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Kinetics and Mechanism of Molecular A-Frame Formation. Reactions of *cyclo*-Octasulfur and Sulfur Dioxide with $Pt_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)_2$ and Related Binuclear Platinum Complexes

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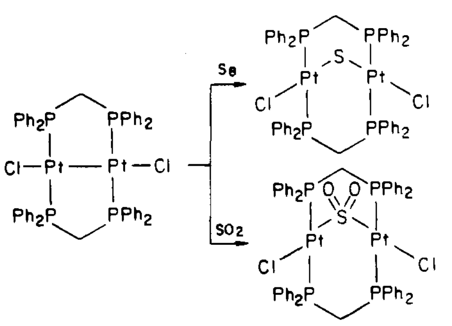
The first reaction referred to in the title follows a second-order rate law in dichloromethane, with $k_{298} = 1.19$ M^{-1} s^{-1} ($\Delta H^{\ddagger} = 15.1 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -7.6 \pm 0.8$ cal mol^{-1} K^{-1}). With a substantial deficiency of elemental sulfur, nearly all eight atoms can (eventually) be incorporated into the bridgehead position. Data were also obtained for complexes having other ligands in place of Cl$^-$, including Br$^-$, I$^-$, pyridine, NH_3, and CO. Complexes with uncharged ligands react very slowly. All of the reactions are substantially accelerated by even trace amounts of a salt such as $R_4N^+X^-$. The diiodide forms two products concurrently, the A-frame and a Pt(II) chelate, $PtI_2(\eta^2\text{-dppm})$; the latter does *not* result from reaction or decomposition of the former. The SO_2 reaction involves preassociation of the reactants, as characterized spectroscopically and kinetically. The adduct appears to be a loose charge-transfer complex, since the phosphorus atoms of dppm remain equivalent in the ^{31}P NMR even at −80 °C and the strength of the interaction is low ($\Delta H°$ and $\Delta G°_{298}$ are −7 and −1.2 kcal, respectively). Kinetic data for both reactions are consistent with a substantial involvement of Pt–Pt bond breaking in the activation process.

Introduction

The "insertion" of an atom or molecule into the platinum–platinum single bond of $Pt_2L_2(\mu\text{-dppm})_2^{n+}$, where dppm = $Ph_2PCH_2PPh_2$, yields a molecular "A-frame" $Pt_2L_2(\mu\text{-Y})(\mu\text{-dppm})_2^{n+}$.[1-3] These products, which are often formed quantitatively in kinetics experiments, have been well characterized preparatively and structurally.[3-11] Heretofore our mechanistic effort has focused on two systems. The one[12] dealt with the insertion of CH_2 from diazomethane and included an evaluation of the kinetic effects of different "terminal" ligands L. The other[13] concerned the special case with L = PPh_3. That reaction proceeds by the initial opening of one arm of the bridging $Ph_2PCH_2PPh_2$ ligand, an interesting process in itself but one that does tend to obscure the insertion step.

This work concerns the insertion of a sulfur atom (from *cyclo*-octasulfur) and a sulfur dioxide molecule, eq 1 and 2, respectively. We report here the kinetics, products, and yields of both. Specific points of interest include the fate of the "rest" of the S_8 molecule once a single S atom has been extruded from it and, for the SO_2 reaction, the kinetic and spectroscopic characterization of a prominent intermediate.



(1)

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Experimental Procedures

Reagents. The starting complexes $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, Br, I), $[Pt_2L_2(\mu\text{-dppm})_2](PF_6)_2$ (L = NH_3, CO, NC_5H_5), and $[Pt_2(CO)Cl(\mu\text{-dppm})_2](PF_6)$ were prepared by literature methods.[14,15] The purity of each compound was checked by UV/visible and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy in CD_2Cl_2. Typically, 5 mg of complex in 0.5 mL solvent was used for a good ^{1}H spectrum, and 15–20 mg in 2 mL for a ^{31}P spectrum. The UV/visible spectra and kinetic data were recorded in CH_2Cl_2. The solvent was washed with concentrated sulfuric acid, 10% potassium carbonate, and deionized water, predried over calcium chloride, and distilled from phosphorus pentoxide. The distilled solvent was stored over 4A molecular sieves. The spectra of the starting materials remained constant over periods much in excess of the reaction times; nonetheless, in most instances freshly prepared solutions were used in the measurements.

Sulfur dioxide (Matheson) was used as received to prepare stock solutions in dichloromethane. Iodometric analysis for [SO_2] in several such solutions gave a mean value of 1.8 ± 0.1 M, which we take to be the approximate concentration of a saturated solution of sulfur dioxide at atmospheric pressure and ambient temperature. A substantial stoichiometric excess of sulfur dioxide over platinum complex was used for kinetics. The residual [SO_2] was analyzed iodometrically at the completion of each kinetic run to avoid reliance on dilution ratios of this volatile solute.

cyclo-Octasulfur, twice recrystallized from carbon disulfide, was used to prepare gravimetrically 0.01–0.25 M stock solutions of S_8 in CS_2. The sulfur concentration to be used in a given experiment was obtained by injecting the required volume into a solution of $Pt_2Cl_2(\mu\text{-dppm})_2$ or other complex in dichloromethane. Generally, this introduced <1 M CS_2, but at the highest [S_8] up to 4 M CS_2 was required to maintain the sulfur in solution. It was shown independently by UV/vis and ^{31}P NMR spectra that $Pt_2Cl_2(\mu\text{-dppm})_2$ remains unchanged in CH_2Cl_2 containing up to 4 M CS_2 for longer than 24 h.[16,17] The rates were also shown to be unaffected by up to 4 M CS_2 by its independent addition.

