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Associative and Dissociative Mechanisms in the Formation of Phthalazine Bridged Organodiplatinum(II) Complexes

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The reaction of phthalazine with the binuclear organoplatinum complexes $[Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtR_2]$, R = Me, Ph, 4-tolyl or $R_2 = (CH_2)_4$, dppm = *bis*(diphenylphosphino)methane, gives the corresponding complexes $[Me_2Pt(\mu\text{-phthalazine})(\mu\text{-dppm})PtR_2]$ by displacement of the bridging dimethylsulfide ligand. The structures of $[Me_2Pt(\mu\text{-}SMe_2)(\mu\text{-dppm})PtMe_2]$ and $[Me_2Pt(\mu\text{-phthalazine})(\mu\text{-dppm})PtMe_2]$ have been determined. Kinetic studies show that the reactions occur mostly by a second order reaction when R = Me or $R_2 = (CH_2)_4$ but entirely by a first order reaction when R = Ph or 4-tolyl. Evidence is presented that the reactions when R = Me or $R_2 = (CH_2)_4$ can occur by either associative or dissociative mechanisms but that the reactions when R = Ph or 4-tolyl occur only by an unusual dissociative mechanism involving formation of an intermediate with a donor−acceptor Pt−Pt bond.

Introduction

Ligand substitution reactions at square planar platinum(II) centers have been thoroughly studied, especially in the contexts of the use of square planar complexes in catalysis and the use of platinum(II) complexes in medicine.[1−3] Classical coordination complexes containing platinum(II) almost always undergo associative ligand substitution, but electron-rich organometallic complexes of the type *cis*-$[PtR_2L_2]$, with R = alkyl or aryl and L = neutral donor ligand, often undergo dissociative ligand substitution.[4] The ligand dissociation step is facilitated by the strong *trans*-influence of the alkyl or aryl group, which weakens the M−L bonds, while the alternative associative mechanism is less favored because the electron-rich platinum center is resistant to nucleophilic attack.[4,5] A typical dissociative reaction mechanism is shown in Scheme 1, involving rate-determining dissociation of a dimethylsulfide ligand from *cis*-$[PtPh_2(SMe_2)_2]$, to give a reactive 14-electron intermediate *cis*-$[PtPh_2(SMe_2)]$, which rapidly adds a new ligand.[4] With chelate ligands such as 2,2′-bipyridine (Scheme 1), the subsequent ring closing step is also fast.[4]

Not all electron-rich platinum(II) complexes undergo dissociative ligand exchange, and the mechanism may depend on the stereochemistry. For example, phosphine ligand exchange is dissociative in *cis*-$[Pt(SiMePh_2)_2(PMe_2Ph)_2]$ but associative in *trans*-$[Pt(SnPh_3)_2(PPh_3)_2]$.[6] Monoalkylplatinum(II) complexes usually undergo associative ligand exchange.[7] In most dissociative reactions, the 14-electron platinum(II) complex intermediates are too shortlived to be detected directly, but a few 14-electron complexes are sufficiently stable to be isolated. Most such compounds have T-shaped stereochemistry, notably the cationic boryl complexes such as $[Pt\{B(NMe_2)_2\}(PCy_3)_2]^+$, but one Y-shaped derivative, $[Pt(SiMe_2Ph)_2(IPr)]$ where IPr = *bis*(2,6-diisopropylphenyl)imidazo-2-ylidene, is also known.[8] The coordinative unsaturation of the T-shaped 14-electron complexes is usually compensated by the presence of an agostic interaction with a ligand CH bond.[8] The 14-electron complexes

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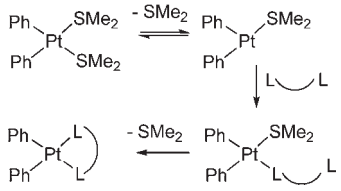
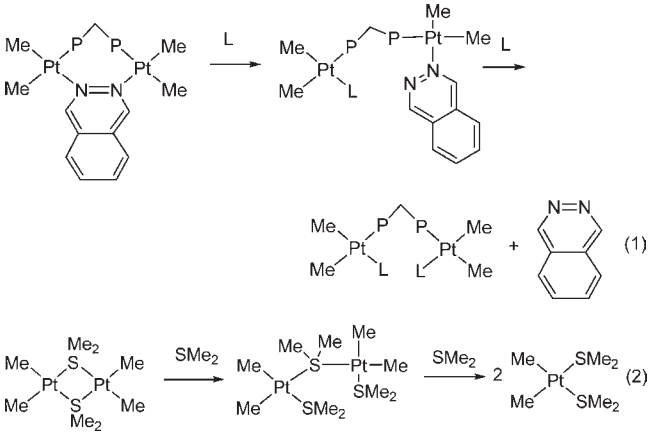
Scheme 1. LL = 2,2′-bipyridine



have been implicated not only in ligand exchange reactions but also in alkyl exchange, insertion/β-elimination, isomerization, and oxidative addition/reductive elimination reactions, at the heart of important catalytic reactions such as polymerization and C−H bond activation, so there is much interest in their formation and reactivity.[4−15]

There have been very few mechanistic studies of ligand substitution in binuclear organoplatinum(II) complexes, although these compounds are now often used as reagents.[16] The two previous studies most relevant to the present work are on the mechanisms of the reactions shown in eqs 1 and 2. The displacement of phthalazine by 2 equiv of triphenylphosphine in eq 1 [PP = bis(diphenylphosphino)methane, dppm; L = PPh_3] and the bridge splitting reaction by dimethylsulfide in eq 2 are both thought to occur by associative mechanisms, with the first step being rate determining in each case.[17,18] These results are somewhat surprising, especially because the ligand exchange in the platinum complexes *cis*-[$PtMe_2(Me_2S{=}O)_2$] and *cis*-[$PtPh_2(SMe_2)_2$] is dissociative,[4,5] and so there is a question whether the binuclear complexes can undergo dissociative ligand substitution. This paper shows that they can, and that there is a dramatic difference between the reactivities at dimethyl- and diphenylplatinum(II) centers.



