Mechanistic Aspects of the Reversible Binding of SO_2 on Arylplatinum Complexes: Experimental and ab Initio Studies

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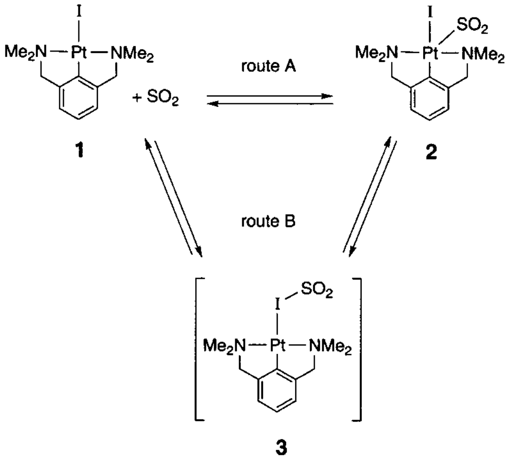
The detailed mechanism of the reversible binding and fast exchange of SO_2 on the organoplatinum(II) complex [PtI(NCN)], **1**, has been studied experimentally in solution ($C_2F_4Br_2$) using low-temperature NMR spectroscopy and theoretically by ab initio calculations. Direct bonding of SO_2 and formation of the thermodynamically most stable product [PtI(NCN)(SO_2)], **2**, was predicted by DFT calculations. Theoretical considerations further indicated the possibility of an alternative and competitive process involving an intermediate [Pt(I−SO_2)(NCN)], **3**, containing an I−S bond, prior to a 1,2-sigmatropic migration of the SO_2 molecule to form ultimately adduct **2**. Temperature-dependent (223−287 K) analysis of the equilibrium constant between complex **1** and the adduct **2** indicated $\Delta H° = -36.6\ (\pm 0.8)$ kJ mol^{-1}, $\Delta S° = -104\ (\pm 3)$ J K^{-1} mol^{-1}, and $K_{298} = 9\ (\pm 4)$ M^{-1}. The exchange of SO_2 on **2** is fast at room temperature, but when the solution was cooled to low temperatures (167−188 K), rate constants were obtained by line-shape analyses of the ^{1}H NMR spectra. The temperature dependence of the exchange rate constants afforded the activation parameters ($\Delta H^\ddagger = +36.2\ (\pm 1.0)$ kJ mol^{-1}, $\Delta S^\ddagger = +33\ (\pm 6)$ J K^{-1} mol^{-1}, $k_{298} = 1.5\ (\pm 0.5) \times 10^8$ s^{-1}, and $k_{174} = 2.34\ (\pm 0.08) \times 10^3$ s^{-1}). From these and concentration-dependent measurements, a dissociative mechanism, D, for the SO_2 exchange on **2** has been deduced involving **1** as an intermediate. This is in line with a direct binding of SO_2 on the platinum center and suggests that the nature of the metal-bound halide has only limited influence on the SO_2 binding. This conclusion is particularly important when fabricating sensor materials for the detection of SO_2 gas that are based on this type of organoplatinum(II) complexes as active sites.

Introduction

Arylplatinum(II) complexes such as [PtI(NCN)], **1** (Scheme 1),[1] containing monoanionic, bis(ortho-)chelating "pincer" ligands of the type $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (abbreviated as NCN)[2] have been shown to be particularly suitable as sensor-active sites for the detection of SO_2 gas.[3] The mode of action of these novel sensors has been studied on a molecular level and consists of reversible η^1-Pt−S bond formation, which is a consequence of the nucleophilicity of the platinum(II) center and the Lewis acidity of the sulfur atom in SO_2.[4] The formed pentacoordinated platinum(II) adduct (e.g., [PtI(NCN)(SO_2)], **2**[5]) gradually loses SO_2 when stored in an atmosphere devoid of SO_2.[6] Here, we report on the detailed mechanism of SO_2 binding onto this class of platinum complexes in solution[7]

Scheme 1. Potential Equilibria between the Arylplatinum(II) Complex **1** and SO_2



