by the examples in Chart 3. In terms of mechanism, the reaction of anionic $[PtMe_2(pz_3BH)]^-$, pz = pyrazolyl, with S_2Ph_2 is thought to occur by a 2-electron (S_N2) mechanism to give $[PtMe_2(SPh)(pz_3BH)]$ and SPh^-, while reactions of neutral complexes $[PtR_2(NN)]$, NN = diimine ligand, are proposed to occur at least in part by free radical mechanisms.[10,11] This paper describes new mechanistic and structural studies in the reactions of di-2-pyridyldisulfide and diphenyldisulfide with dimethylplatinum(II) complexes.

Results

Reactions of Di-2-pyridyldisulfide. The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[12] with di-2-pyridyldisulfide occurred rapidly at room temperature to give the platinum(IV) complex $[PtMe_2(2\text{-}Spy)_2]$, **1**, py = pyridyl, according to eq 1. The reaction involves oxidative addition of the S−S bond of the disulfide to platinum(II) with displacement of weakly bound dimethylsulfide ligands from platinum. Because there are precedents for both coordination of di-2-pyridyldisulfide to transition metals (**F** and **G**, Chart 2) and undergoing cleavage of the S−S bond to give 2-pyridylthiolate complexes (**H**, Chart 2), the reaction was monitored by low temperature NMR spectroscopy in an attempt to identify reaction intermediates. The reaction occurred over a period of about one hour at −15 °C, but no reaction intermediates were detected. As the resonances for $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $S_2(2\text{-py})_2$ decayed, those for complex **1** increased in intensity. The only complication was that, at intermediate stages, resonances for *cis*-$[PtMe_2(SMe_2)_2]$, formed by reaction of displaced SMe_2 with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$,[12] were observed (eq 1). Thus, it seems that the slow step in the reaction is the initial coordination of di-2-pyridyldisulfide to platinum, and that the oxidative addition and complete displacement of dimethylsulfide occur rapidly after that.



The stereochemistry of complex **1** could be deduced from the ^1H NMR spectrum and was confirmed by a structure determination. The methylplatinum resonance occurred at δ = 1.51 with $^2J(PtH)$ = 76 Hz, in the range expected for a methylplatinum(IV) complex with methyl *trans* to nitrogen.[10−13] The H^6 proton of the pyridyl group appeared at δ = 8.11 with $^3J(PtH)$ = 21 Hz, and the low value of the coupling constant indicates that the pyridyl group is *trans* to methyl.[10−13] The structure of complex **1** is shown in Figure 1. It confirms the predicted structure, with mutually *trans* sulfur atoms. There are two independent molecules which have similar chiral structures. Distortions from regular octahedral geometry at platinum(IV) arise through the constraints of the 4-membered chelate rings.

Reaction of di-2-pyridyldisulfide with $[PtMe_2(bipy)]$, **2a**, bipy = 2,2′-bipyridine, in CD_2Cl_2 immediately gave a black precipitate which slowly redissolved to give a yellow solution. Complex **1** could be crystallized from this solution. A similar reaction was monitored by ^1H NMR as the solution in CD_2Cl_2 was warmed from −80 °C to room temperature. Complex **2a** was almost completely consumed at −10 °C and the major product was identified as the binuclear complex $[\{PtMe_2(Spy)(bipy)\}_2]$, **3a** (Scheme 2). As the mixture was warmed to room temperature, complex **3a** reacted further to give $[PtMe_2(Spy)_2(bipy)]$, **4a**, and then **4a** underwent dissociation of 2,2′-bipyridine to give the final product $[PtMe_2(2\text{-}Spy)_2]$, **1**. There was an equilibrium between **1** and free 2,2′-bipyridine and complex **4a** (Scheme 2), but the equilibrium strongly favored **1** and free 2,2′-bipyridine, with only *ca.* 5% **4a** present at the concentration used. In addition, both $[Pt(Spy)Me_3(bipy)]$, with $\delta(^1H)$ = 0.28 [s, 3H, $^2J(PtH)$ = 62 Hz, PtMe *trans* to S]

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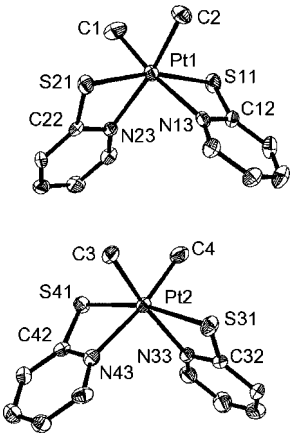


Figure 1. Structure of complex **1**. Selected bond parameters for molecule 1, which are similar for molecule 2: Pt(1)−C(1) 2.045(13); Pt(1)−C(2) 2.057(11); Pt(1)−N(23) 2.160(8); Pt(1)−N(13) 2.168(9); Pt(1)−S(21) 2.362(3); Pt(1)−S(11) 2.364(3) Å; N(23)−Pt(1)−S(21) 68.3(2); N(13)−Pt(1)−S(11) 68.0(2); S(21)−Pt(1)−S(11) 164.6(1)°.

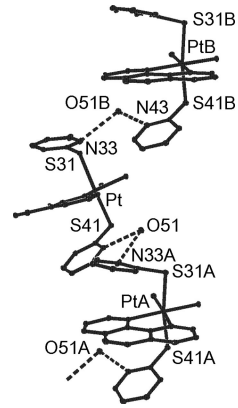
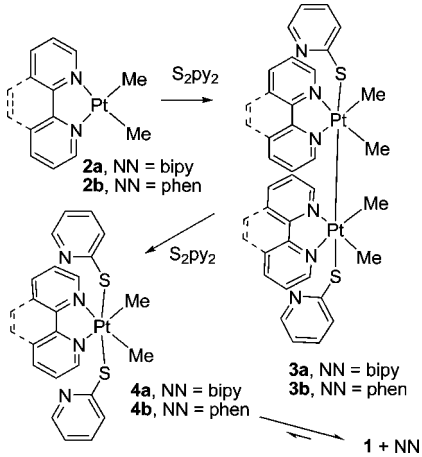


Figure 2. Structure of complex **4b**·H_2O. Selected bond parameters: Pt−C(1) 2.06(1); Pt−C(2) 2.10(1); Pt−N(22) 2.153(9); Pt−N(11) 2.17(1); Pt−S(41) 2.343(3); Pt−S(31) 2.396(3) Å; S(41)−Pt-S(31) 171.3(1); C(32)−S(31)−Pt 105.4(4); C(42)−S(41)−Pt 104.0(4) °. H-bonding distances: O(51)···N(43) 2.87(1); O(51)···N(33A) 3.22(2) Å.

Scheme 2



and $\delta(^1H) = 1.28$ [s, 6H, $^2J(PtH) = 70$ Hz, PtMe *trans* to N], and [$PtClMe_3$(bipy)], with $\delta(^1H) = 0.39$ [s, 3H, $^2J(PtH) = 75$ Hz, PtMe *trans* to Cl] and $\delta(^1H) = 1.22$ [s, 6H, $^2J(PtH) = 70$ Hz, PtMe *trans* to N], were identified in *ca.* 2% yield from their characteristic ^1H NMR spectra.[14] Remarkably, a similar reaction of **2a** with S_2py_2 in $CDCl_3$ solution was very much slower, with only about 10% decay of resonances for **2a** in one hour at room temperature. The product mixture was complex, with some products arising from reaction with solvent.[15]

The loss of 2,2′-bipyridine (bipy) from **4a** to give **1** under mild conditions was not expected, so the reaction was also studied for the 1,10-phenanthroline (phen) complex **2b**. The greater rigidity of the phen ligand compared to bipy makes its displacement much more difficult. The reaction in CD_2Cl_2 solution also occurred according to Scheme 2, but there were significant differences. The initial reaction was very similar and led to formation of the black binuclear complex **3b** in high yield. This step was complete in a few minutes at 0 °C. The next step to give **4b** (Scheme 2) was slower than in the similar reaction with **2a** and decay of **3b** was complete in about one day at room temperature. There were several byproducts formed during this period, among which the complexes [Pt(Spy)Me_3(phen)] and [$PtClMe_3$(phen)] were identified by their ^1H NMR spectra. Complex **4b** only partly decomposed to give **1** over a period of a week at room temperature. Because complex **3b** was longlived in solution, many attempts were made to crystallize it, but only **4b** could be crystallized from this and similar reaction mixtures.