Others have found that some reactions of *cyclo*-octasulfur, such as the reaction between S_8 and triphenylphosphine,[18,19] are subject to large

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(16) Note, however, that $Pt_2Cl_2(\mu\text{-dppm})_2$ has been reported to react with CS_2 when refluxed for a long time in dichloromethane, yielding $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-dppm})_2$, an A-frame with η^2-bound CS_2.[17] The ^{1}H and ^{31}P NMR spectra are quite characteristic, however, and do not match those of $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$. We were also able to prepare the latter complex from $Pt_2Cl_2(\mu\text{-dppm})_2$ and S_8 *without* addition of carbon disulfide. This product and that from the kinetic experiments are spectroscopically identical. Thus insertion of CS_2 occurs so slowly as to be unimportant under the conditions employed here.

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catalytic and photochemical effects. We thus took particular efforts in all of the experiments, especially those involving sulfur, to ensure that the reactions were not influenced by impurities in the solvents or reagents. For that reason all the materials were purified by distillation or recrystallization. To ensure that the kinetic data were not affected by any acceleration due to the effect of light on the reactions or their components, the reagents, solvents, and stock solutions were stored out of light and the reaction solutions made up in foil-wrapped spectrophotometer cells or NMR tubes. The reproducibility in the kinetic data is the best indication that these procedures were successful; three different experimentalists[20] working independently were able to obtain reproducible kinetic data for the compound most extensively investigated, $Pt_2Cl_2(\mu\text{-dppm})_2$. These data sets included numerous independent batches of reagents and solvents. In one respect, however, the existence of interesting, and we think, quite mechanistically significant, catalytic effects of anions was noted. As reported in a subsequent section of this publication, the reactions are strongly accelerated by otherwise "innocent" salts such as chlorides. Remarkable anion effects on other reactions of these dinuclear platinum complexes have recently been investigated.[21]

Measurements. Rate constants were determined by using UV/visible spectrophotometry. In the case of $Pt_2Cl_2(\mu\text{-dppm})_2$, the most extensively studied complex, the reaction with SO_2 was monitored at 400 or 380 nm, and that with S_8 at a wavelength in the range 380–440 nm, with most determinations being at 400 nm. In every case the wavelength choice altered neither the rate constants nor the agreement between the absorbance changes observed and those calculated from the independently determined molar absorptivities. With S_8 and SO_2 used in large stoichiometric excess over the platinum complex, the reactions followed pseudo-first-order kinetics to at least 90% completion. The rate constants were evaluated by standard least-squares or graphical analysis. Data were often acquired and analyzed by using automated spectrophotometers; Cary Model 219/Apple II$^+$ and Cary Model 14/OLIS 3820 systems were used. Most kinetic runs were conducted with reagents and solvents from which oxygen had been removed by a stream of an inert gas, although no observations were different in the few cases where that was not done.

Routine ^1H spectra were determined at 300 MHz with a Nicolet NT-300 spectrometer. The $^{31}P\{^1H\}$ spectra were recorded at 121.5 MHz by using a Bruker WM 300 spectrometer. Quantitative, simultaneous determinations of $Pt_2Cl_2(\mu\text{-dppm})_2$ and $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$ were obtained from the areas of their ^{31}P peaks, pulsing only every 10 s in the FT mode, to allow sufficient time for spin–lattice relaxation.[13]

Results and Discussion

Reaction with S_8: Platinum Products. We surmise that the slowly reacting cationic complexes form A-frames, as they do when CH_2 is inserted.[12] More rapidly reacting platinum complexes such as the dihalides, $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, Br), can be shown to yield exclusively the A-frames, $Pt_2X_2(\mu\text{-S})(\mu\text{-dppm})_2$. The UV/visible and ^1H and ^{31}P NMR spectra of the products in kinetic experiments agreed with those of the authentic materials (see Table I).

Assignments are suggested for the α and β methylene protons of dppm in the A-frames, as shown in Table I. (The proton endo to the bridgehead is labeled as H_α.) With terminal Cl ligands, changing the bridging group (CH_2, S, and SO_2) causes the resonance that lies further downfield to shift appreciably (3.80, 4.42, and 4.94 ppm, respectively), whereas the other resonance changes hardly at all (2.90, 2.84, and 2.76 ppm). On the other hand, in the series of μ-S A-frames, the change in terminal ligand (Cl, Br, and I) shifts the former hardly at all (4.94, 4.97, and 4.99 ppm) but the latter quite perceptibly (2.76, 2.85, and 3.05 ppm). The basis for the suggested assignment is this: It seems reasonable that the bridging group will affect the nearby endo proton, H_α, to a much greater extent than the more remote H_β, whereas the terminal ligand with the opposite proximity should have the effects reversed.

UV/visible spectral scans during the course of the reactions were consistent with the smooth conversion of reactant to product. Similarly, ^{31}P spectra taken during the reaction of the dichloride showed only its resonance and that of the $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$ product. The A-frame $Pt_2Br_2(\mu\text{-S})(\mu\text{-dppm})_2$ was prepared by two methods, the one route being analogous to the chloride method[11] (i.e., S_8 + $Pt_2Br_2(\mu\text{-dppm})_2$) and the other involving prolonged (>48 h) stirring of $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$ with Et_4NBr in dichloromethane, precipitation with isooctane, and recrystallization (dichloromethane/isooctane). The ^{31}P spectra of these materials agreed, and matched that of the material obtained from kinetic runs.