Results and Discussion

The reactions studied in this work are shown in Scheme 2. The complexes **1a**− **1d** and **2a**, **2b** have been reported previously,

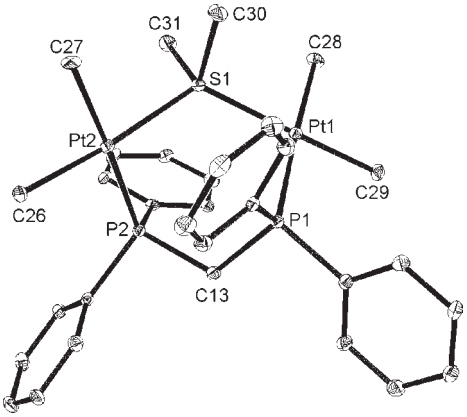
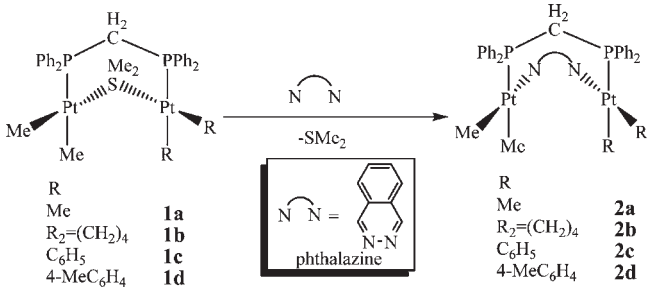


Figure 1. View of the structure of complex **1a**. Selected bond parameters: Pt(1)−C(29) 2.070(8); Pt(1)−C(28) 2.104(8); Pt(1)−P(1) 2.272(2); Pt(1)−S(1) 2.371(2); S(1)−Pt(2) 2.384(2); Pt(2)−C(26) 2.072(8); Pt(2)−C(27) 2.102(8); Pt(2)−P(2) 2.286(2) Å; P(1)−Pt(1)−S(1) 91.28(8); P(2)−Pt(2)−S(1) 91.28(7); Pt(1)−S(1)−Pt(2) 122.25(9)°.

Scheme 2



and the new complexes **2c** and **2d** were prepared according to Scheme 2.[19−21] Qualitatively, the rates of the reactions with phthalazine (Scheme 2) followed the sequence **1a**, **1b** > **1c**, **1d**, indicating that the introduction of diarylplatinum centers in place of dialkylplatinum centers reduces the rate of reaction. The reaction was successful if there was at least one dialkylplatinum group present [$PtMe_2$ in **1a**, **1c** **1d**, or $PtMe_2$ and platinacyclopentane in **1b**] but no reaction occurred between [$Pt_2Ph_4(\mu\text{-}SMe_2)(\mu\text{-dppm})$][22] and phthalazine, indicating that the introduction of two diphenylplatinum centers is strongly deactivating.

Characterization of the Complexes. Further spectroscopic and structural characterization of the binuclear platinum(II) complexes **1** and **2** was carried out to give insight into reactivity trends.[19−21] The structure of complex **1a** is shown in Figure 1. Each platinum center has square planar stereochemistry and the 6-membered Pt_2SP_2C ring adopts a twist-boat conformation. The only indicator of possible ring strain

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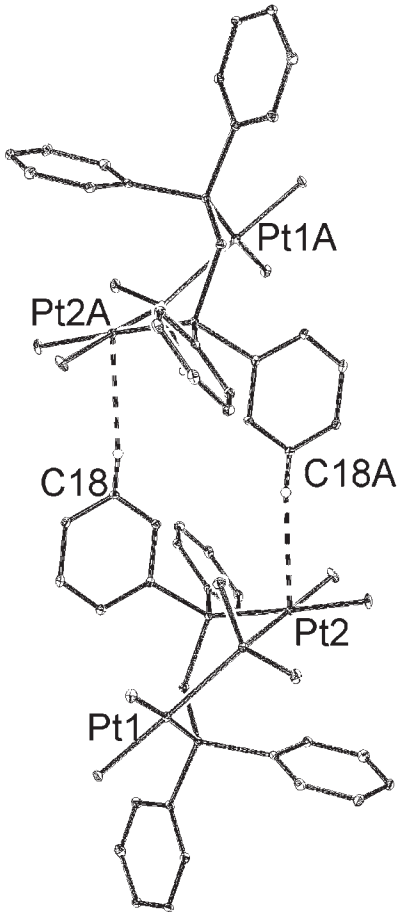

Figure 2. Formation of loosely held dimers of complex **1a**, emphasizing the accessibility of the open face of the Pt(2) center.

is the opening of the angle at the bridging dimethylsulfide, Pt(1)S(1)Pt(2) = 122.25(9)°, which can be compared to an average value of 100.3° in $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, 100.45° in $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$, and 116.3° in $[Pt_3Ph_6(\mu\text{-}SMe_2)_3]$.[23] This angle distortion at sulfur allows the incorporation of the larger bridging ligand dppm, and the associated ring strain will enhance the reactivity to ligand substitution.

In the conformation adopted by **1a** in the solid state, each platinum(II) center has one face protected by a phenyl group of the dppm ligand and one open face. The complexes form loose dimers in the crystal through formation of pairwise CH···Pt interactions at the open face of the Pt(2) center, as shown in Figure 2. The significance of these interactions with Pt(2)···H(18A) about 2.8 Å is probably very small, but it does give a view of the direction in which a ligand is likely to approach the open face of a square planar platinum(II) center in **1a**.