The structure of **4b**, which crystallized as a water solvate, is shown in Figure 2. It confirms the *trans* orientation of the two 2-pyridylthiolate ligands, as found in related complexes.[10,11] The C−S−Pt angles are less than the tetrahedral angle, which allows π-stacking of the pyridyl and phenanthroline rings. Individual molecules are self-assembled into polymeric chains through hydrogen bonding between pyridyl groups and the water molecules, N···HOH···N, as shown in Figure 2.

The characterization of the binuclear complexes **3a** and **3b** depends in large part on the ^1H NMR spectra. Consider the case of formation of **3a** from **2a**. If the reaction with di-2-pyridyldisulfide is carried out in a 1:1 ratio, only half of the disulfide is consumed in forming **3a**, and the stoichiometry of the product is readily confirmed by integration of the ^1H NMR spectrum. Complex **3a** is much longer lived when formed in the absence of excess di-2-pyridyldisulfide. The complex gives a single methylplatinum resonance and the coupling constant $^2J(PtH) = 75$ Hz is in the range expected for 6-coordinate platinum and considerably less than in **2a**, which gives $^2J(PtH) = 86$ Hz. The resonance for the *ortho* hydrogen, N=CH^6, of the bipy ligand occurs at $\delta = 9.28$ in **2a** but at 8.70 and 8.04 in **4a** and **3a** respectively. Similarly, the *ortho*-hydrogen of the 2-pyridylthiol unit, S=CH^3, is at $\delta = 7.62$ in the parent ligand S_2py_2 but at $\delta = 6.78$ and 6.22 in **4a** and **3a** respectively. These shifts must arise primarily through ring shielding effects, and indicate more extensive π-stacking of the aromatic rings in **3a** than in **4a**. The shielding effects are even more pronounced in the 1,10-phenanthroline complex **3b** as illustrated in Figure 3. The spectra indicate apparent C_{2v} symmetry of the [$Pt_2Me_4(NN)_2$] units in **3a** and **3b**, indicating easy rotation of the 2-pyridylsulfide groups as well as easy libration about the Pt−Pt bond at room temperature. Both the methylplatinum peaks and the 1,10-phenanthroline peaks in **3b** (except the H^5 resonance) are broadened at low temperature, indicating the slowing of rotation about the Pt−Pt bond but not about the Pt−S bond, under these conditions.

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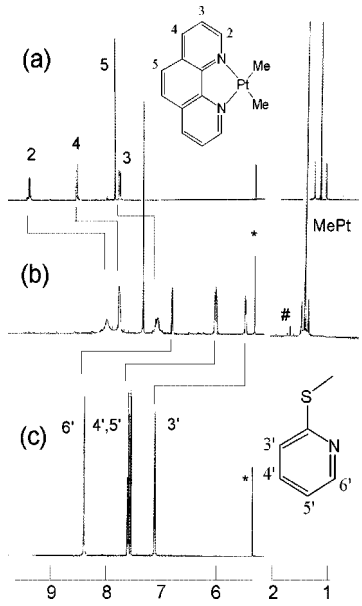


Figure 3. ^{1}H NMR spectra in CD_2Cl_2 solution of (a) [$PtMe_2$(phen)], **2b** (400 MHz, 20 °C); (b) [Pt_2Me_4(Spy)$_2$(phen)$_2$], **3b** (600 MHz, −20 °C); (c) S_2py_2 (400 MHz, 20 °C). The correlation lines show the chemical shift changes in **3b** compared to the reagent molecules primarily as a result of the π-stacking. The peak marked * is due to $CHDCl_2$, while that marked # in (b) is due to impurity of complex **4b**.

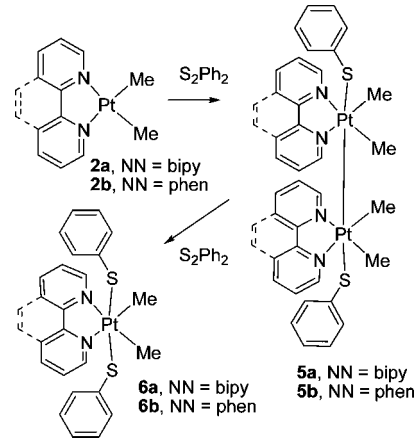
Further evidence for the proposed binuclear structure of **3a** and **3b** was obtained by ESI-MS of reaction mixtures in dichloromethane solution. The first step of the reaction of [$PtMe_2$(bipy)], **2a**, with S_2py_2 was complete in ten minutes and the base peak was at m/z = 491, corresponding to [$PtMe_2$(bipy)(Spy)]$^+$. Lower intensity peaks were observed at m/z = 981 [(**3a**-H)$^+$], 825 [(**3a**-bipy-H)$^+$] and also at m/z = 1092 [(**3a**+Spy)$^+$]. Over a period of one hour, the peak at m/z = 1092 decayed and a peak at m/z = 505 [($PtMe_3$(bipy)(Spy)-H)$^+$] grew in intensity. Analogous results were obtained for the reaction with [$PtMe_2$(phen)], **2b**, in which the ESI-MS gave a base peak was at m/z = 515, corresponding to [$PtMe_2$(phen)(Spy)]$^+$, with lower intensity peaks at m/z = 1029 [(**3b**-H)$^+$], 849 [(**3b**-phen-H)$^+$], 1140 [(**3b**+Spy)$^+$] and 529 [($PtMe_3$(phen)(Spy)-H)$^+$].

Reactions of Diphenyldisulfide. The reaction of [$PtMe_2$(phen)], **2b**, with diphenyldisulfide was studied previously but, with the instrumentation available at that time, it was not possible to obtain satisfactory NMR data on the initial product.[11] A reinvestigation with both **2a** and **2b** has now shown that the reactions occur according to Scheme 3.

The course of the reaction is similar to the first steps in the reaction with di-2-pyridyldisulfide (Scheme 2). If the reactions are carried out with a 1:1 ratio of **2a** or **2b**: Ph_2S_2, the reaction mixture becomes black on mixing and much of this black product (**5a** or **5b**) precipitates. On stirring, the black material slowly redissolves to give **6a** or **6b**, which can be isolated as yellow crystalline solids. If the reaction is carried out in a 2:1 ratio of **2a** or **2b**: Ph_2S_2, the black products **5a** or **5b** are more persistent, but it has not been possible to crystallize them. The structures of **6a** and **6b** are shown in Figures 4 and 5. They confirm the overall product of *trans* oxidative addition of diphenyldisulfide to **2a** or **2b**, with π-stacking of the phenyl groups with the bipy or phen units.[10,11]

The ^{1}H NMR spectra of complexes **5a** and **5b** were, like those of the 2-pyridylthiolate analogs **3a** and **3b**, greatly influenced

Scheme 3



by π-stacking of the aromatic groups. For example, in Ph_2S_2, **6b** and **5b**, the *ortho*-hydrogen atoms of the PhS groups appeared at δ = 7.48, 6.18 and 5.35 respectively as π-stacking increased. Similarly, in **2b**, **6b**, and **5b**, the *ortho*-hydrogen atoms of the phen groups appeared at δ = 9.51, 8.89 and 7.99 respectively, confirming mutual shielding of aromatic protons of both the phenylthiolate and 1,10-phenanthroline groups with increasing π-stacking. Complex **5b** gives a single methylplatinum resonance at δ = 1.32 with ^2J(PtH) = 76 Hz.