Table I. NMR Spectra

(1) ^1H NMR Spectra[a]

complex	chem shift/ppm[b] H_β, H_α	coupling const/Hz ^2J(H,H)	^3J(Pt,H)	^2J(P,H)
$Pt_2Cl_2(\mu\text{-SO}_2)$-	2.84	14	31.0	
$(\mu\text{-dppm})_2$[c]	4.42		11.2	
$Pt_2Cl_2(\mu\text{-S})$-	2.76	12.9	63.9	3.3
$(\mu\text{-dppm})_2$[c]	4.94		12.7	
$Pt_2Br_2(\mu\text{-S})$-	2.85	13.2	60	3.6
$(\mu\text{-dppm})_2$[d]	4.97		13.2	
$Pt_2I_2(\mu\text{-S})$-	3.05	13.2	57.9	3.3
$(\mu\text{-dppm})_2$[d]	4.99		12.6	

(2) $^{31}P\{^1H\}$ Spectra[a]

complex	δ (^1J(Pt,P)/Hz; ^2J(Pt,P)/Hz)
$Pt_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2$	19.5 (3588; 273)[c,e] 21.7 (3645; 280)[d,f]
$Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$	1.45 (2884; –)[c,e] 4.06 (2888; ~40[g])[d,f]
$Pt_2Br_2(\mu\text{-S})(\mu\text{-dppm})_2$	4.14 (2784; ~40[b])[d,f]
$Pt_2I_2(\mu\text{-S})(\mu\text{-dppm})_2$	4.47 (2840; ~40[g])[d,f]

[a] At ambient temperature in CD_2Cl_2 or $C_2D_2Cl_4$. [b] Relative to Me_4Si; the resonance further downfield is assigned to the CH_2 proton of dppm that is endo with respect to the bridgehead group (see text). [c] References 11 and 17; at 60 Hz and 343 K. [d] This work; ^1H spectra at 300 MHz and ^{31}P spectra at 121.5 MHz. [e] Relative to trimethyl phosphate; at 36.4 MHz. [f] Relative to external 85% phosphoric acid in CD_2Cl_2; at 22 °C. [g] Estimated from unresolved satellites.

Thus the reaction proceeds without the intervention of an intermediate that attains an appreciable concentration and is not complicated by the formation of appreciable byproducts. It was verified by ^{31}P NMR that $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$ in dichloromethane-d_2 is indefinitely stable to carbon disulfide and sulfur.

Reaction with S_8: Chelate Formation. There were, however, complications in the reaction of the diiodide, and the UV/visible kinetic data appeared to follow a biphasic pattern. This reaction was shown by ^{31}P NMR to yield partially the mononuclear chelate complex $PtI_2(\eta^2\text{-dppm})$. (This is a known[15] material; it was prepared as described and found to have a ^{31}P chemical shift of −70.15 ppm and ^1J(Pt,P) = 2989 Hz, which match exactly the values for the observed byproduct.) A larger proportion of the A-frame was formed when an iodide salt was added. Addition of free iodide also increased the reaction rate (see below).

Formation of a Pt(II) chelate is, of course, a redox process. Consistent with that, these solutions had the definite aroma of hydrogen sulfide, which was not noted in any other system.

This side reaction precluded the isolation of a clean A-frame product from this reaction, although the latter was readily obtained by the reaction of $Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2$ with NaI in acetone. The A-frame was characterized by its NMR spectrum, which was much like those of its analogues (see Table I). With the spectrum known, it was then possible to monitor the progress of the reaction by ^{31}P NMR.

These experiments clearly showed that the reaction with S_8 forms the A-frame and the chelated byproduct concurrently. Indeed, the authentic A-frame is stable toward S_8 and CS_2 at these concentrations. Both observations are consistent with the assignment of *concurrent* pathways leading to the separate products but not with *consecutive* formation and decomposition of the A-frame.

Reaction with S_8: Stoichiometry. With S_8 in excess, as it was in the rate determinations, the reaction proceeds to completion. This situation might be as represented by eq 3. On a molecular

$$Pt_2Cl_2(\mu\text{-dppm})_2 + (1/8)S_8 = Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2 \quad (3)$$

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[20] We are grateful to R. J. Blau for performing the third set of independent kinetic measurements.

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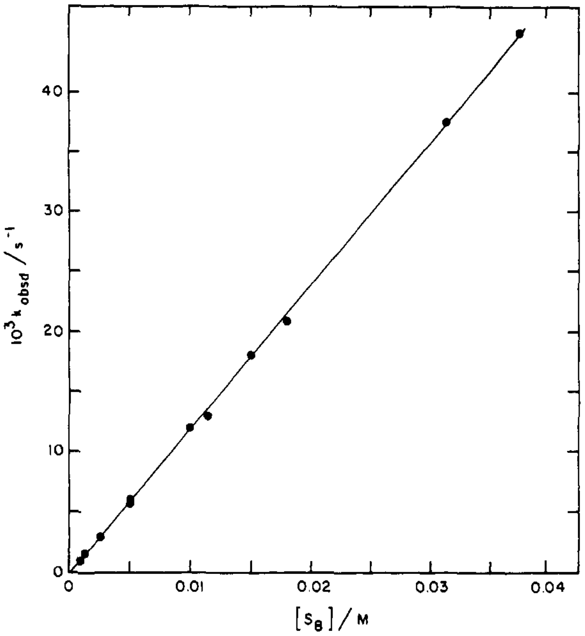

Figure 1. Pseudo-first-order rate constant for the reaction of $Pt_2Cl_2(\mu\text{-dppm})_2$ with excess S_8 as a linear function of $[S_8]$. The data shown are for reactions in CH_2Cl_2 at 25.0 °C.