The structure of the phthalazine bridged complex **2a** is shown in Figure 3. Each platinum(II) center has square planar stereochemistry, and there are no large distortions of the bond angles from 90°. The 7-membered $Pt_2N_2P_2C$ ring can be considered to adopt an extended twist-boat conformation, in which the dimethylplatinum centers are folded above one another in such a way that the non-bonding separation Pt(1)···Pt(2) = 3.42 Å is significantly shorter than in the 6-membered ring of complex **1a** with Pt(1)···Pt(2) = 4.16 Å. In this conformation an incoming ligand could clearly

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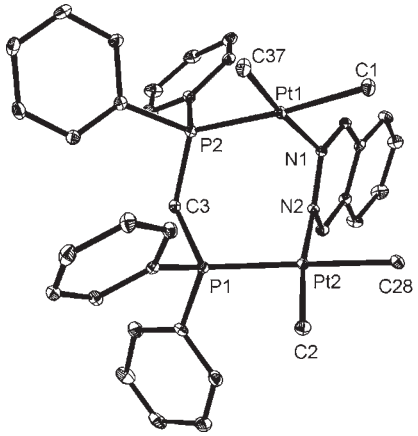

Figure 3. View of the structure of complex **2a**. Selected bond parameters: Pt(1)−C(1) 2.096(5); Pt(1)−C(37) 2.051(5); Pt(1)−P(2) 2.291(1); Pt(1)−N(1) 2.130(4); Pt(2)−N(2) 2.115(4); Pt(2)−C(2) 2.053(4); Pt(2)−C(28) 2.106(4); Pt(2)−P(1) 2.268(1) Å; P(2)−Pt(1)−N(1) 90.15(10); P(1)−Pt(2)−N(2) 93.1(1); Pt(1)−N(1)−N(2) 116.1(3); Pt(2)−N(2)−N(1) 116.8(3)°.

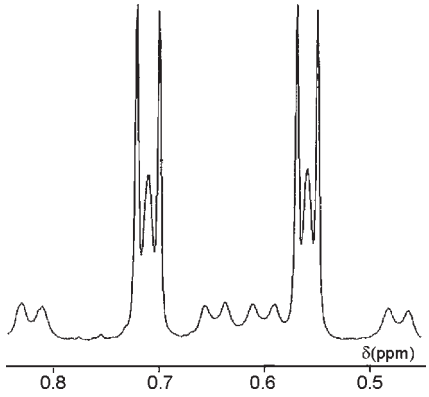

Figure 4. ^{1}H NMR spectrum (Pt-Me region) of *cis*,*cis*-$[Me_2Pt(\mu\text{-}NN)(\mu\text{-}dppm)PtMe_2]$, **2a**, in CD_2Cl_2 at room temperature.

approach a platinum center only from the outside face (or the ligand leave a 5-coordinate intermediate from the outside face).

The ^{1}H NMR spectrum in CD_2Cl_2 solution of complex **2a** in the methylplatinum region is shown in Figure 4.[19] There are two equal intensity resonances for the methylplatinum groups *trans* to phosphorus [δ = 0.56, ^2J(PtH) = 70 Hz, ^3J(PH) = 8 Hz] and sulfur [δ = 0.71, ^2J(PtH) = 88 Hz, ^3J(PH) = 8 Hz] respectively. The unusual appearance of the main resonances, an apparent doublet with a broad central peak, arises because the ^{1}H and ^{31}P atoms in each $H_3CPtPCPPtCH_3$ unit comprise a second order $A_3XX'A'_3$ spin system with an intermediate value of the coupling ^2J(PP) = 51 Hz.[24] The doublet splitting is given by the sum of the coupling constants ^3J(PH) + ^5J(PH) but, because ^5J(PH) is close to zero, it is equal to ^3J(PH).

The ^{31}P NMR spectrum in CD_2Cl_2 solution of complex **1a** is shown in Figure 5a. There is a single resonance [δ = 17.1, ^1J(PtP) = 1910 Hz, ^3J(PtP) = 33 Hz, ^2J(PP) = 51 Hz]. In the isotopomer containing a single ^{195}Pt atom, the ^{31}P and ^{195}Pt atoms give an AA′X spin system, with inner and outer double satellites around the center peak. However, in

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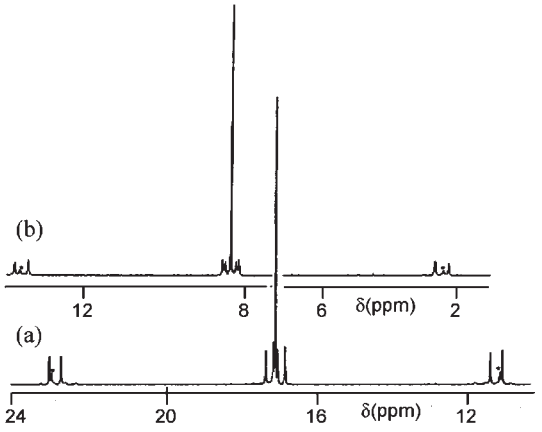

Figure 5. ^{31}P NMR spectra of (a) [$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$], **1a**, and (b) *cis*,*cis*-[$Me_2Pt(\mu$-NN)$(\mu$-dppm)$PtMe_2$], **2a**, in CD_2Cl_2.

the isotopomer containing two ^{195}Pt atoms, the ^{31}P and ^{195}Pt atoms give a second order AA′XX′ spin system, with outer peaks separated by ^1J(PtP) + ^3J(PtP) = 1910 + 33 = 1943 Hz. These low intensity peaks are indicated by asterisks in Figure 5a, and their position shows that ^1J(PtP) and ^3J(PtP) have the same sign (both positive). The magnitudes of the long-range coupling constants ^3J(PtP) and ^2J(PP) are in the range expected for complexes with no metal−metal bonding.[25] A similar analysis can be applied to the ^{31}P NMR spectrum of complex **2a**, which is shown in Figure 5b [δ = 8.4, ^1J(PtP) = 1928 Hz, ^3J(PtP) = 14 Hz, ^2J(PP) = 62 Hz]. These data indicate that the structures established crystallographically for complexes **1a** and **2a** are maintained in solution, and that potential isomers with metal−metal bonding are not present.