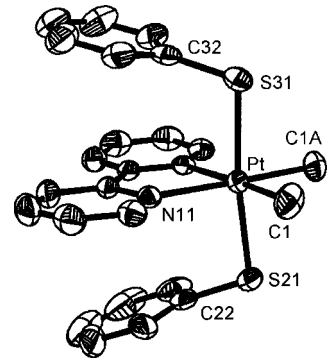


Figure 4. Structure of complex **6a**. Selected bond parameters: Pt−C(1) 2.055(6); Pt−N(11) 2.163(4); Pt−S(21) 2.366(2); Pt−S(31) 2.381(2) Å; C(1)−Pt−S(21) 87.2(2); N(11)−Pt−S(21) 92.91(11); C(1)−Pt−S(31) 87.7(2); N(11)−Pt−S(31) 92.56(11); S(21)−Pt−S(31) 173.06(9); C(22)−S(21)−Pt 105.6(3) °. Symmetry equivalent atoms: A, x, $-y+1/2$, z.

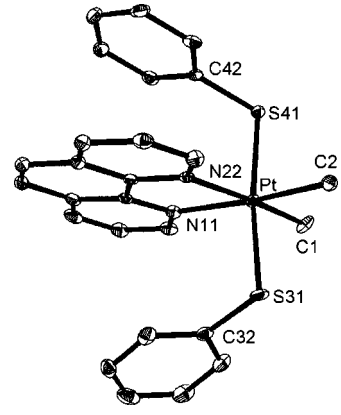
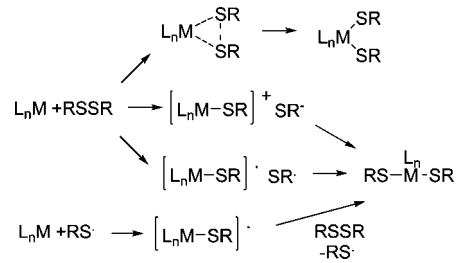


Figure 5. Structure of complex **6b**. Selected bond parameters: Pt−C(2) 2.050(7); Pt−C(1) 2.059(8); Pt−N(11) 2.161(5); Pt−N(22) 2.174(6); Pt−S(31) 2.364(2); Pt−S(41) 2.374(2) Å; C(32)−S(31)−Pt 106.5(2); C(42)−S(41)−Pt 106.3(1) °.

Scheme 4



When the reaction of **2b** with diphenyldisulfide was carried out in acetone solution, a trace product formed along with **6b** was identified as the product of *cis* oxidative addition, *cis,cis*-$[PtMe_2(SPh)_2(phen)]$.[11] This product is not formed in the reaction in dichloromethane solution, but a minor product was identified as $[PtClMe_3(phen)]$.[14] It was formed in only about 2% yield, and was identified near the end of the slower step of the overall reaction to form **6b** from **5b** and Ph_2S_2 in dichloromethane solution.

Discussion

There are several potential mechanisms of oxidative addition of S−S bonds to transition metal complexes as outlined in Scheme 4. A concerted mechanism is expected to give the product of *cis* oxidative addition, but this stereochemistry is observed only when there are geometrical constraints (for example **I**, Chart 3), and is clearly impossible for formation of the binuclear complexes **3** and **5**.[9−11] The polar mechanism, forming the intermediate $[L_nMSR]^+SR^-$, has precedents in oxidative addition of halogens and finds support in oxidative addition to anionic complexes.[10] However, disulfides rarely act as simple electrophiles as required in this mechanism.[4,5] Free radical nonchain or chain mechanisms have more precedents in disulfide chemistry,[4] and there is some evidence for these in oxidative addition of disulfides or diselenides to platinum(II), including complex kinetics and enhancement by photons.[10,11] However, attempts to detect radical intermediates by EPR or CIDNP have not been successful. Any of the polar or radical mechanisms can give *trans* oxidative addition (Scheme 4). A major complication in the reactions studied here is the kinetic preference for formation of the binuclear complexes **3** and **5**. To gain insight into the mechanism of S−S bond activation, calculations have been carried out using density functional theory (DFT).

Concerted Mechanism of S−S Bond Cleavage. The simplest reaction is the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with S_2py_2 to give complex **1** and the calculated energies of some potential intermediates are shown in Scheme 5. There are several ways in which S_2py_2 may chelate to a dimethylplatinum(II) unit after displacement of dimethylsulfide. The calculations indicate, as do the precedents in Chart 2,[8] that the N,N or N,S chelate, **7** or **8**, is preferred. The 5-membered chelate ring in **8** is favored over the 4-membered chelate ring in **8′**. Coordination of both sulfur atoms in **9** or **10** leads to considerable weakening of the S−S bond and then concerted oxidative addition leads to the *cis* 5-coordinate platinum(IV) complex **11**. Complex **11** has an essentially barrier-free route to the *trans* 5-coordinate isomer **12** and then coordination of the free pyridyl group gives **1**. It is also possible for **11** to give the product of *cis* oxidative addition **13**, and **13** is calculated to lie only about 10 kJ mol^{-1} higher in energy than **1** (Scheme 5). Complex **13** is not observed because the rearrangement of **11** to **12** (in which both sulfur π-donors are *cis* to the vacant coordination site in the 16-electron platinum(IV) complex and which is calculated to be 72 kJ mol^{-1} more stable than **11**) is faster than the pyridine coordination step. The activation enthalpy is calculated to be 130 kJ mol^{-1}.

In the reaction of S_2py_2 or S_2Ph_2 with **2a**, the bipy ligand cannot be displaced by the neutral disulfide ligand so the above mechanism is not possible. A search for a concerted mechanism of oxidative addition in this system was unsuccessful, so calculations were carried out with a model system of S_2H_2 with *cis*-$[PtMe_2(NH_3)_2]$ in order to gain insight into this problem. The results are shown in Scheme 6. The disulfide first adds to give the square pyramidal disulfide complex **14**.[16] As the second sulfur atom approaches the platinum atom the SS bond is weakened and, near the transition state, **15**, one of the ammine ligands is essentially dissociated and then recoordinates in the product of *cis* oxidative addition **16**. The situation is reminiscent of the oxidative addition of nonpolar C−H or C−C bonds to platinum(II) in which coordinative unsaturation is needed[17,18] but, of course, the disulfide case differs in that the sulfur atoms carry lone pairs of electrons and so **15** would be a 20-electron complex intermediate if the ligand dissociation did not occur. There is another route, with slightly lower activation energy, which involves intermediate ligand displacement (Scheme 6). One ammine ligand is displaced from **14** by way of a trigonal bipyramidal transition state **17** to give the κ^1-disulfide complex **18**.[16] The concerted *cis* oxidative addition from **18** through **19** to give the dithiolate complex **20** occurs easily as the Pt−S−S angle distorts to allow a second Pt···S interaction, and there is then an easy route to the *trans* isomer **21** and then to product of *trans* oxidative addition **22**. The ease of reaction of **18** to give **20** and **21**, suggests an alternative route to **1** from di-2-pyridyldisulfide and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ by direct rearrangement of $[PtMe_2(SMe_2)(\kappa^1\text{-}S\text{-}S_2py_2)]$ to give $[PtMe_2(SMe_2)(Spy)_2]$, followed by displacement of dimethylsulfide to give **1**. Calculations indicate a similar activation energy as for the oxidative addition step in Scheme 5. What is clear from these calculations is that a concerted mechanism of oxidative addition is possible provided that a disulfide complex of platinum(II) with a square planar 16-electron configuration can be formed as an intermediate. However, a concerted mechanism of reaction is not favored with complexes such as **2a** and **2b** which have no easily displaced ligand.[18]