scale, however, there is no assurance that all eight sulfur atoms—or even more than one—are utilized. Should the known molecule S_7 be formed in an initial reaction step, its sulfur atoms are not necessarily incorporated into further A-frame product, although some or all may be. If not, the limiting situation shown in eq 4

$$Pt_2Cl_2(\mu\text{-dppm})_2 + S_8 = Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2 + S_7 \quad (4)$$

would represent the reaction stoichiometry, with a maximum of one sulfur atom per *cyclo*-octasulfur molecule utilized in A-frame formation. (The example using S_7 as the product is arbitrary. The same issues would pertain if S_6 etc. were considered. Sulfur fragments smaller than S_8 are stable molecules that have been identified.[19,22-25])

To address that point, mixtures prepared from $Pt_2Cl_2(\mu\text{-dppm})_2$ and variable but insufficient amounts of S_8 were analyzed by ^{31}P NMR. Four solutions, each 1.5 mM $Pt_2Cl_2(\mu\text{-dppm})_2$ in CD_2Cl_2, were treated with different amounts of S_8. After 24 h each contained considerable proportions of product from which the efficiency of sulfur atom utilization can be calculated. A reaction having a S_8/Pt_2 complex mole ratio of 0.25, incorporated 3.0 S atoms per S_8 molecule into the A-frame product. Other values: 0.125, 4.0; 0.063, 5.3; 0.031, 5.3. The solution with a mole ratio of 0.063, reanalyzed later, showed evidence of further sulfur incorporation: 7.2 and 7.6 S atoms per S_8 molecule had been incorporated after 48 and 60 h, respectively. We infer from this that essentially all the sulfur content of S_8 can be utilized in A-frame formation, given enough time.

Reaction with S_8: Kinetics. Typical concentrations of the dinuclear platinum complex were 5×10^{-6}–2×10^{-4} M. In the reaction with $Pt_2Cl_2(\mu\text{-dppm})_2$, $[S_8]$ was varied over wide limits, 7.5×10^{-5}–3.75×10^{-2} M. The pseudo-first-order rate constants at 25.0 °C in dichloromethane ranged from 9.27×10^{-5} to 4.5×10^{-2} s^{-1}. The plot of k_{obsd} vs. $[S_8]$ is linear over the entire range and passes through the origin, as shown in Figure 1. The slope of this plot yields a second-order rate constant of 1.19 ± 0.03 M^{-1} s^{-1} at 25.0 °C. Studies over a wider temperature range, 5.0–25.0 °C, yielded the activation parameters shown in the expression

$$k = (RT/Nh) \exp[(-15.1 \pm 0.3 \text{ kcal mol}^{-1})/RT] \times \exp[(-7.6 \pm 0.8 \text{ cal mol}^{-1} \text{ K}^{-1})/R] \quad (5)$$

Table II. Rate Constants (M^{-1} s^{-1}) for Reactions of $Pt_2L_2(\mu\text{-dppm})_2{}^{n+}$ with S_8 and CH_2N_2 in Dichloromethane

complex	S_8 (25 °C)[a]	CH_2N_2 (2 °C)[b]
$Pt_2Cl_2(\mu\text{-dppm})_2$	1.19 ± 0.03	41.2
$Pt_2Br_2(\mu\text{-dppm})_2$	0.16 ± 0.06	204
$Pt_2I_2(\mu\text{-dppm})_2$	0.15 ± 0.03	73
$[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$	$(4.1 \pm 0.2) \times 10^{-4}$	20.6
$[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$		1.0
$[Pt_2(NC_5H_5)_2(\mu\text{-dppm})_2]^{2+}$	$\sim 1.4 \times 10^{-3}$	$<10^{-2}$
$[Pt_2(NH_3)_2(\mu\text{-dppm})_2]^{2+}$	$\sim 2 \times 10^{-4}$	$<10^{-2}$

[a] This work. [b] Reference 12.

Rates were also measured for complexes in which the terminal chlorides were replaced by other anions or by uncharged ligands. These measurements proceeded analogously, except for the biphasic pattern seen in the reaction of the iodide complex and non-pseudo-first-order kinetics for the dicarbonyl complex (a system that was not examined further). The very slow reactions of the cationic complexes yielded data of lower precision. Such substitutions have marked effects on the rate of reaction, which tend to be qualitatively similar to those observed for CH_2 insertion, particularly the point that the cationic complexes are substantially less reactive than the uncharged dihalides. This affirms the earlier[12] finding that transfer of the electron pair out of the metal–metal bond is a substantial component of the activation process. Rate constants for both S_8 and CH_2 reactions are summarized in Table II.

Perhaps the most noteworthy difference was found for the half-substituted chloro–carbonyl complex $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$. It reacts with diazomethane only about half as fast as the dichloride does, and the dicarbonyl dicationic complex is much less reactive. In contrast, both of these cationic carbonyls are *much* less reactive toward *cyclo*-octasulfur than is the dichloride.

Reaction with S_8: Anion Effects. Some difficulty was initially encountered in obtaining reproducible results with the dichloride. This was traced to contamination of some samples by HCl used in the preparation. When the sample was treated with Et_3N and then washed well with methanol, the problem disappeared, and uniformly consistent results were obtained. During this stage of the investigation, however, it was learned that the reactions are strongly accelerated by halides, even at extremely low concentrations (1–50 μM). The apparent rate constants varied linearly with their concentrations. The second-order rate constant (M^{-1} s^{-1} units) for the Pt_2Cl_2 compound is given by $k = (1.19 \pm 0.03) + 1.8 \times 10^3[Et_4N^+Cl^-]$, for the bromide by $(0.16 \pm 0.06) + 1.1 \times 10^2[Et_4N^+Br^-]$, and for the iodide (much more approximately, owing to the biphasic kinetics) by $(0.15 \pm 0.03) + 16[n\text{-}Bu_4N^+I^-]$.