Kinetics of Ligand Substitution. The dimethylsulfide bridged complexes **1** are colorless or pale yellow, whereas the phthalazine bridged complexes **2** are intensely yellow or orange in solution, so the formation of the complexes **2** (Scheme 2) could be followed conveniently by UV−visible spectroscopy. A series of scans from the reaction of complex **1a** with phthalazine to form **2a** is shown in Figure 6. The kinetics were studied at varying temperatures in the nonpolar solvent benzene and more polar solvent acetone. The reactions were carried out under pseudo-first order conditions by using excess phthalazine reagent. There was no evidence in any case studied for the formation of long-lived intermediates, and so it is concluded that the substitution of the first Pt−S bond is rate-determining and that the cleavage of the second Pt−S bond is then rapid.[17,18] Independent study by NMR also showed that no intermediates were formed in detectable amounts. Preliminary reactions with phthalazine were also studied in the presence of excess free dimethylsulfide but, in these binuclear complexes, new unidentified products were also formed so the kinetics were not easily interpreted. Under the conditions described below the reactions occurred cleanly and simply.

Figure 7 shows a plot of the pseudo-first order rate constants for the reaction of complex **1a** with phthalazine at 30 °C in benzene and in acetone. The plots show a linear dependence of the rate constants on concentration of

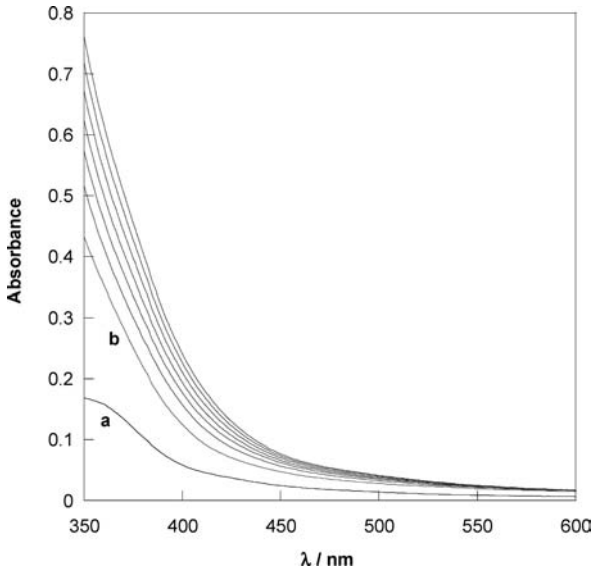

Figure 6. Changes in the UV−visible spectrum during the reaction of complex of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$], **1a** (3×10^{-4} M) and phthalazine (0.1 M) in acetone at T = 20 °C: (a) initial spectrum (before adding phthalazine) and (b) spectrum at t = 30 s; successive spectra were recorded at intervals of 2 min.

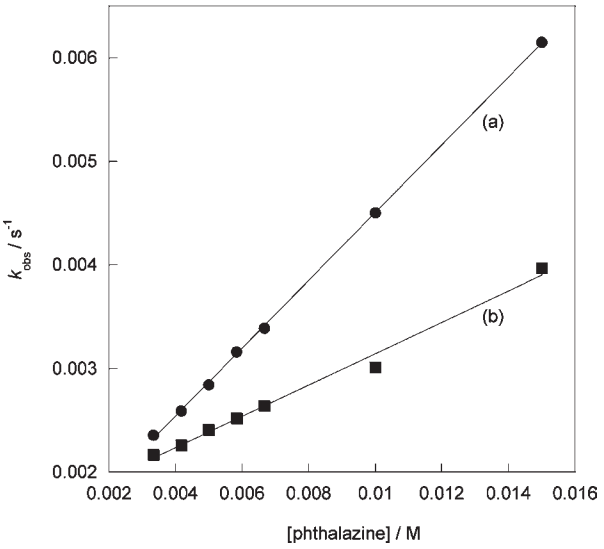

Figure 7. Plots of first-order rate constants (k_{obs}/s^{-1}) vs [phthalazine] for the reaction of complex **1a** with phthalazine at T = 30 °C in (a) benzene and (b) in acetone.

phthalazine (NN) but the lines do not pass through the origin, indicating that the reactions have both a second order and a first order component, with k(obs) = k_1 + k_2[NN]. The resulting rate constants are listed in Table 1. The second order rate constants in benzene are about double the values of the rate constants in acetone. The dependence of the rate constants on temperature is illustrated in Figure 8. The resulting activation parameters are listed in Table 1. The entropies of activation for the k_2 component of the reaction in both solvents benzene and acetone are significantly negative. This is a strong indicator of an associative mechanism of reaction for the k_2 component of the reaction.[1,17,18] The interpretation of the mechanism associated with the first order component is less obvious, because it could result from either a dissociative mechanism or an associative mechanism

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Table 1. Rate Constants[a] and Activation Parameters[b] for Reaction of the Complex *cis,cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtMe_2$], **1a**, with NN in Benzene or Acetone

Reaction in Benzene							
	rate constants at different temperatures						
	20 °C	25 °C	30 °C	35 °C	50 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
$10^2 k_2$ /L mol^{-1} s^{-1}	10.8	18.9	32.4	47.7	179.0	70.4 ± 1.7	−23 ± 6
$10^2 k_1$/s^{-1}	0.04	0.07	0.12	0.27	1.80	98.9 ± 4.1	27 ± 13
Reaction in Acetone							
	rate constants at different temperatures						
	15 °C	20 °C	25 °C	30 °C	35 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
$10^2 k_2$ /L mol^{-1} s^{-1}	4.2	6.6	9.2	15.1	17.7	29.0	46.9 ± 3.5	−107 ± 12
$10^2 k_1$/s^{-1}	0.02	0.04	0.09	0.16	0.40	1.42	106.8 ± 2.6	55 ± 9

[a] Estimated errors in rate constants are ±5%. [b] Calculated from temperature dependence of rate constants using the Eyring equation.