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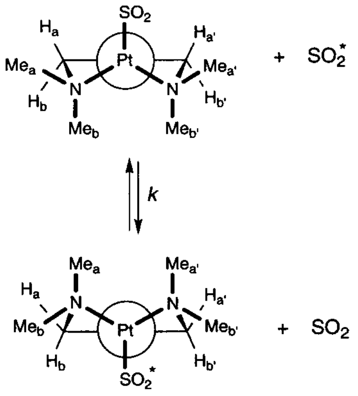
10.1021/ic0009019 CCC: $20.00

because this knowledge is obviously important for improving the sensor activity (e.g., signal amplification, decrease of threshold limits).[8]

Two different reaction routes can be distinguished for the formation of adduct **2** from **1**. In route A, direct binding of SO_2 onto the platinum center occurs (i.e., direct transformation of **1** to **2**; Scheme 1). In the second route B, initial binding of SO_2 onto a ligand site can take place (the iodide is shown), followed by a subsequent intramolecular shift of the SO_2 molecule from the ligand to the metal center. Various groups in **1** can be considered as potential sites for (initial) binding of SO_2. Whereas no evidence has been provided thus far for the (transient) formation of arene$-$$SO_2$ adducts,[9] amines and halides are known to form stable complexes with SO_2.[10] A mechanism involving initial amine coordination would require prior decoordination of the ortho NMe_2 ligand from the platinum center. This possibility can be discarded because of the high stability of the Pt$-$N bond in complex **1**, which is best demonstrated by the inertness of these complexes toward excess of aqueous HCl (no quaternization of the amino groups is observed[11]).

The role of the metal-bound halide in complex **1** is more complicated because the iodide ion is comparable to the platinum center in terms of size and nucleophilicity. Moreover, Pt$-$I bond dissociation has been observed in polar solvents to give the ion pair complex [Pt(NCN)(S)](I) (S = MeCN, for example),[12] where the dissolved iodide ion may act as the initial SO_2 binding site and subsequently transport the SO_2 molecule to the platinum center. The square-planar complex $[Pt(I-SO_2)(NCN)]$, **3** (Scheme 1), would then be an important intermediate in such a mechanism (Scheme 1). Interestingly, such an analogue has indeed been isolated from a related square-planar platinum(II) iodide complex: $[Pt(Me)(I)(PPh_3)_2]$. Addition of SO_2 did not lead to the pentacoordinate adduct but promoted the formation of $[Pt(Me)(I-SO_2)(PPh_3)_2]$ containing an iodide-bound SO_2 molecule. This species may, in fact, represent a "frozen intermediate" in the binding process.[13] Furthermore, spectroscopic evidence has been obtained recently that the formation of related pentacoordinate square-pyramidal arylplatinum(II) complexes containing I_2 instead of SO_2 in the apical position includes initial binding of the iodine molecule on the metal-bound halide, thus forming the intermediate $[Pt(I_3)(NCN)]$.[12] Since the bonding principles of the platinum complexes to I_2 are very similar to those established for SO_2, an analoguous reaction pathway must be carefully evaluated for SO_2 bonding on arylplatinum(II) complexes. On the basis of ab initio calculations and NMR experiments at low temperature, we present herein evidence for an SO_2 binding mechanism that involves direct binding of the SO_2 molecule onto the platinum center rather than an indirect process via precoordination to the metal-bound halide.

Scheme 2. Newman Projection of **2** along the Pt$-$C Axis, Emphasizing the Diastereotopic Nature of the Two Benzylic Protons and the NMe_2 Methyl Groups



Results and Discussion

Solution Measurements Using UV$-$Vis Spectroscopy. Initial attempts to follow the adduct formation of the arylplatinum(II) complex [PtI(NCN)], **1**, with SO_2 have concentrated on UV$-$vis measurements using stopped-flow techniques. Mixing of toluene solutions containing **1** (4.76×10^{-4} M) and SO_2 (2.9×10^{-3} M) at 188 K (toluene) revealed that the reaction was completed in less than 0.020 s and only the final pentacoordinate product **2** was observed. This reaction time corresponds to the mixing time at this temperature because of the increased viscosity of the solvent and thus indicates a fast binding process.