The remarkable catalytic effect of anions on the reactions of this family of dinuclear platinum complexes has been noted,[21] and it applies both to A-frame-forming reactions and to ligand-substitution reactions; indeed, we have established[13,21] that in certain circumstances the two types of chemical processes may proceed through one or more common intermediates. The powerfully catalytic role of halide and pseudohalide (and other) anions in the substitution reactions of polynuclear complexes has been noted previously.[26-28]

Reaction with SO_2: Product. The reaction of $Pt_2Cl_2(\mu\text{-dppm})_2$ with SO_2 ultimately produced the A-frame quantitatively. This was proved by comparison of the spectra (UV/visible, ^1H and ^{31}P

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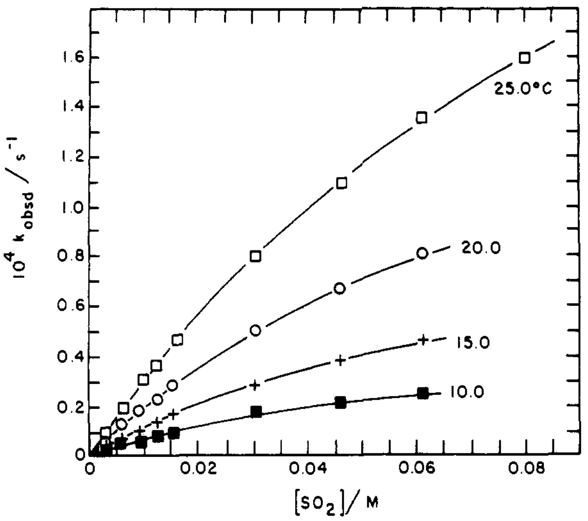

Figure 2. Pseudo-first-order rate constant as a nonlinear function of $[SO_2]$, signaling the presence of an independently confirmed association between $Pt_2Cl_2(\mu\text{-dppm})_2$ and SO_2 (eq 7). The lines show the least-squares fit from eq 9–10.

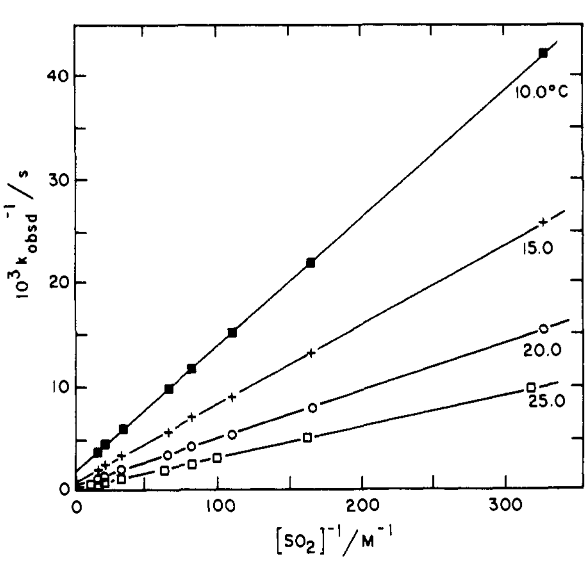

Figure 3. Double-reciprocal plots of the kinetic data for eq 2 according to a rearranged form of eq 6. Notation is as in Figure 2.

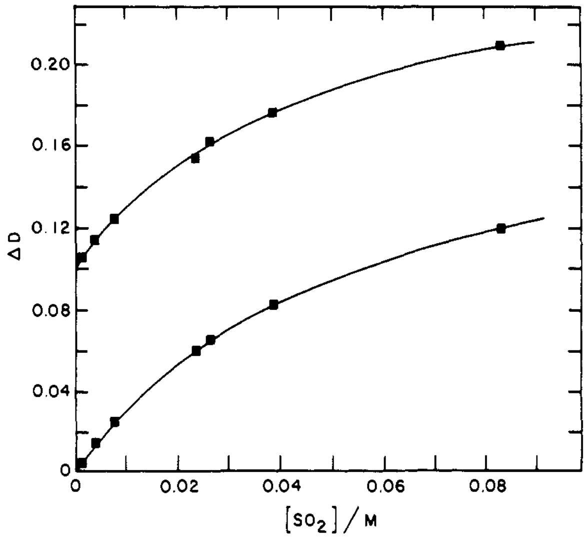

Figure 4. Independent evidence of SO_2 preassociation shown by the nonlinear absorbance changes in the series of kinetic runs at 400 (upper, offset by 0.100 absorbance unit) and 380 nm (lower). The data refer to experiments with $[Pt_2]_0 = 1.00 \times 10^{-4}$ M at 5.0 °C; absorbance values are normalized to a 1.00-cm optical path. Analysis according to eq 5 gave $K = 19$ and 18 M^{-1} at $T = 5$ °C.

NMR) with those of the authentic material; see, for example, Figure 5B. The spectra of such solutions remain unchanged for several days, indicating that the product is quite stable. This agrees with reports[11] that SO_2 is not lost when N_2 is passed through a solution of $Pt_2Cl_2(\mu\text{-dppm})_2$ or when this complex is boiled in CH_2Cl_2 or heated under vacuum. The complex did, however, decompose in $C_2H_2Cl_4$ after 2 h at 80 °C.