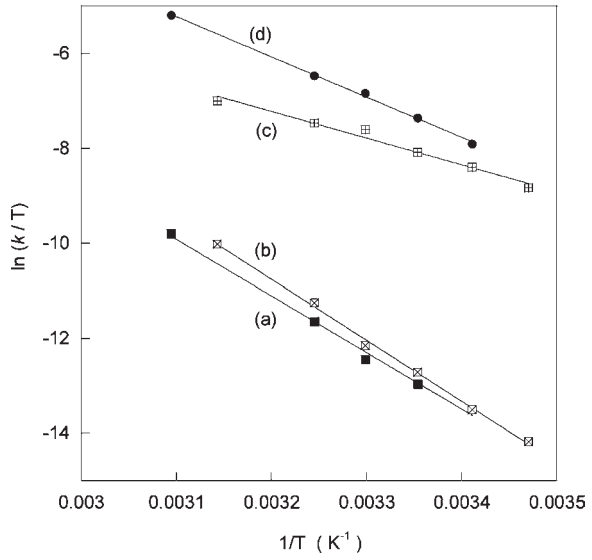


Figure 8. Eyring plots for the reaction of complex **1a** with phthalazine in benzene [(a) k_1 path, (d) k_2 path] and acetone [(b) k_1 path, (c) k_2 path].

involving solvent.[1,4,5,17,18] The data in Table 1 show that there is only a small difference between the values of k_1 in benzene or acetone at a given temperature and that the entropy of activation is positive in both cases. A solvent assisted associative mechanism would be expected to give a significantly higher value of k_1 in acetone than in benzene and perhaps a negative value of the entropy of activation (note that in a binuclear complex, cleavage of one Pt−S bond does not give two independent particles so the entropy of activation for a dissociative reaction should be less positive than in a comparable mononuclear complex).[1,4,5,17,18] Therefore, it is concluded that the k_1 term arises from a dissociative mechanism.

The kinetic data for reaction of phthalazine with the platinacyclopentane complex **1b** to give **2b** (Scheme 2) followed the same kinetics as for **1a**, and the associated rate constants are given in Table 2. The second order rate constants k_2 are smaller for **1b** than for **1a**, most likely because **1b** is more electron rich and so less susceptible to nucleophilic attack. In similar platinum(II) complexes containing either the $Pt(CH_2)_4$ or the $PtMe_2$ group, the platinacyclopentane is more reactive in oxidative addition because it is more electron rich and so oxidized more easily.[26] The values of k_1 are also slightly lower for **1b** than for **1a** (Tables 1 and 2).

The kinetics of the reaction of phthalazine with **1c** and **1d** are different from **1a** and **1b**. With complexes **1c** and **1d**, the rates are slower and the pseudo-first order rate constants are independent of the concentration of phthalazine, as shown by the plots in Figure 9 for the reactions of **1d** in benzene at 30 °C and in acetone at 40 °C (compare Figure 7). At a given temperature, the rates are essentially the same in benzene or acetone. This lack of dependence of the rate on the nucleophilicity of the solvent suggests that a dissociative mechanism operates.[1,4,5]

The first order rate constants and activation parameters for the reactions of **1c** and **1d** are listed in Tables 3 and 4. The observation of slightly faster rates for **1d** over **1c** is consistent with the expected greater σ-donor ability of 4-tolyl over phenyl, which should stabilize a dissociative intermediate but destabilize an associative one. Similarly, the values of k_1 are lower for **1c** (Table 3) than for **1a**, Table 1, consistent with the lower σ-donor ability of phenyl compared to methyl. A puzzling result is that the entropies of activation for reactions of both **1c** and **1d** are large and negative (Tables 3, 4), in contrast to the observation of positive values of the entropy of activation associated with the first order component of the reactions of **1a** and **1b** (Tables 1, 2).

Conclusions

The proposed associative and dissociative mechanisms of reaction of phthalazine with complex **1a** are shown in Scheme 3. The associative mechanism dominates in this case. The primary step in the associative mechanism is ligand addition to give intermediate ***A***, while in the dissociative mechanism it is cleavage of a Pt−S bond to give intermediate ***B***. Square pyramidal intermediate ***A*** can rearrange to intermediate ***C*** by displacement of a Pt−S bond, via a trigonal bipyramidal intermediate,[1] while the same intermediate ***C*** can be formed from ***B*** by addition of phthalazine. Finally intermediate ***C*** undergoes displacement of the SMe_2 ligand to give the product **2a**. The kinetics give no information on the mechanism of this fast step, but it is likely to involve an intramolecular associative ligand substitution through nucleophilic attack by the free nitrogen atom of intermediate ***C***. The reaction of phthalazine with complex **1b** is

(26) Rashidi, M.; Esmaeilberg, A. R.; Shahabadi, N.; Tangestaninejad, S.; Puddephatt, R. J. *J. Organomet. Chem.* **1998**, *568*, 53.

Table 2. Rate Constants[a] and Activation Parameters[b] for Reaction of the Complex *cis,cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$Pt(CH_2)_4$], **1b**, with NN in Benzene or Acetone

Reaction in Benzene

	rate constants at different temperatures						
	20 °C	25 °C	30 °C	35 °C	50 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_2 /L mol^{-1} s^{-1}	1.9	3.4	6.0	8.2	29.0	67.8 ± 3.0	−46 ± 10
10^2k_1/s^{-1}	0.03	0.05	0.10	0.21	1.23	96.9 ± 2.8	18 ± 9

Reaction in Acetone

	rate constants at different temperatures							
	15 °C	20 °C	25 °C	30 °C	35 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_2 /L mol^{-1} s^{-1}	1.0	1.7	3.7	5.0	7.7	21.0	73.7 ± 3.5	−27 ± 12
10^2k_1/ s^{-1}	0.01	0.03	0.05	0.12	0.25	0.65	103.2 ± 5.8	39 ± 19

[a] Estimated errors in rate constants are ±5%. [b] Calculated from temperature dependence of rate constants using the Eyring equation.