NMR Spectroscopy in Toluene-*d*$_8$. Similar results have been obtained by NMR spectroscopy in toluene. At room temperature, no species have been detected whose symmetry elements appear to reflect complexes of lower than idealized C_{2v} symmetry in nature. Lower symmetry would be expected, however, from the structures of several $[PtX(NCN)(SO_2)]$ complexes in the solid state, which all clearly reveal the inequivalence in the five-coordinate structure of axial and equatorial methyl groups and benzylic protons (Scheme 2).[6] In solution, however, one species is observed that presumably has time-averaged C_{2v} symmetry, suggesting that **2** is involved in a fast equilibrium that renders the diastereotopic NMe_2 methyl groups and the diastereotopic CH_2 protons enantiotopic. Various possible explanations for this observation exist. The most likely processes include a fast *inter*molecular exchange of SO_2, either associative or dissociative, which may even be catalytic in SO_2, or an *intra*molecular shift of the SO_2 molecule, perhaps along the Pt$-$I bond (1,2-sigmatropic migration).[3,6] Either route must be fast on the NMR time scale at room temperature, since even at -85 °C (toluene solution), a C_{2v}-symmetrical complex is observed.

Temperature- and Concentration-Dependent ^{1}H NMR Spectroscopy. Consequently, further measurements toward the elucidation of the SO_2 coordination and decoordination process were performed in 1,2-dibromotetrafluoroethane ($C_2F_4Br_2$) using variable temperature ^{1}H NMR spectroscopy. When a solution of **1** (1.1×10^{-2} M) and SO_2 (2.4×10^{-2} M) is (stepwise) cooled from 293 to 185 K, a gradual change of the chemical shift values is observed. The resonances due to the benzylic

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(7) For a solid-state investigation, see the following. Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.

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(9) However, $SO_2$$-$diene adducts have been reported. (a) Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, K. W., II.; Kuczowski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 4732. (b) Fernandez, T.; Sordo, J. A.; Monnat, F.; Deguin, B.; Vogel, P. *J. Am. Chem. Soc.* **1998**, *120*, 13276. (c) Solari, E.; Floriani, C.; Schenk, K. *J. Chem. Soc., Chem. Commun.* **1990**, 963.

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ArCH_2N protons are diagnostic; at high temperatures, they are located at a frequency identical to the one observed for the corresponding protons in **1** ($\delta_H = 4.07$ at 287 K) and shift continuously to lower field upon cooling. At 193 K, the observed chemical shift value ($\delta_H = 4.36$) corresponds to that of adduct **2** obtained in the presence of a large excess of SO_2.[3] At this low temperature, only one coalesced signal for H_A and H_B (Scheme 2) is observed because of the very fast exchange between dissolved and platinum-bound SO_2 (viz., **2**). This correlation of the observed chemical shift values with temperature allows for the determination of the concentrations of **1** and adduct **2**, knowing the total complex concentration, $[Pt]_{tot} = [\mathbf{1}] + [\mathbf{2}]$, and the total SO_2 concentration, $[SO_2]_{tot} = [SO_2] + [\mathbf{2}]$, and using the relation $\delta_{obs} = \delta_1[\mathbf{1}]/([\mathbf{1}]+[\mathbf{2}]) + \delta_2[\mathbf{2}]/([\mathbf{1}]+[\mathbf{2}])$. A slight temperature dependence of the chemical shift values of the individual complexes was taken into account, which was quantified by measuring the arylplatinum complex either in a pure $C_2F_4Br_2$ solution (solely complex **1**) or in a solution that was previously saturated with SO_2 (only complex **2** present).[14] Hence, the corresponding equilibrium constant *K* was determined as a function of temperature:

$$\mathbf{1} + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{2} \qquad (1)$$

A plot of ln(*K*) against the reciprocal temperature is linear and hence gives directly the standard entropy and enthalpy with $\Delta H° = -36.6\ (\pm 0.8)$ kJ mol^{-1} and $\Delta S° = -104\ (\pm 3)$ J K^{-1} mol^{-1}.[15] Importantly, the Gibbs free energy difference at 298 K between the adduct and the SO_2-free platinum complex is $\Delta G°_{298} = -5.5\ (\pm 1.2)$ kJ mol^{-1} ($K_{298} = 9\ (\pm 4)$ M^{-1}) and is relatively small. The previously determined value of $K_{292} = 9.8\ (\pm 1.4)$ M^{-1}, obtained from UV−vis spectroscopy by titration experiments at 292 K in C_6H_6 solution, is in good agreement with these results.[3]