Reactions with SO_2: Kinetics. The reaction rates were determined in CH_2Cl_2 with $[SO_2]_0 \gg [Pt_2]_0$. The data followed precise pseudo-first-order kinetics. The variation of k_{obsd} with $[SO_2]$ was nonlinear, as depicted in Figures 2 and 3. This pattern suggested the intervention of an intermediate formed in a rapid preequilibrium. This has been confirmed by direct spectroscopic detection, as described subsequently. The dependence of k_{obsd} on $[SO_2]$ is described by

$$\frac{-d[Pt_2Cl_2(\mu\text{-dppm})_2]}{dt} = k_{obsd}[Pt_2Cl_2(\mu\text{-dppm})_2] = \frac{kK[Pt_2Cl_2(\mu\text{-dppm})_2]_{tot}[SO_2]}{1 + K[SO_2]} \quad (6)$$

where K is the constant of association between $Pt_2Cl_2(\mu\text{-dppm})_2$ and SO_2, eq 7. Independent evidence for this preequilibrium was

$$Pt_2Cl_2(\mu\text{-dppm})_2 + SO_2 = Pt_2Cl_2(\mu\text{-dppm})_2{\cdot}SO_2 \quad (7)$$

obtained by direct spectrophotometry. Absorbance changes were recorded immediately upon mixing but before the occurrence of appreciable overall reaction. Values of the absorbance jump (ΔD, optical path 1 cm) measured at 380 and 400 nm were analyzed as a function of $[SO_2]$ according to eq 8, where $\Delta\epsilon$ represents the

$$D = \frac{(\Delta\epsilon)K[SO_2]}{1 + K[SO_2]}[Pt_2]_{tot} \quad (8)$$

difference in molar absorptivity between adduct and reactant, and K the association constant for eq 7. Combination of these data[29] (Figure 4) and the kinetic analysis yielded values of k and K. At 25.0 °C $k = (3.06 \pm 0.12) \times 10^{-2}$ M^{-1} s^{-1} and $K = 8.0 \pm 0.1$ M^{-1}. Over the full temperature range

$$k_{SO_2} = (RT/Nh)\exp[(-22.2 \pm 0.2\ \text{kcal mol}^{-1})/RT] \times \exp[(4.9 \pm 0.4\ \text{cal mol}^{-1}\ \text{K}^{-1})/R] \quad (9)$$

$$K = \exp[(7.0 \pm 0.2\ \text{kcal mol}^{-1})/RT] \times \exp[(-19.3 \pm 0.7\ \text{cal mol}^{-1}\ \text{K}^{-1})/R] \quad (10)$$

Kinetic data are reported only up to 0.2 M SO_2; above that, the kinetic data and the UV spectra indicate additional complications. Such data were excluded from the data treatment presented. Although not examined in detail, it appears that this effect signals that a new path and a new absorbing intermediate are beginning to contribute under this concentration extreme. Some confirmation for this point was obtained from the NMR spectra, as presented in the next section and in Figure 5A.

Reaction with SO_2: Intermediate Formation. The intervention of an SO_2-containing intermediate was particularly evident in the $^{31}P\{^1H\}$ NMR spectrum. When the reactants were mixed and held at −20 °C, three prominent resonances were evident. Two were clearly identified: $Pt_2Cl_2(\mu\text{-dppm})_2$ at 6.8 ppm and the A-frame product, $Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$, at 21.7 ppm. The resonance at 10.6 ppm is characteristic of the intermediate. When the solution was allowed to warm to room temperature for a few hours and its ^{31}P NMR spectrum then recorded after cooling to −20 °C,

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(29) The molar absorptivities of the adduct derived from this analysis are 1.9×10^3 and 2.42×10^3 M^{-1} cm^{-1} at 380 and 400 nm, respectively. In comparison, the respective values are 1.9×10^3 and 6.0×10^2 for $Pt_2Cl_2(\mu\text{-dppm})_2$ and 4.4×10^3 and 1.9×10^3 for $Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$.