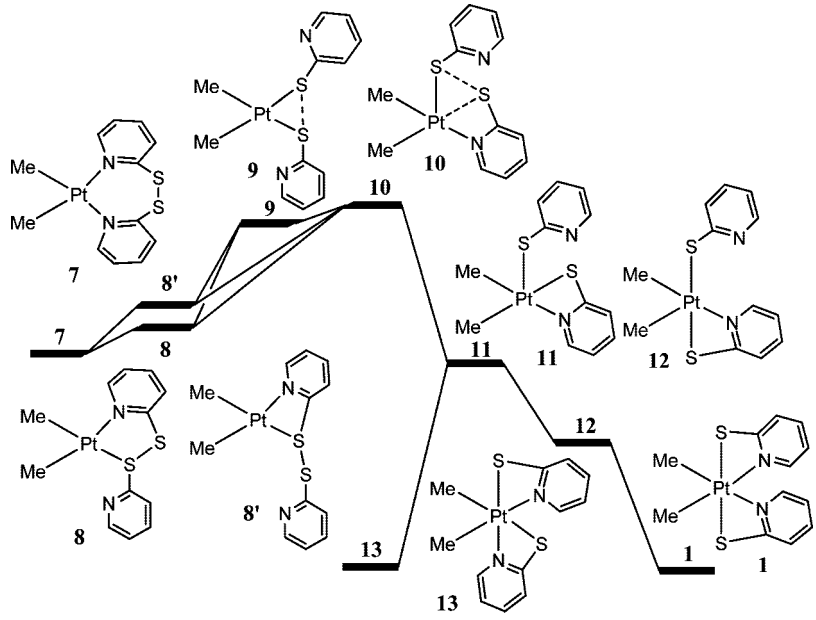
Nonconcerted Mechanisms of S−S Bond Cleavage. Schemes 7 shows potential mechanisms of oxidative addition of diphenyldisulfide to complex **2a** to give $[Pt(SPh)_2Me_2(bipy)]$, **6a**, a reaction which does not occur in practice. Calculations suggest a weak bonding between **2a** and S_2Ph_2 to give **23** which might then undergo S−S bond homolysis or heterolysis to give **24** and PhS$^\cdot$ or **25** and PhS^-, respectively.[16] Recombination of the radicals or ions would then give **6a**. In the radical chain mechanism, a phenylthiyl radical is formed in an initiation step, then reacts with **2a** to give **24**, which reacts with S_2Ph_2 to give **6a** and PhS$^\cdot$, to continue the chain.

(16) For a discussion, from a theoretical perspective, of 5-coordinate intermediates in substitution reactions of platinum(II): Cooper, J.; Ziegler, T. *Inorg. Chem.* **2002**, *41*, 6614.

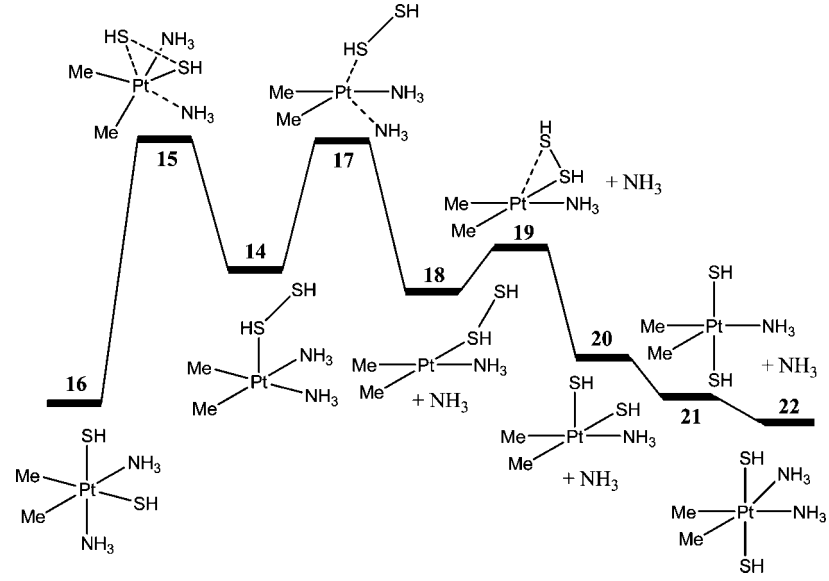
(17) (a) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456. (b) Gilbert, T. M.; Hristov, I.; Ziegler, T. *Organometallics* **2001**, *20*, 2669. (c) Hoover, J. M.; Freudenthal, J.; Michael, F. E.; Mayer, J. M. *Organometallics* **2008**, *27*, 2238.

(18) Arguments have been made for either concerted or polar (S_N2) mechanisms for oxidative addition of the O−O bond of peroxides to dimethylplatinum(II) complexes: (a) Taylor, R. A.; Law, D. J.; Sunley, G. J.; White, A. J. P.; Britovsek, G. J. P. *Chem. Commun.* **2008**, 2800. (b) Thorshaug, K.; Fjeldahl, I.; Romming, C.; Tilset, M. *J. Chem. Soc., Dalton Trans.* **2003**, 4051. (c) Rashidi, M.; Nabavizadeh, M.; Hakimelahi, R.; Jamali, S. *J. Chem. Soc., Dalton Trans.* **2001**, 3430. (d) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608.

Scheme 5. Calculated S−S Distances are 7 = 2.35, 8 = 2.42, 8′ = 2.49, 9 = 3.03, 10 (Transition State) = 3.31, 11 = 3.70, 12 = 4.90, 13 = 4.08, 1 = 4.99 Å



Scheme 6. Calculated S−S Distances: 14, 2.56; 15, 2.89; 17, 2.41; 18, 2.53; 19, 2.76 Å



Coordination of S_2Ph_2 to give **23** is calculated to lead to lengthening of the S−S distance from 2.42 to 2.57 Å, arising from backbonding from filled d-orbitals on platinum into the S−S σ^*-orbital of the disulfide. Nevertheless, either homolysis to give PhS$^{\cdot}$ and **24** or heterolysis to give PhS$^-$ and **25** in the gas phase requires a high activation energy (Scheme 8). Solvation effects in solution will certainly stabilize the polar intermediates but probably not by enough to favor the polar mechanism.[19] Once the intermediates are formed, collapse to give **6a** is highly favorable. Hence the fact that **6a** is not a primary product must be associated with the high barrier to the activation of **23**. If free phenylthiyl radicals can be formed, the addition to **2a** to give **24**, followed by further reaction to give **6a**, should be easy in a chain reaction (Scheme 7, 8), but there may be no easy source of the initiating radicals under the mild reaction conditions used.

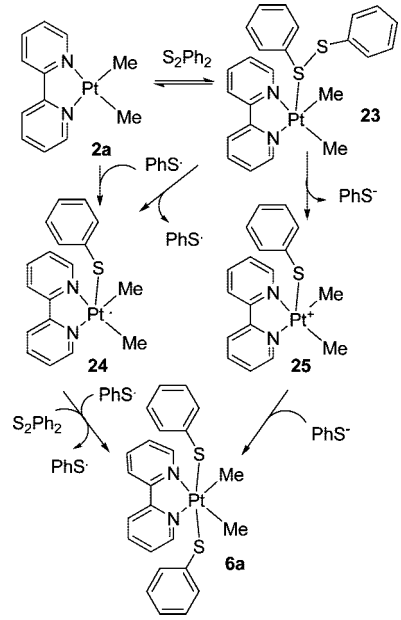
It is well-known that square planar platinum(II) complexes with 2,2′-bipyridine or 1,10-phenanthroline can form π-stacked dimers, which involve attractions between aromatic groups sometimes enhanced by secondary Pt···Pt bonding, in solution or solid states.[20,21] In the solid state structure of [$PtMe_2$(bipy)], **2a**, neighboring pairs of molecules are separated by 3.48 Å.[21] We therefore explored the potential involvement of the dimer [PMe_2(bipy)]$_2$, **26**, in the reaction with diphenyldisulfide. The results should be treated with caution because DFT is not the

(19) For a detailed theoretical study of solvation effects during the model reaction of oxidative addition of methyl iodide to *cis*-[$PtMe_2(NH_3)_2$] by the S_N2 mechanism, see: (a) Hayaki, S.; Yokogawa, D.; Sato, H.; Sakaki, S. *Chem. Phys. Lett.* **2008**, *458*, 329.