Hence, at 224 K and at the given concentration of SO_2, the arylplatinum complex exists predominantly as the pentacoordinate adduct and the equilibrium constant *K* is large ($K \gg 1$). Raising the temperature gradually favors the existence of the four-coordinate species. At 287 K, the equilibrium is shifted markedly to the square-planar platinum complex **1** and solvated SO_2.

When the temperature is further decreased (i.e., $T < 200$ K, where only complex **2** is present according to ^1H NMR spectroscopy), a broadening of the characteristic NMR resonances is noted. This suggests that a dynamic process is operating in solution. Indeed, at 150 K decoalescence of both the resonances assigned to the ArCH_2N and the NMe_2 groups was unambiguously established. This behavior is attributed to the SO_2 exchange process (Scheme 2), which has become slow at these temperatures. At the slow exchange limit, the signal due to the NMe_2 groups is split into two singlets at $\delta_H = 3.36$ and 3.25 and the benzylic protons appear as two doublets centered at $\delta_H = 4.80$ and 3.84 (400 MHz). The coupling constant ($^2J_{HH} = 14.4$ Hz) is indicative of geminal H−H coupling in a complex of lower than C_{2v} symmetry as displayed by the pentacoordinate platinum complex **2**.

Line shape analysis of the benzylic signals was performed in order to obtain the observed rate constant *k* for this SO_2 exchange reaction (Figure 1). Variable SO_2 concentration measurements, using solutions of complex **2** (1.1×10^{-2} M) and SO_2 (0.6×10^{-2} to 7.2×10^{-1} M) in $C_2F_4Br_2$ at 174 K showed that the rate constant is barely influenced by the changes in concentration of free SO_2, hence following a rate law that is first order in arylplatinum complex and zero order in SO_2, which strongly points to a dissociative process.

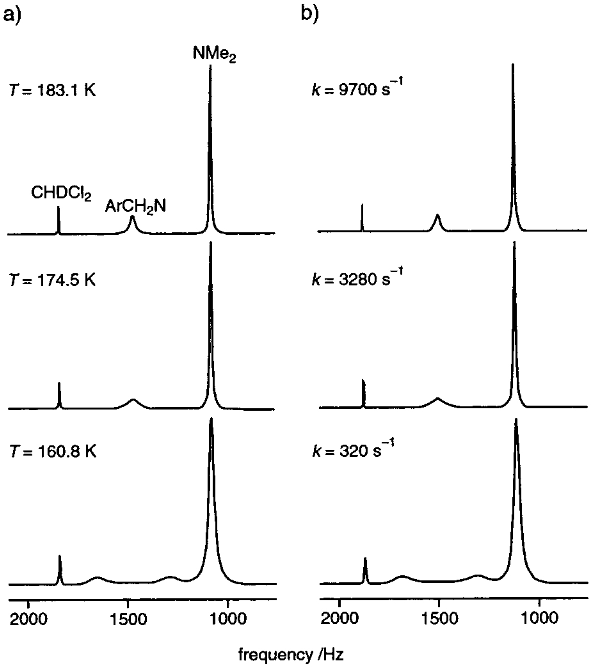

Figure 1. Measured (a) and simulated (b) temperature-dependent ^1H NMR spectra of **2** (400 MHz, $C_2F_4Br_2$ solution).

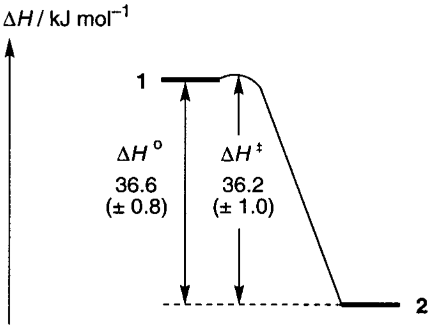

Figure 2. Energy diagram of the postulated binding process and the fast SO_2 exchange on the platinum center. $\Delta H^\ddagger$ denotes the activation energy determined for the release of SO_2 from adduct **2** and formation of the SO_2-free complex **1**.