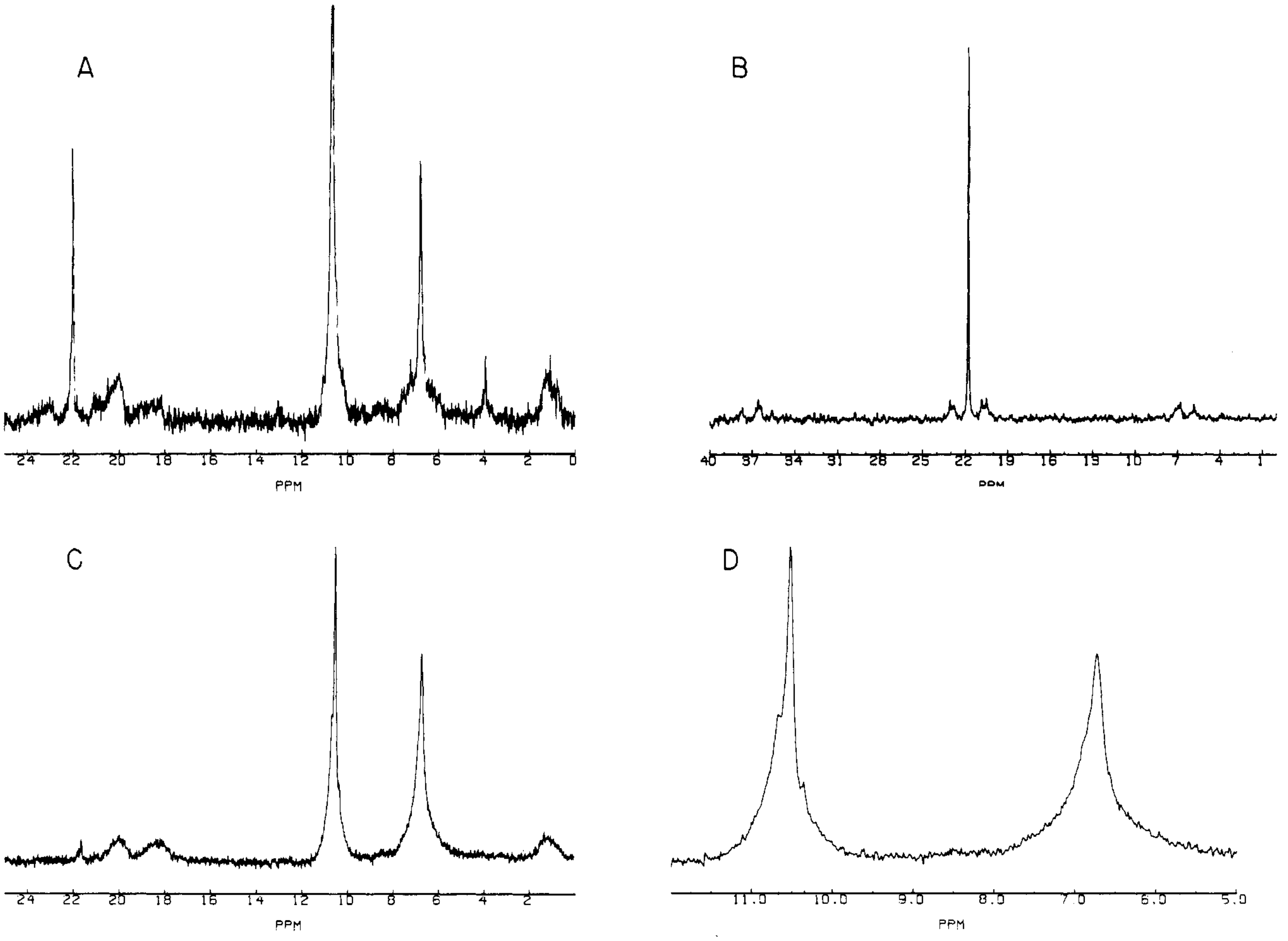

Figure 5. $^{31}P\{^1H\}$ NMR spectra at low temperatures in CD_2Cl_2, taken during the reaction of $Pt_2Cl_2(\mu\text{-dppm})_2$ with SO_2: (A) at −20 °C (a new resonance at +10.6 ppm being seen along with reactant and product, at 6.8 and 21.7 ppm); (B) after warming the solution to room temperature for a few hours and then recooling to −20 °C; (C) at −80 °C, before any A-frame product had formed. Part D is an amplified portion of spectrum C. Further comments on these spectra are given in the text and in ref 30.

only the single resonance of the A-frame was evident. These spectra are illustrated in Figure 5.[30]

An equilibrium constant $K = 70 \pm 2$ M^{-1} at −20 °C was calculated by integrating the ^{31}P NMR peak areas. Extrapolation of the spectrophotometric data to −20 °C gives $K = 66$ M^{-1}. Agreement between the two methods is quite satisfactory.

Possible structures for the intermediate were considered since SO_2 is known to coordinate to and bridge between transition-metal centers in a variety of geometrical arrangements.[31] The 10.6 ppm resonance of the intermediate in the ^{31}P spectrum remains a singlet at −80 °C (Figure 5C) with no appreciable broadening or splitting that would suggest an inequivalence in the phosphorus atoms of dppm. These spectra allow the assignment of coupling constants as $^1J(\text{Pt,P}) = 2286$ Hz and $^2J(\text{Pt,P}) = 45$ Hz. The former is considerably smaller than that for the A-frames, including the $\mu\text{-}SO_2$ compound with $^1J = 3645$ Hz (Table I); note also that the coupling constant for $Pt_2Cl_2(\mu\text{-dppm})_2$ is 2764 Hz.

Attempts were made to measure reliable proton spectra at −80 °C. It appeared that the methylene protons might be inequivalent in the intermediate, as they are in the A-frame, but small shifts with temperature of the spectra of reactant and product make it difficult to assert this with confidence.

Whatever the actual molecular structure of the intermediate, it is necessarily one in which all the phosphorus atoms of dppm remain equivalent, as they are in the reactant and in the A-frame product. Either that, or the intermediate is fluxional between forms having inequivalent dppm's. We tend to discount the latter possibility owing to the low temperatures at which the intermediate shows a singlet in the ^{31}P spectrum. This rules out a structure in which the SO_2 has associated with a single platinum of the dinuclear reactant. The one-bond, P,Pt coupling constant of this resonance is 2286 Hz, weaker than that in the reactant or A-frame, but still significant. One possible structure of the intermediate that is suggested by the NMR results, for which there is no other supporting evidence, however (nor, it would seem, a precedent), is an O-bound $\mu\text{-}O_2S$ group that bridges the platinum atoms of a complex in which the metal–metal bond is retained. It should be noted that the bond strength of the interaction is merely 7 kcal/mol (eq 10). Perhaps some much looser and more labile association (i.e., a charge-transfer complex) occurs. Such a species could remain fluxional even at −80 °C. In the absence of other

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(30) Some details of Figure 5 deserve further amplification. The closely spaced ^{195}Pt satellites of the product are clearly evident in spectrum B, determined to high precision to identify the product and to establish its purity as it is formed in an actual reaction solution. Note that no resonances of the starting material (6.8 ppm) or intermediates (4 and 10.6 ppm), as seen in spectrum A, remain after completion of the reaction. Spectra A and C, on the other hand, were determined with a wider window (−10 to +80 ppm) and a shorter accumulation time, since the intent was first to determine an accurate concentration of the intermediate, to confirm the spectrophotometric value of K, and second, by the use of a wide window, to ensure that all resonances had been detected and thus establish whether the phosphorus atoms of dppm remain equivalent in the intermediate. The satellites of the 10.6 ppm intermediate are the features centered at about 1 and 20 ppm, seen in both spectra A and C. The satellites appear relatively broad because of fine structure in them, as seen in the spectra of stable materials run at high resolution. Also, some broadening may result because spectral resolution in general is not nearly as good at low temperatures owing to problems in shimming the magnet. The small signal in Figure 5A at 4 ppm corresponds to a species that is absent in the product (spectrum B) and is entirely unimportant at −80 °C (spectrum C). This resonance may arise from the second intermediate, seen in the spectrophotometric kinetics at $[SO_2] > 0.2$ M. This intermediate does not occur along a major or well-characterized kinetic pathway and is not a species of known structure.