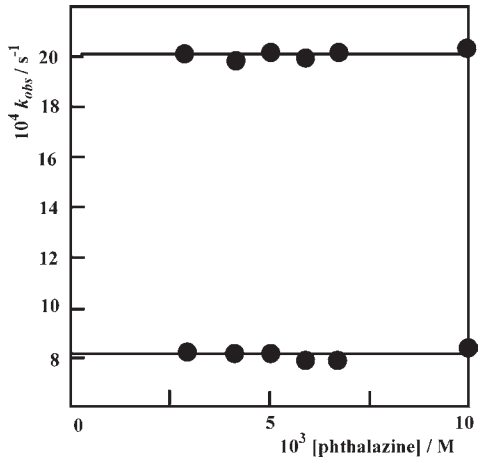


Figure 9. Plots of first-order rate constants (k_{obs}) for the reaction of complex **1d** with phthalazine (a) at T = 30 °C (in benzene) and (b) T = 40 °C (in acetone).

proposed to occur similarly. In this case the initial associative or dissociative step could occur at either the $PtMe_2$ or the $Pt(CH_2)_4$ center and, because no intermediates are directly detected, there is no direct information on which is preferred. However, because the overall rate constants k_1 and k_2 are similar for reactions of **1a** and **1b**, it is likely that the discrimination is small.

Potential associative mechanisms of reaction of phthalazine with the unsymmetrical complex **1c** (PP = dppm, NN = phthalazine) are shown in Scheme 4. The kinetic results show clearly that these mechanisms are not followed, but it is important to consider reasons for this. Primary attack could occur at the dimethylplatinum or diphenylplatinum center to give intermediate ***D*** or ***E*** respectively. Steric effects of the phenylplatinum groups will prevent formation of ***E*** (Scheme 4) but should not interfere with formation of ***D***. The potential route from ***D*** to **2c** would involve formation of ***F*** followed by displacement of dimethylsulfide from the diphenylplatinum center (Scheme 4), and it is likely that the final associative step is blocked by steric effects of the diphenylplatinum unit.

Potential dissociative mechanisms of reaction of phthalazine with complex **1c** (PP = dppm, NN = phthalazine) are shown in Scheme 5. By analogy with the dissociative mechanism proposed in Scheme 3 for complex **1a**, complex **1c** might react through the sequence **1c**, ***G***, ***F***, **2c** (by initial cleavage of the Me_2Pt-S bond) or **1c**, ***H***, ***I***, **2c** (by initial cleavage of the Ph_2Pt-S bond). Now, by analogy with Scheme 4, the reaction of ***F*** to give **2c** by displacement of dimethylsulfide ligand is expected to be blocked by steric effects of the diphenylplatinum group, so the sequence **1c**, ***H***, ***I***, **2c** (Scheme 5) must be considered more probable. The only problem with this mechanism is that it is expected to give a positive value of the entropy of activation, associated with opening of the ring structure of **1c**, as was observed for the dissociative component of the reaction with **1a** (Scheme 3, Table 1), whereas a large negative value is observed (Table 3). An alternative mechanism might involve cleavage of a Pt−S bond in **1c** accompanied by formation of a donor−acceptor metal−metal bond to give an intermediate ***J*** or ***L*** (Scheme 5). These could then proceed through either sequence **1c**, ***J***, ***K***, **2c** or **1c**, ***L***, ***M***, **2c** to give the product **2c**, as shown in Scheme 5. Intermediate ***J*** can be ruled out because steric effects prevent formation of a 5-coordinate diphenylplatinum center, but the sequence **1c**, ***L***, ***M***, **2c** appears consistent with all of the kinetic data.

There are several precedents for formation of donor−acceptor PtPt bonds, notably in the structurally characterized complex cation $[Pt_2Me_3(\mu\text{-dppm})_2]^+$, ***N***, but also in the neutral complex $[Me_2(Me_2S)Pt(\mu\text{-}NC_5H_4PPh_2)PtMe(O_2CCF_3)]$, ***O***, which is easily formed from its isomer with a bridging dimethylsulfide group (Chart 1).[27] The analogous complex ***L*** (Scheme 5) has the electron-rich dimethylplatinum center as donor and the less electron-rich diphenylplatinum center as acceptor, and so should be favored by electronic as well as steric factors compared to its isomer ***J***. Of course, the formation of the donor−acceptor bond reduces the electron density at the dimethylplatinum center, in particular by donation from the $5d_{z^2}$ orbital, and this should increase the reactivity toward nucleophilic attack by phthalazine. Hence the reaction of intermediate ***L*** to give ***M*** is expected to occur easily. The conversion of ***M*** to **2c** just requires replacement of the metal−metal bond by the free nitrogen donor. The formation of a more rigid 5-membered ring in ***L*** from the more flexible 6-membered ring in **1c**, with associated loss of degrees of rotational freedom from several substituents as the size of the molecule is reduced and steric interactions correspondingly increase, may then be responsible

(27) (a) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500. (b) Rashidi, M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 2612. (c) Sterenberg, B. T.; McDonald, R.; Cowie, M. *Organometallics* **1997**, *16*, 2297.

Table 3. Rate Constants[a] and Activation Parameters[b] for Reaction of the Complex *cis,cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$PtPh_2$], **1c**, with NN in Benzene or Acetone

Reaction in Benzene							
	rate constants at different temperatures						
	20 °C	30 °C	35 °C	40 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_1/ s^{-1}	0.04	0.08	0.12	0.13	0.16	40.9 ± 4.7	−170 ± 15
Reaction in Acetone							
	rate constants at different temperatures						
	20 °C	30 °C	35 °C	40 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_1/ s^{-1}	0.04	0.08	0.12	0.14	0.16	41.8 ± 4.6	−167 ± 15

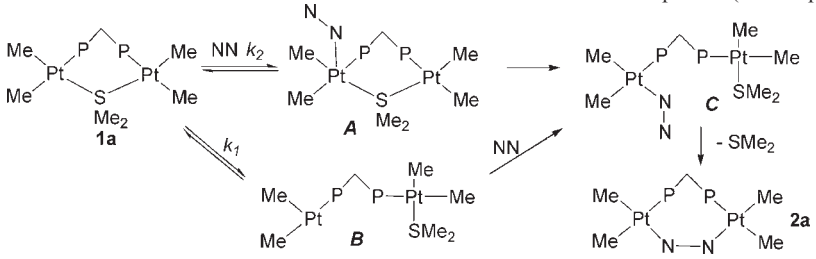
[a] Estimated errors in rate constants are ±5%. [b] Calculated from temperature dependence of rate constants using the Eyring equation.