The variable temperature rate constants were fitted to the Eyring equation, which resulted in a rate constant $k_{174} = 2.34\ (\pm 0.08) \times 10^3$ s^{-1}, an activation enthalpy $\Delta H^\ddagger = +36.2\ (\pm 1.0)$ kJ mol^{-1}, and entropy $\Delta S^\ddagger = +33\ (\pm 6)$ J K^{-1} mol^{-1}. Extrapolation of the observed rate constant to room temperature gave $k_{298} = 1.5\ (\pm 0.5) \times 10^8$ s^{-1}.

From the positive entropy of activation, a dissociative mechanism, D, is assumed. Furthermore, the values of $\Delta H°$ for the reversible adduct dissociation and $\Delta H^\ddagger$ for the SO_2 exchange process (+36.6 and +36.2 kJ mol^{-1}, respectively) are very similar, indicating that the two processes, i.e., the transformation of **2** to **1** and vice versa and the fast SO_2 exchange, are related with each other. This strongly suggests **1** as an intermediate in the exchange process. This is in accordance with a dissociative mechanism and implies a negligible activation energy for the binding of SO_2 on **1** to form adduct **2** (Figure 2).

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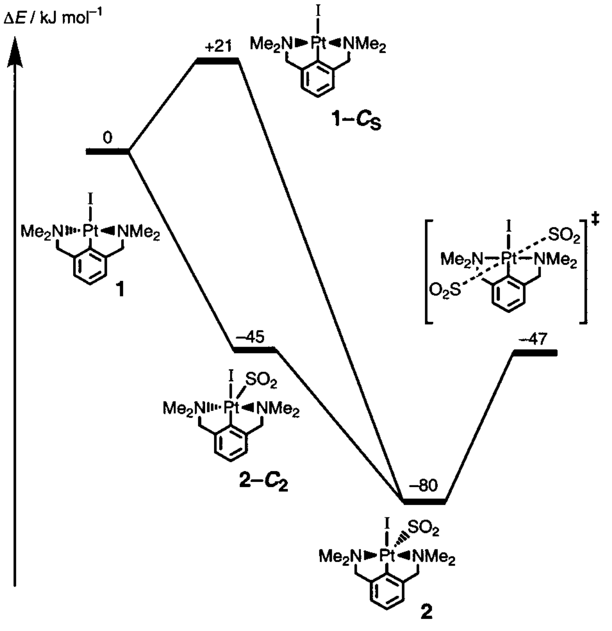
(14) For further details, see Supporting Information.

(15) Günther, H. *NMR Spektroskopie*; Georg Thieme: Stuttgart, Germany, 1973; pp 239.

Scheme 3. Energy Diagram of a Binding Process Covering Direct Coordination of the SO_2 Molecule on the Platinum Center



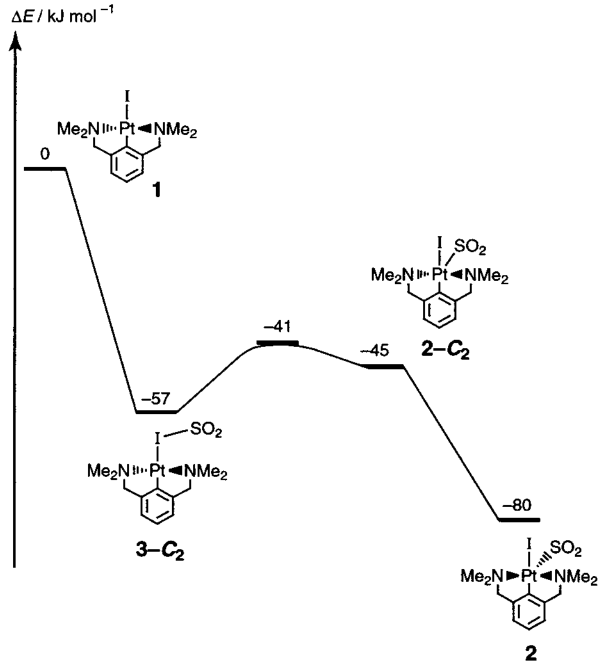
Such a mechanism is also supported by the solvent dependence of the coalescence temperature. Polar and (weakly) coordinating solvents such as THF are often considered to increase the rate of substrate coordination to the metal center and therefore lower the activation energy. Indeed, when the solvent was changed to THF-d_8, measurements at temperatures as low as 160 K uniformly resulted in spectra that show broadened signals only. Further cooling to identify any decoalescence behavior of the relevant resonances is prevented by solvent freezing. Importantly, no signals other than those of complex **2** have been detected at any temperature in either solvent that could originate from an adduct **3** containing an iodide-bound SO_2 molecule. This provides further support for a mechanism comprising direct SO_2 coordination to the metal center.