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evidence, the latter seems the more conservative interpretation.

There is a second transient species seen at 4 ppm in the ^{31}P NMR spectrum shown in Figure 5A. Because this feature disappears in the spectrum of the principal intermediate recorded at −80 °C and is also absent in the reaction product, we suggest that it can be attributed to a second intermediate. There is no real proof of this assignment and certainly no suggestion as to what its structure and composition might be, but the kinetic and spectrophotometric complications that appear at $[SO_2] > 0.2$ M lend credence to this suggestion. Whatever its role, it is clearly a species not important under the conditions used in most of the experiments reported herein.

Oxidation of $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$. It has been shown that S_7 can be smoothly converted to S_7O by using CF_3CO_3H[25] and that $Pd_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$ can be converted to $Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$ by using m-chloroperoxybenzoic acid.[32] Experiments were conducted with $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$ by mixing the reagents at −30 °C in CD_2Cl_2 and recording the ^{31}P NMR spectra at −20 °C. When the amount of MCPBA was stoichiometric or less, $Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$ was indeed the major product, although small amounts of unidentified oxidation products were seen. With excess MCPBA, the μ-SO_2 A-frame was absent, and only oxidation products were found.

Conclusions. The principal findings of the work can be summarized as follows. The insertion of sulfur dioxide into the Pt–Pt bond yields an A-frame known to have a structure in which the sulfur atom is bound to both platinums with equivalent and noncoordinated oxygen atoms. This reaction proceeds by way of an intermediate readily observed and characterized in a consistent manner by both spectroscopy and kinetics. The structure of the intermediate cannot be defined unambiguously but is most probably a loosely bound charge-transfer complex.

A single S atom from S_8 inserts into the Pt–Pt bond. The reaction is able to utilize all or nearly all of the sulfur atoms of the reactant under suitable reaction conditions. The rate of this reaction, like that of diazomethane, is strongly dependent on the terminal ligands bound to the metal. In both cases the rate is much lower when halides are replaced by uncharged Lewis bases (CO, py, NH_3). (In qualitative experiments, the same was found for sulfur dioxide insertion). Clearly, then, the mechanism is not nucleophilic attack of the inserting reagent on the metal center, a process that would be accelerated by increased positive charge at the attack site. These data suggest that cleavage of the Pt–Pt bond occurs during the activation step, not subsequent to it. The rate constants for both reactions are characterized by sizable activation enthalpies, 15.1 and 22.2 kcal/mol, for S_8 and SO_2, respectively. That, too, speaks to compensating bond making and bond breaking in the activated complex, since (for example) the former value is considerably low than the S–S bond energy.

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Registry No. S_8, 10544-50-0; SO_2, 7446-09-5; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2Br_2(\mu\text{-dppm})_2$, 61250-66-6; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4; $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$, 64387-53-7; $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$, 68851-45-6; $[Pt_2(NC_5H_5)_2(\mu\text{-dppm})_2]^{2+}$, 68851-56-9; $[Pt_2(NH_3)_2(\mu\text{-dppm})_2]^{2+}$, 68851-54-7; $Pt_2Br_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 102494-78-0; $Pt_2I_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 102494-79-1; $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 68851-48-9.

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Kinetics of Reduction of a Series of Pentaaquo(pyridine)chromium(III) Ions by 1-Hydroxy-1-methylethyl Radicals: Evidence for Electron Transfer to Pyridine

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The title reaction was investigated for a series of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ ions. The rate constants are correlated by the Hammett equation. These data, in comparison to other cases in the literature, provide support for a mechanism in which a pyridyl radical, coordinated to Cr(III), is first formed. Subsequent intramolecular electron transfer to produce Cr^{2+} and pyH^+ occurs more rapidly. Additional members of the series of free pyridinium ions, $C_5H_4XNH^+$, were also investigated.

Introduction

A question of continuing interest to us[1] and others[2–9] concerns the site of electron transfer in transition-metal complexes. At issue for any given family of outer-sphere reactions is whether the reaction occurs via prior ligand reduction ("chemical mechanism") or directly at the metal center ("resonance transfer").[10] The issue is particularly pertinent when one or more ligands is known independently to be redox active,[2] such as a phenanthroline[3] or a pyridine,[1,11] and when the reaction has a large thermodynamic driving force. The latter is the case for $^{\bullet}C(CH_3)_2OH$, a powerful reductant ($E^\circ \sim -1.3$ V), and for alkyl radicals,[3] which are strong oxidants. A method for deciding the mechanism in a specific case or in general, is not readily at hand. Product analysis, for example, is not definitive since additional reactions often occur immediately after the initial step.

We recently suggested[1,11] that a helpful approach in certain instances can be based on a linear free energy relationship (LFER). Applied to reactions of $(NH_3)_5Co(py)^{3+}$ (where py = NC_5H_5 and

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