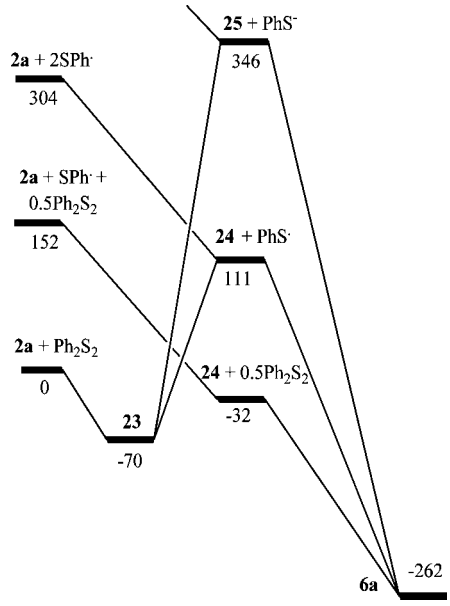
(20) (a) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1989**, *28*, 1529. (b) Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 6261. (c) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913. (d) Kato, M.; Kosuge, C.; Morii, K.; Ahn, J. S.; Kitagawa, H.; Mitani, T.; Matsushita, M.; Kato, T.; Yano, S.; Kimura, M. *Inorg. Chem.* **1999**, *38*, 1638. (e) Momeni, B. Z.; Hamzeh, S.; Hosseini, S. S.; Rominger, F. *Inorg. Chim. Acta* **2007**, *360*, 2661.

(21) Achar, S.; Catalano, V. J. *Polyhedron* **1997**, *16*, 1555.

Scheme 7. Possible Mechanisms of Oxidative Addition



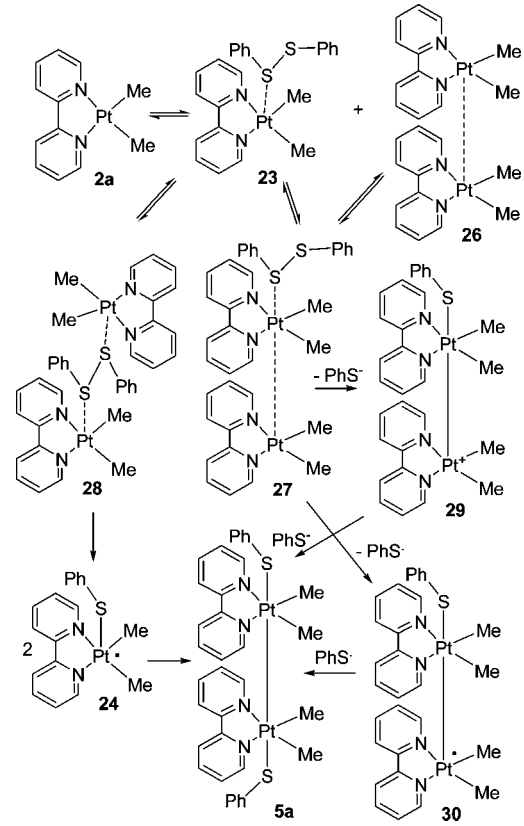
Scheme 8. Calculated Activation Enthalpies (kJ mol^{-1}) for Gas Phase Reaction of 2a to Give Ionic or Radical Intermediates En Route to 6a



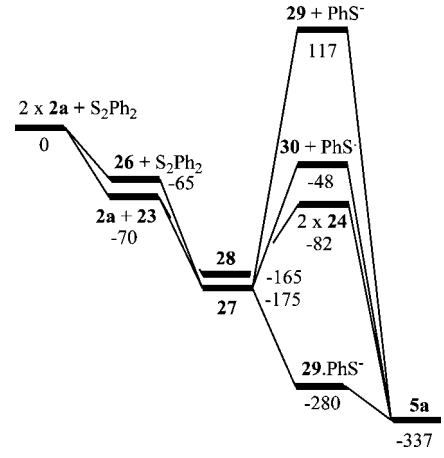
best theory for modeling weak interactions, but the overall picture obtained is useful.

The calculated energies of the intermediates defined in Schemes 9 are shown in Scheme 10. The enthalpy change for formation of **26** is similar to that for addition of S_2Ph_2 to **2a** to give **23**. The addition of S_2Ph_2 to **26**, or the addition of [$PtMe_2$(bipy)] to **23**, can then give **27**, and this is also calculated to be favorable (Scheme 10). Alternatively, complex **23** can react with [$PtMe_2$(bipy)] to give the bridging diphenyldisulfide complex **28**, and this is also easy and favorable. There are then three possible routes to **5a**, involving heterolysis or homolysis of the S−S bond to give **29** or **30**, followed by recombination of the ions **29** and PhS^- or the radicals **30** and PhS·, respectively, to give **5a**, or involving homolysis of the S−S bond of **28** to give two radicals [$PtMe_2$(SPh)(bipy)]·, **24**, which then recombine to form **5a** (Scheme 9 and 10). For the homolytic cleavage mechanisms, the activation energies to form **24** from

Scheme 9. Possible Mechanisms of Formation of Complex 5a



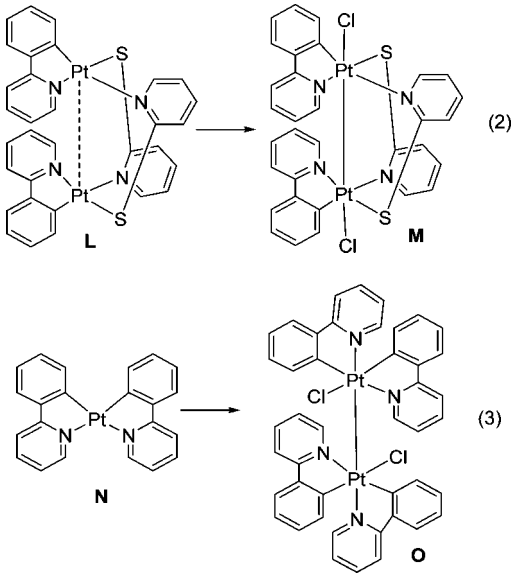
Scheme 10. Calculated Energies (kJ mol^{-1}) for the Complexes and Intermediates Defined In Scheme 8



23 (Scheme 8), **30** from **27** and 2 × **24** from **28** (Scheme 10) are 181, 127, and 83 kJ mol^{-1}, respectively, and these values correlate well with the calculated S−S distances in **23**, **27**, and **28** of 2.57, 2.67, and 2.71 Å, respectively. The calculated activation energy for gas phase heterolysis of the S−S bond of **27** (292 kJ mol^{-1}) is similarly much lower than in **23** (416 kJ mol^{-1}). As the S−S bond of the intermediate **27** is cleaved to give **29** or **30**, the calculations indicate that both the Pt−Pt and Pt−S bonds are strengthened [Pt−Pt = 3.35, 2.94, 2.95 Å; Pt−S = 2.81, 2.57, 2.55 Å in **27**, **29**, and **30** respectively]. Similarly, cleavage of the S−S bond in **28** to give two molecules of the radical **24** is accompanied by strengthening of both Pt−S bonds [Pt−S = 2.72, 2.58 Å in **28** and **24**, respectively]. These calculations correspond to formation of ions or radicals separated at infinity in the gas phase. Calculations of units **29** + PhS^- or