Table 4. Rate Constants[a] and Activation Parameters[b] for Reaction of the Complex *cis,cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)$Pt(p$-tolyl$)_2$], **1d**, with NN in Benzene or Acetone

Reaction in Benzene							
	rate constants at different temperatures						
	20 °C	30 °C	35 °C	40 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_1/ s^{-1}	0.05	0.08	0.09	0.18	0.21	43.7 ± 7.3	−160 ± 24
Reaction in Acetone							
	rate constants at different temperatures						
	20 °C	30 °C	35 °C	40 °C	45 °C	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
10^2k_1/ s^{-1}	0.05	0.09	0.10	0.20	0.26	49.2 ± 7.0	−141 ± 23

[a] Estimated errors in rate constants are ±5%. [b] Calculated from temperature dependence of rate constants using the Eyring equation.

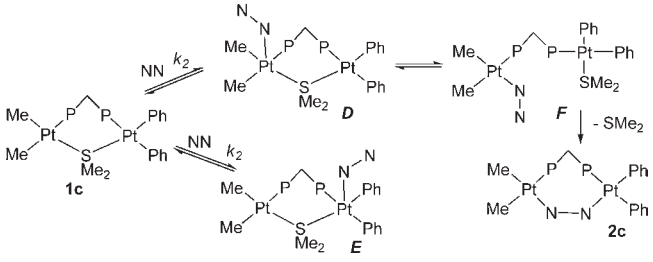
Scheme 3. Proposed Associative and Dissociative Mechanisms of Reaction of Phthalazine with Complex **1a** (PP = dppm, NN = phthalazine)



for the large negative values of the entropy of activation (Tables 3 and 4). We cannot rule out the formation of a similar intermediate ***P*** (Chart 1) in the reaction of **1a** but the observation of a positive entropy of activation argues against it. Complex ***L*** (Scheme 5) is also favored over ***P*** by the Thorpe−Ingold effect of the bulkier phenyl groups, favoring small ring formation.

Overall, three different mechanisms are proposed to account for the kinetic data. A relatively fast associative mechanism is observed for reaction of complexes **1a** and **1b**, and accounts for the major part of the reaction (Scheme 3). A minor part of the reaction, characterized by a modestly positive entropy of activation, is proposed to occur by a simple dissociative mechanism (Scheme 3). In the reactions of complexes **1c** and **1d**, the second order reaction is completely blocked and only a first order reaction is observed. The reaction is characterized by a significantly negative entropy of activation, and it is proposed that the dissociation of a Pt−S bond is accompanied by formation of a metal−metal bond in the intermediate ***L*** (Scheme 5). This intermediate reacts rapidly with phthalazine to give the corresponding product **2c** (Scheme 5) or **2d**. This appears to be the first evidence from kinetic studies of a dissociative mechanism of ligand substitution in a binuclear platinum(II) complex.[1,4,5,17,18]

Scheme 4. Potential Associative Mechanisms of Reaction of Phthalazine with Complex **1c** to Give **2c** (PP = dppm, NN = phthalazine)



Scheme 5. Potential Dissociative Mechanisms of Reaction of Phthalazine with Complex **1c** to Give **2c** (PP = dppm, NN = phthalazine)

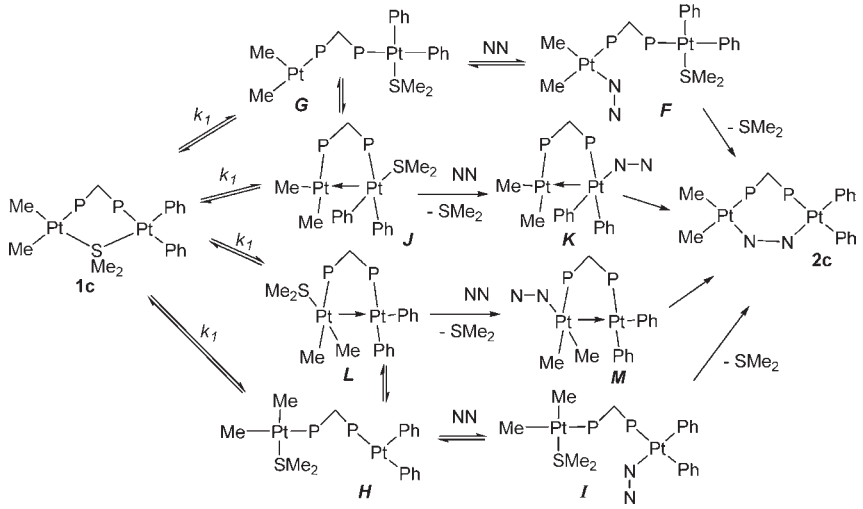


Chart 1. P = PPh_2, X = CF_3CO_2

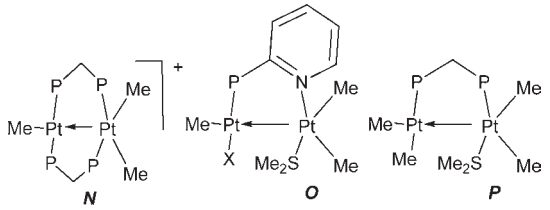


Table 5. Crystal Data and Structure Refinement for Complexes **1a**·CH_2Cl_2 and **2a**

	1a·CH_2Cl_2	**2a**
formula	$C_{32}H_{42}Cl_2P_2Pt_2S$	$C_{37}H_{40}N_2P_2Pt_2$
fw	981.74	964.85
T/K	150(2)	150(2)
λ/Å	0.71073	0.71073
cryst. syst.	triclinic	orthorhombic
space gp.	$P\bar{1}$	$P2_12_12_1$
cell dimens.		
a/Å	9.583(2)	11.2916(5)
b/Å	13.409(3)	16.2609(8)
c/Å	14.552(3)	18.6217(9)
α	108.76(3)	90
β	93.82(3)	90
γ	108.33(3)	90
V/Å^3	1651.2(6)	3419.2(3)
Z, d(calc)/Mg m^{-3}	2, 1.975	4, 1.874
μ/ mm^{-1}	8.806	8.296
data/restr./param.	7626/0/354	6931/0/392
R_1 [$I > 2\sigma(I)$]	0.0392	0.0222
wR_2 [all data]	0.1437	0.0378