An important conclusion emanating from these kinetic results is that the exchange rate of SO_2 on these arylplatinum(II) complexes at ambient temperature is extremely rapid (extrapolation to room temperature gives $k_{298} = 1.5 \times 10^8$ s^{-1}) and comparable to the fastest enzymatic reactions.[16] This demonstrates that the signal response of sensor devices, which are based on the metal units as diagnostic sites, is very fast,[8] and therefore, such materials are suitable for true on-line monitoring for the presence of SO_2.

Ab Initio Calculations. Theoretical studies concentrated on both mechanistic pathways, viz. involving (i) direct coordination of SO_2 to the metal center and (ii) prior binding of SO_2 to the metal-bound iodide and subsequent migration to the metal center (Scheme 1). Energies (ΔE) were calculated for structures in the gas phase and focused predominantly on the identification of potential intermediates and therefore correspond to $\Delta H°$. In a few cases, reaction pathways were further detailed, and transition states and hence activation energies ΔE_a (corresponding to $\Delta H^{\ddagger}$) were also taken into account.

1. Direct Coordination of SO_2 to the Platinum Center. Direct coordination of SO_2 on platinum may occur either on

Scheme 4. Energy Diagram of an SO_2 Binding Process Involving an Intermediate Containing an Iodide-Bound SO_2 Molecule and a Subsequent 1,2-Sigmatropic Shift of SO_2 to the Platinum Center[a]



[a] Only the route involving C_2 type nitrogen coordination of the pincer ligand is shown.

complex **1** (identical with **1**−$\boldsymbol{C_2}$) comprising a C_2-symmetric pincer ligand or on complex **1**−$\boldsymbol{C_S}$ with both metallacycles puckered in the same direction. Such a conformation was calculated to be considerably less stable (by 20.9 kJ mol^{-1}) than the crystallographically characterized complex **1**.[1b] Complex **1**−$\boldsymbol{C_S}$ displays a preorganized conformation for direct SO_2 bonding and formation of the adduct **2** (identical with **2**−$\boldsymbol{C_S}$), whereas bonding of SO_2 on **1** would lead to **2**−$\boldsymbol{C_2}$. An intramolecular rearrangement of **1** to **1**−$\boldsymbol{C_S}$ is accompanied by a rehybridization on the platinum center (between 5d and 6p orbitals), which gives the occupied donor orbitals a higher amplitude on the side the Pt−S bond is formed. This effect is reflected in a large energy difference for SO_2 bonding on platinum in **1**−$\boldsymbol{C_S}$ to give **2** ($\Delta E = -100.5$ kJ mol^{-1}), which is more than twice as large as $\Delta E = -45.2$ kJ mol^{-1} for the corresponding process starting from **1** to form **2**−$\boldsymbol{C_2}$ (Scheme 4). Notably, formation of **2**−$\boldsymbol{C_2}$ circumvents the initial activation barrier of 21 kJ mol^{-1} required for the formation of **1**−$\boldsymbol{C_S}$. The theoretical calculations further predict that the most favorable conformation of adduct **2** is characterized by a C_s-symmetric pincer ligand, since inversion of the puckering of the metallacycles in the adduct **2** is a significantly slower process than in the SO_2-free complex **1** ($\Delta E = 34.3$ kJ mol^{-1} in **2** vs 20.9 kJ mol^{-1} in **1**). However, the most likely binding process involves presumably SO_2 binding, which is in concert with the transformation of the binding mode of the pincer ligand from C_2 type to C_s-symmetric and hence does not involve a well-defined intermediate ($\Delta E_a = -79.6$ kJ mol^{-1}).