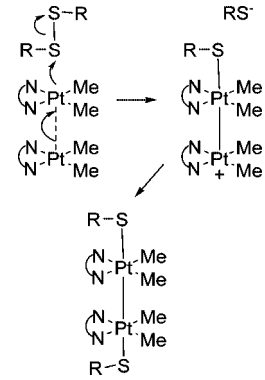
30 + PhS˙ in geometries corresponding to gas phase tight ion pairs or radical pairs give lower energies, the most favorable of which studied corresponds to the ion pair **29** + PhS^- in which the thiolate ion is π-stacked with the bipyridyl ligand on the platinum cation (i.e., close to the product). In geometries closer to the initial transition state, the radical pair structure is favored. It is likely that solvation effects would favor the ion pair structure in these cases but calculation of these effects is difficult in such a complex system.[19]

Related Reactions and a Proposed Mechanism. Binuclear oxidative addition reactions are well-known in ligand-bridged binuclear precursor complexes,[22−24] but they are rare in unbridged complexes.[25] Some examples with platinum(II) precursors are shown in eqs 2 and 3. Equation 2 shows an example with bridging ligands to anchor the binuclear unit, and the oxidation exhibits easy electrochemical reversibility.[22] The formation of complex **O** from **N** (eq 3) can involve oxidation by [AuCl(SMe$_2$)] or *N*-chlorosuccinimide, and the reaction is thought to occur by a 1-electron mechanism involving sequentially the intermediates [ClPt(C$_6$H$_4$py)$_2$]˙ and [ClPt(C$_6$H$_4$py)$_2$-Pt(C$_6$H$_4$py)$_2$]˙.[25] However, oxidation of complex **N** with PhICl2 gives simple oxidation to [PtCl$_2$(C$_6$H$_4$py)$_2$], evidently by a polar mechanism.[23]



There are several pieces of evidence against a free radical mechanism in formation of the binuclear complexes **3** (Scheme 2) and **5** (Scheme 3) in dichloromethane or acetone solution at concentrations used in monitoring by NMR. We have failed to observe CIDNP effects in NMR spectra, there are no byproduct of the type expected from platinum radical intermediates, there are no induction periods, and the reactions are not retarded by traces of free radical scavengers. Although none of this constitutes a definitive proof, the combination is strongly indicative.[14] Evidence for an ionic mechanism was obtained by ESI-MS of reaction mixtures, in which compounds [Pt$_2$Me$_4$(NN)$_2$(Spy)(S$_2$py$_2$)]$^+$, NN = bipy or phen, were observed in reactions leading to **3a** or **3b**. These are likely to be formed by trapping of the corresponding intermediates [Pt$_2$Me$_4$-(NN)$_2$(Spy)]$^+$ by the reagent S$_2$py$_2$. The ion [Pt$_2$Me$_4$(NN)$_2$-(Spy)]$^+$ was not observed, but the most abundant ion was [PtMe$_2$(NN)(Spy)]$^+$ which would be formed by cleavage of its Pt−Pt bond. A general mechanism which is consistent with the data is shown in Scheme 11. It is suggested, based on the data in Schemes 8 and 10, that the activation energy for direct reaction of [PtMe$_2$(NN)], NN = bipy or phen, with R$_2$S$_2$ is too high to allow easy reaction.[26] However, the weakly bonded dimer [Pt$_2$Me$_4$(NN)$_2$] is in easy equilibrium with [PtMe$_2$(NN)], and then a neighboring group effect leading to acceleration of the reaction is possible. A similar effect has been proposed previously for bridged binuclear complexes, but this appears to be the first evidence for such an effect in simple mononuclear complexes.[22−25] The puzzling solvent effect on the reaction rate, in which the reaction of **2a** or **2b** with S$_2$Ph$_2$ or S$_2$py$_2$ was much faster in CD$_2$Cl$_2$ than in CDCl$_3$, can be understood in terms of this mechanism. Thus, it has been shown that electron rich dimethylplatinum(II) complexes can interact with chloroform through Pt···HCCl$_3$ bonding and this is likely to prevent the association between units of **2a** or **2b** in CDCl$_3$ solution.[27]

Scheme 11. Proposed Mechanism of Binuclear Oxidative Addition of S−S Bonds



The mechanism of reaction of the binuclear platinum(III) complexes **3** or **5** with a disulfide to give **4** or **6** is likely to involve radical intermediates. These reactions are faster in the light than in the dark, and they occur with formation of byproducts including [PtMe$_3$(SR)(NN)] and [PtClMe$_3$(NN)]. The platinum centers in **3** and **5** are sterically inaccessible, so radical attack at platinum is not possible. In the light it is possible that homolysis of the Pt−Pt bond might occur. Otherwise, thiol radical attack at a thiolate ligand followed by loss of disulfide might generate the reactive intermediate [PtMe$_2$(SR)(NN)]˙ and [PtMe$_2$(NN)]. In either case, the reactive intermediate [PtMe$_2$(SR)(NN)]˙ can abstract an RS group to give **4** or **6**, or abstract a methyl group to give [PtMe$_3$(SR)(NN)].

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(23) (a) Koshiyama, T.; Omura, A.; Kato, M. *Chem. Lett.* **2004**, *33*, 1386. (b) Koshiyama, T.; Kato, M. *Acta Cryst. C* **2005**, *C61*, m173.

(24) The bridging must allow face-to-face orientation of the two square planar units in order to see binuclear oxidative addition: (a) Jain, V. K.; Jain, L. *Coord. Chem. Rev.* **2005**, *249*, 3075. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (c) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2522.

(25) (a) Yamaguchi, T.; Kubota, O.; Ito, T. *Chem. Lett.* **2004**, *33*, 190. (b) Whitfield, S. R.; Sanford, M. S. *Organometallics* **2008**, *27*, 1683. (c) Dick, A. S.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2005**, *24*, 482.

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(27) Zhang, F.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2004**, *23*, 1396.

Table 1. Crystal Data and Structure Refinements

complex	**1**	**4b**·H_2O	**6a**	**6b**
formula	$C_{12}H_{14}N_2PtS_2$	$C_{24}H_{24}N_4OPtS_2$	$C_{24}H_{24}N_2PtS_2$	$C_{26}H_{24}N_2PtS_2$
fw	445.46	643.68	599.66	623.68
T/ K	150(2)	150(2)	300(2)	150(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
cryst. syst.	Triclinic	monoclinic	orthorhombic	monoclinic
Space gp.	$P\bar{1}$	*Pn*	*Pnma*	$P2_1/n$
cell dimens.				
a/Å	9.4800(5)	9.6789(5)	14.1299(3)	7.6899(2)
b/Å	12.3371(6)	11.2501(6)	12.5587(2)	15.7816(5)
c/Å	13.5806(6)	10.5571(6)	12.6883(3)	18.7901(6)
α/°	78.662(3)	90	90	90
β/°	70.699(3)	91.340(3)	90	96.913(2)
γ/°	74.273(3)	90	90	90
V/Å^3	1432.9(1)	1149.2(1)	2251.6(1)	2263.8(1)
Z	4	2	4	4
d_c/Mg m^{-3}	2.065	1.860	1.769	1.830
Abs. coeff./ mm^{-1}	10.064	6.311	6.430	6.399
Reflns	17835	13428	28275	19085
Data/restr./param.	5044/0/311	5107/267/297	2406/0/144	3943/0/259
$R_1[I > 2\sigma(I)]$	0.0474	0.0538	0.0345	0.0467
*wR*2[all data]	0.1159	0.1355	0.0901	0.1343

In conclusion, the oxidative addition reactions of disulfides to platinum(II) are surprisingly complex. Most oxidative addition reactions to dimethylplatinum(II) complexes of the type [$PtMe_2$(NN)], with NN = bipy or phen, give mononuclear platinum(IV) products, whether they occur by polar or free radical mechanisms.[9−15,28] This includes reactions of E−E bonds with E = O, S, Se.[9−11,18] The formation of the diplatinum(III) complexes **3** and **5** by reaction of [$PtMe_2$(NN)] with disulfides is therefore unusual,[25,28] and most precedents for binuclear oxidative addition involve reactions to bridged binuclear complexes.[22−25,28,29] The combination of experimental and computational work described above suggests that the unusual reactivity arises for the following combination of reasons.