Experimental Section

The ^{1}H NMR spectra were recorded by using either a Bruker Avance DRX 500 spectrometer (in acetone-d^6), or a Varian Mercury 400 spectrometer (in CD_2Cl_2), with TMS as reference. The ^{31}P NMR spectra were recorded either on a Bruker Avance DRX 500 spectrometer (in acetone-d^6 or $CDCl_3$) or on a Varian Mercury 400 spectrometer (in CD_2Cl_2), with 85% H_3PO_4 as reference, and ^{195}Pt NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (in acetone-d^6 or $CDCl_3$), with aqueous Na_2PtCl_4 as reference. Kinetic studies were carried out by using a Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. The microanalyses were performed using a Termofinnigan Eager 300 CHN-O elemental analyzer. The complexes *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)(\mu$-dppm)PtR_2], **1a**−**1d**,[19] *cis*,*cis*- [$Me_2Pt(\mu$-NN)(μ-dppm)$PtMe_2$], **2a**,[20] and [$Me_2Pt(\mu$-NN)(μ-dppm)Pt{$(CH_2)_4$}], **2b**,[21] were prepared by the literature methods.

[$Me_2Pt(\mu$-NN)(μ-dppm)$PtPh_2$], 2c. To a solution of [Me_2Pt-(μ-SMe_2)(μ-dppm)$PtPh_2$], **1c**, (110 mg, 0.10 mmol) in acetone (20 mL) was added phthalazine, NN, (13 mg, 0.10 mmol) at room temperature. The mixture was stirred for 3 h, the solvent was then removed under reduced pressure, and the residue was triturated with ether (3 mL) and *n*-pentane (3 mL) to give the product as an orange solid, which was separated and dried under vacuum. Yield: 65 mg, 60%. mp: 150 °C (dec). Anal. Calcd. for $C_{45}H_{43}N_2P_2Pt_2$: C, 51.8; H, 4.0; N, 2.5. Found: C, 52.1; H, 4.2; N, 2.6. NMR data in acetone-d^6: δ(^{1}H) = 0.45 [d, ^3J(PH) = 6.8 Hz, ^2J(PtH) = 67.4 Hz, Me *trans* to phosphorus, 3H], 0.52 [d, ^3J(PH) = 6.3 Hz, ^2J(PtH) = 85.5 Hz, Me *trans* to nitrogen, 3H], 3.60 [m, CH_2 group of dppm, 2H], CH groups of phthalazine adjacent to the coordinating N atoms: 9.1 [s, ^3J(PtH) = not measured, 1H] and 9.7 [s, ^3J(PtH) = not measured, 1H]; δ(^{31}P) = 0.6 [d, ^2J(PP) = 65 Hz, ^1J(PtP) = 1728 Hz, P *trans* to Ph ligand], δ = 11.5 [d, ^2J(PP) = 65 Hz, ^1J(PtP) = 1928 Hz, P *trans* to Me ligand]; δ(^{195}Pt) = −3150 [br. d, ^1J(PtP) = 1730 Hz, Pt connected to Ph ligands], −3230 [br. d, ^1J(PtP) = 1925 Hz, Pt connected to Me ligands].

The complex [$Me_2Pt(\mu$-NN)(μ-dppm)$Pt(p$-$MeC_6H_4)_2$], **2d**, was prepared similarly, using appropriate starting materials: Yield, 70%. mp: 148 °C (dec). Anal. Calcd. for $C_{49}H_{48}N_2P_2Pt_2$: C, 52.6; H, 4.3; N, 2.5. Found: C, 52.8; H, 4.3; N, 2.5. NMR data in acetone-d^6: δ(^{1}H) = 0.60 [d, ^3J(PH) = 8.1 Hz, ^2J(PtH) = 64.9 Hz, Me *trans* to phosphorus, 3H], 0.85 [d, ^3J(PH) = 8.3 Hz, ^2J(PtH) = 87.6 Hz, Me *trans* to nitrogen, 3H], 3.60 [m, CH_2 group of dppm, 2H], CH groups of phthalazine adjacent to the coordinating N atoms: 9.2 [s, ^3J(PtH) = 7.0 Hz, 1H] and 9.7 [s, ^3J(PtH) = 12.0 Hz, 1H]; δ(^{31}P) = 1.2 [d, ^1J(PtP) = 1785 Hz, ^2J(PP) = 63 Hz, P *trans* to tolyl ligand], δ = 12.5 [d, ^1J(PtP) = 1965 Hz, ^2J(PP) = 63 Hz, P *trans* to Me ligand]; δ(^{195}Pt) = −2220 [br. d, ^1J(PtP) = 1780 Hz, Pt connected to tolyl ligands], −2295 [br. d, ^1J(PtP) = 1960 Hz, Pt connected to Me ligands].

Kinetic Studies. In a typical experiment, a solution of complex **1a** in benzene (3 mL, 3×10^{-4} M) in a cuvette with a 1 cm path length was thermostatted at 20 °C, and a known excess of phthalazine (100 μL, 0.1 M in benzene) was added using a microsyringe. After rapid stirring, the absorbance at λ = 355 nm was monitored with time. Summarized data are given in the tables and complete data are listed in the Supporting Information.

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 corrections were 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 structures by direct methods. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. Details are given in Table 5.

Acknowledgment. We thank the Shiraz University research council and the NSERC Canada for financial support.

Supporting Information Available: Tables of X-ray data for the complexes in cif format. Tables of kinetic data in PDF format (8 pp). This material is available free of charge via the Internet at http://pubs.acs.org.