1. A concerted mechanism of oxidative addition to 16-electron platinum(II) complexes is generally unfavorable and has a high activation energy, unless an easy ligand dissociation or displacement step can occur easily (see Scheme 6). This conclusion applies to reactions involving many nonpolar bonds, including H−H, C−H, C−C, N−N, O−O, and S−S bonds.[17,18,28] Hence a simple concerted oxidative addition of an S−S bond to [$PtMe_2$(NN)] is not favored.

2. The activation energy for a polar (S_N2) or free radical reaction mechanism of reaction is too high to allow easy reaction, owing to the low reactivity of disulfides in oxidative addition (Schemes 7 and 8).[26] If the first step in Scheme 7 were possible, a simple oxidative addition would be expected, as is observed with the more reactive diselenide reagents.[9−11]

3. Easy association between dimethylplatinum(II) complexes can occur, and a neighboring group effect of the second platinum atom leads to a much lower activation energy for oxidative addition (Schemes 9 and 10). The bond activation step leads to strengthening of the PtPt bond and so this bond remains intact through to formation of the products **3** or **5**. The effect of weak association of platinum(II) complexes on spectral properties is well-known,[20] but the effect on chemical reactivity is not well documented. This work suggests that binuclear oxidative addition with complexes [$PtMe_2$(NN)] will be favored in stepwise reactions with substrates which have intrinsically low reactivity.

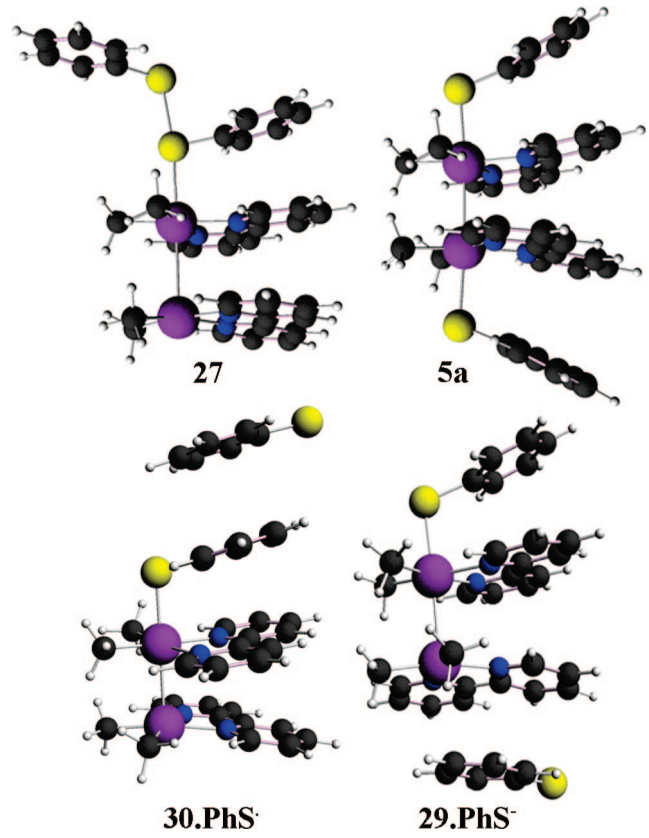

Figure 6. Calculated structures of complex **5a** and potential intermediates **27**, **29**·PhS^-, and **30**·$PhS^{\cdot}$.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques, unless otherwise specified. NMR spectra were recorded using Varian Mercury 400 or Varian Inova 400 or 600 spectrometers. ESI mass spectra were recorded using a Micromass LCT spectrometer, with an injection flow rate of 20 μL/min, and were calibrated with NaI at a concentration of 2 μg/μL in 50:50 propan-2-ol/water. The injection flow rate at 20.0 μL/min was used throughout all experiments. The complexes [$Pt_2Me_4(\mu$-$SMe_2)_2$], [$PtMe_2$(bipy)], and [$PtMe_2$(phen)] were prepared by the literature methods.[12]

[$PtMe_2$(2-$SC_5H_4N)_2$], 1. A mixture of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (26.1 mg, 0.045 mmol) and di-2-pyridyldisulfide (20 mg, 0.091 mmol) in CD_2Cl_2 (1 mL) was allowed to react for 10 min. The ^{1}H NMR spectrum showed formation of **1** and free SMe_2 [$\delta(^1H) = 2.10$] only. Evaporation of the solution gave complex **1**, as a yellow-orange solid, which was crystallized from CH_2Cl_2/pentane. Anal. Calc. for $C_{12}H_{14}N_2PtS_2$: C, 32.36; H, 3.17; N, 6.29. Found: C, 32.01; H, 3.05; N, 6.28%. NMR in CD_2Cl_2: $\delta(^1H) = 1.51$ [s, 6H, ^2J(PtH) = 76 Hz, PtMe]; 6.87 [m, 2H, H^5]; 6.91 [m, 2H, H^3]; 7.43 [m, 2H, H^4]; 8.11 [m, 2H, ^3J(PtH) = 21 Hz, H^6]. A similar reaction was monitored from −15 to 0 °C and showed formation of **1**, SMe_2 and *cis*-[$PtMe_2(SMe_2)_2$],[12] identified by resonances at $\delta(^1H) = 0.68$ [s, 6H, ^2J(PtH) = 81 Hz, PtMe] and 2.39 [s, 12H, ^3J(PtH) = 23 Hz, SMe], at intermediate stages.

[{$PtMe_2$(Spy)(bipy)}$_2$], 3a, and [$PtMe_2$(Spy)$_2$(bipy)], 4a. To a solution of [$PtMe_2$(bipy)], **2a** (10 mg, 0.026 mmol) in CD_2Cl_2 (0.5 mL) was added a solution of di-2-pyridyldisulfide (5.8 mg, 0.026 mmol) in CD_2Cl_2 (0.5 mL). The solution became black and a black

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precipitate formed, which redissolved to give a yellow solution after 2 h. This solution was shown to contain a mixture of **1**, free 2,2′-bipyridine and **4a**. A similar reaction was carried out at low temperature and was monitored by ^{1}H NMR as it warmed to room temperature. At −10 °C, complex **2a** was almost completely consumed and the major product was **3a**. After 1 h at 20 °C, the major product was **4a**, but **1** and **3a** were also major products along with free 2,2′-bipyridine. After 1 day, complex **1** and free 2,2′-bipyridine were the major products, with only *ca.* 5% **4a**. Both [Pt(Spy)Me$_3$(bipy)] and [PtClMe$_3$(bipy)] were identified in *ca.* 2% yield from their characteristic ^{1}H NMR spectra. **3a**: δ(^{1}H) = 1.15 [s, 12H, ^2J(PtH) = 75 Hz, PtMe]; 6.22 [m, 2H, H$^{3'}$]; 6.45 [m, 2H, H$^{4'}$]; 6.62 [m, 2H, H$^{5'}$]; 7.38 [m, 2H, H$^{6'}$]; 7.39 [m, 4H, H^3]; 7.63 [m, 8H, H^{4,5}]; 8.04 [m, 4H, H^6]. **4a**: δ(^{1}H) = 1.56 [s, 6H, ^2J(PtH) = 70 Hz, PtMe]; 6.58 [m, 2H, H$^{4'}$]; 6.78 [m, 2H, H$^{3'}$]; 6.92 [m, 2H, H$^{5'}$]; 7.62 [m, 2H, H$^{6'}$]; 7.45 [m, 2H, H^3]; 7.83, 7.88 [m, each 2H, H^{4,5}]; 8.70 [m, 2H, H^6]. A similar reaction in CDCl$_3$ was complete in about 7 days to give **1**, free 2,2′-bipyridine and several unidentified minor products. Only complex **1** could be isolated in pure form from this reaction.

[{PtMe$_2$(Spy)(phen)}$_2$], 3b, and [PtMe$_2$(Spy)$_2$(phen)], 4b. To a solution of [PtMe$_2$(phen)], **2b** (10.7 mg, 0.026 mmol) in CD$_2$Cl$_2$ (0.5 mL) was added di-2-pyridyldisulfide (5.8 mg, 0.026 mmol) in CD$_2$Cl$_2$ (0.5 mL) at −78 °C and ^{1}H NMR spectra were recorded as the mixture warmed to room temperature. At 0 °C complex **2b** was almost completely consumed and the major product was **3b**. After several hours at 20 °C, the major product was **4b**, but **3b**, [Pt(Spy)Me$_3$(phen)] and [PtClMe$_3$(phen)] were also major products along with a minor amount of **1** and free 1,10-phenanthroline. After 1 day, the solution was allowed to evaporate slowly to give **4b** as a yellow crystalline solid. Anal. calcd for C$_{24}$H$_{22}$N$_4$PtS$_2$: C, 46.07; H, 3.54; N, 8.95. Found: C, 45.74; H, 3.32; N, 8.68%. NMR in CD$_2$Cl$_2$: **3b**: δ(^{1}H) = 1.40 [s, 12H, ^2J(PtH) = 75 Hz, PtMe]; 5.51 [m, 2H, H$^{3'}$]; 6.04, 6.09 [m, each 2H, H$^{4',5'}$]; 6.84 [m, 2H, H$^{6'}$]; 7.12 [m, 4H, H^3]; 7.40 [s, 4H, H^5]; 7.86 [m, 4H, H^4]; 8.05 [m, 4H, H^2]. **4b**: δ(^{1}H) = 1.72 [s, 6H, ^2J(PtH) = 70 Hz, PtMe]; 6.31 [m, 2H, H$^{5'}$]; 6.45 [m, 2H, H$^{3'}$]; 6.57 [m, 2H, H$^{4'}$]; 7.22 [m, 2H, H$^{6'}$]; 7.63 [m, 2H, H^5]; 7.65 [m, 2H, H^3]; 8.12 [m, 2H, H^4]; 8.62 [m, 2H, H^2]. [Pt(Spy)Me$_3$(phen)]: δ(^{1}H) = 0.41 [s, 3H, ^2J(PtH) = 62 Hz, PtMe *trans* S]; δ(^{1}H) = 1.46 [s, 6H, ^2J(PtH) = 70 Hz, PtMe]. [PtClMe$_3$(phen)]: δ(^{1}H) = 0.73 [s, 3H, ^2J(PtH) = 73 Hz, PtMe *trans* Cl]; 1.44 [s, 6H, ^2J(PtH) = 70 Hz, PtMe]. In a similar reaction in CDCl$_3$, very little reaction occurred in 1 h at 20 °C. For a typical ESI-MS experiment, a mixture of [PtMe$_2$(bipy)], **2a** (10 mg, 0.026 mmol) and pySSpy (5.8 mg, 0.026 mmol) were dissolved in CH$_2$Cl$_2$ (1 mL). Samples of the solution were injected into the ESI-MS at ten minute intervals over a period of 100 min.

[{PtMe$_2$(SPh)(phen)}$_2$], 5b, and [PtMe$_2$(SPh)$_2$(phen)], 6b. The complex [PtMe$_2$(phen)], **2b** (100 mg, 0.247 mmol) and PhSSPh (53.9 mg, 0.247 mmol) were dissolved in CH$_2$Cl$_2$ (4 mL) and stirred overnight. The mixture became black in color with formation of a black precipitate, which slowly redissolved to give an orange/yellow solution. After 1 day, the solution was allowed to evaporate slowly to give **6b** as a yellow crystalline solid, which was washed with pentane and dried under vacuum. Yield: 86.3 mg, 56%. Anal. calcd for C$_{26}$H$_{24}$N$_2$PtS$_2$: C, 50.07; H, 3.88; N, 4.49. Found: C, 49.80; H, 3.76; N, 4.33%. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 1.63 [s, 6H, ^2J(PtH) = 71 Hz]; 6.18 [m, 4H, SPh, H^o]; 6.19 [m, 4H, SPh, H^m]; 6.43 [m, 2H, SPh, H^p]; 7.70 [s, 2H, H^5]; 7.75 [m, 2H, H^3]; 8.28 [m, 2H, H^4]; 8.89 [m, 2H, ^3J(PtH) = 19 Hz, H^2]. The reaction was monitored by dissolving [PtMe$_2$(phen)], **2b** (10.7 mg, 0.026 mmol) and PhSSPh (3.0 mg, 0.014 mmol) in CD$_2$Cl$_2$ (1 mL) at −60 °C, then recording 1H NMR spectra as the solution was warmed to room temperature. At 0 °C, the product was very largely **5b**: NMR in CD$_2$Cl$_2$: δ(^{1}H) = 1.32 [s, 6H, ^2J(PtH) = 76 Hz, PtMe]; 5.35 [m, 2H, SPh, H^o]; 5.74 [m, 2H, SPh, H^m]; 6.18 [m, 1H, SPh, H^p]; 7.07 [m, 2H, H^3]; 7.34 [s, 2H, H^5]; 7.76 [m, 2H, H^4]; 7.99 [m, 2H, H^2]. An analytical sample was prepared as above, followed by precipitation with *n*-pentane at 0 °C. Anal. calcd for C$_{40}$H$_{38}$N$_4$Pt$_2$S$_2$: C, 46.69; H, 3.72; N, 5.44. Found: C, 47.04; H, 3.78; N, 5.09%.

[{PtMe$_2$(SPh)(bipy)}$_2$], 5a, and [PtMe$_2$(SPh)$_2$(bipy)], 6a Were Prepared Similarly from Complex 2a. Complex **5a**: Anal. calcd for C$_{36}$H$_{38}$N$_4$Pt$_2$S$_2$: C, 44.08; H, 3.90; N, 5.71. Found: C, 44.47; H, 3.80; N, 5.43%. NMR in CD$_2$Cl$_2$: δ(^{1}H) = 1.09 [s, 12H, ^2J(PtH) = 76 Hz, PtMe]; 5.87 [m, 4H, H^o]; 6.49 [m, 4H, H^m]; 6.50 [m, 2H, H^p]; 7.2−7.5 [m, 12H, H^{3,4,5}]; 8.01 [m, 4H, H^6]. Complex **6a**: Anal. calcd for C$_{24}$H$_{24}$N$_2$PtS$_2$: C, 48.07; H, 4.03; N, 4.67. Found: C, 47.81; H, 3.79; N, 4.52%.NMR in CD$_2$Cl$_2$: δ(^{1}H) = 1.50 [s, 6H, ^2J(PtH) = 71 Hz, PtMe]; 6.41 [m, 2H, SPh, H^o]; 6.50 [m, 2H, SPh, H^m]; 6.74 [m, 1H, SPh, H^p]; 7.43 [m, 2H, H^5]; 7.58 [s, 2H, H^3]; 7.81 [m, 2H, H^4]; 8.61 [m, 2H, ^3J(PtH) = 19 Hz, H^6].

Structure Determinations. Data were collected using a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997−2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski and Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. 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. The crystal data and refinement parameters are listed in Table 1.

DFT Calculations. Calculations were made using the Amsterdam Density Functional program based on the Becke-Perdew functional, with first-order scalar relativistic corrections.[30] Transition state structures were located using a linear transit scan.[17b]

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Supporting Information Available: X-ray data for the complexes **1**, **4b**, **6a**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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