For the exchange of SO_2 on **2** (Scheme 2), a dissociative mechanism, D, would account for the exact microscopic reverse of the process described above for the coordination of SO_2. Consequently, the SO_2-free complex **1** represents a classical intermediate of such a mechanism ($\Delta E_a \geq -79.6$ kJ mol^{-1}). The apparent discrepancy between the measured energy values

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(16) Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman and Company: New York, 1985.

($\Delta H° = -36.6$ kJ mol^{-1}) and the calculated ones has been attributed predominantly to solvent effects (vide infra).

Alternatively, an associative mode of activation must be considered that involves a transition state characterized by a platinum(II) center of octahedral geometry containing two SO_2 molecules in a mutual trans disposition (associative interchange mechanism, I_a; Scheme 3). Such a transition state, with a competitive interaction of both molecules of SO_2 with the d_{z^2} orbital of platinum, is less stable than the corresponding SO_2 adduct **2** ($\Delta E = +32.7$ kJ mol^{-1}) but seems kinetically preferred to the SO_2-free complex **1** (i.e., the intermediate of a dissociative mechanism) by -46.9 kJ mol^{-1}. This process may become important in the presence of excess SO_2, i.e., in a situation where solvent effects have a less pronounced effect.

2. Binding of SO_2 on Iodide and Subsequent Shift to Platinum. As pointed out above, structure **3** is an interesting representative of a potential intermediate for the binding of SO_2 and also for the fast exchange of SO_2. This is confirmed by the low calculated barrier for the migration of the iodide-bound SO_2 molecule from one face of the metal coordination plane to the other, which does not exceed 12 kJ mol^{-1}. Binding of SO_2 on iodide that is bound to a platinum complex containing the pincer ligand in a C_2 type conformation[17] (viz., formation of **3**$-$***C*₂**; Scheme 4) lowers the relative energy of the adduct by $\Delta E = -56.5$ kJ mol^{-1}, which is 11.3 kJ mol^{-1} more than for coordination at platinum to form **2**$-$***C*₂**. A subsequent 1,2-sigmatropic shift of SO_2 along the I$-$Pt bond is predicted to require an activation energy $\Delta E_a = +15.5$ kJ mol^{-1} for the forward reaction (iodide-to-platinum shift starting from complex **3**$-$***C*₂**) and a $\Delta E_a = +4.2$ kJ mol^{-1} for the reverse process (Pt-to-I migration of the SO_2 molecule beginning with structure **2**$-$***C*₂**). The final transformation of the coordinated amine groups from C_2 to C_s corresponds to the formation of the product **2** and is identical to the one calculated for the SO_2 binding directly on the metal center (Scheme 4). Again, this is probably not a stepwise process but involves a shift of the SO_2 molecule that occurs in concert with the C_2-C_s isomerization of the pincer ligand.

Combination of Theory and Experiment. Notably, the calculated bonding energies refer to structures that were optimized in the gas phase, and solvent effects were consequently ignored. This may explain the uniformly larger energy values obtained from calculations compared to the experimentally determined ones, since solvation is assumed to increase the stability of certain intermediates. For example, interestingly all the optimized structures show a distinct interaction of both oxygen atoms of SO_2 with protons of the NMe_2 groups (Figure 3b). This interaction may be less important in solvated systems and accounts for at least 16 kJ mol^{-1}, as was derived from the calculated energy differences upon rotation of the SO_2 molecule in **3** along the I$-$S bond axis. Furthermore, coordinating or halogenated solvents are anticipated to stabilize SO_2 by similar donor$-$acceptor interactions as calculated for the I$-$S bond in **3**, thus making the thermodynamics of the Pt$-$S bond dissociation much more balanced. Moreover, the presence of solvents certainly has a direct influence on the thermodynamic energy values of various configurations at the platinum center, in particular when comparing metal complexes with different coordination numbers (e.g., octahedral vs square-planar geometry).

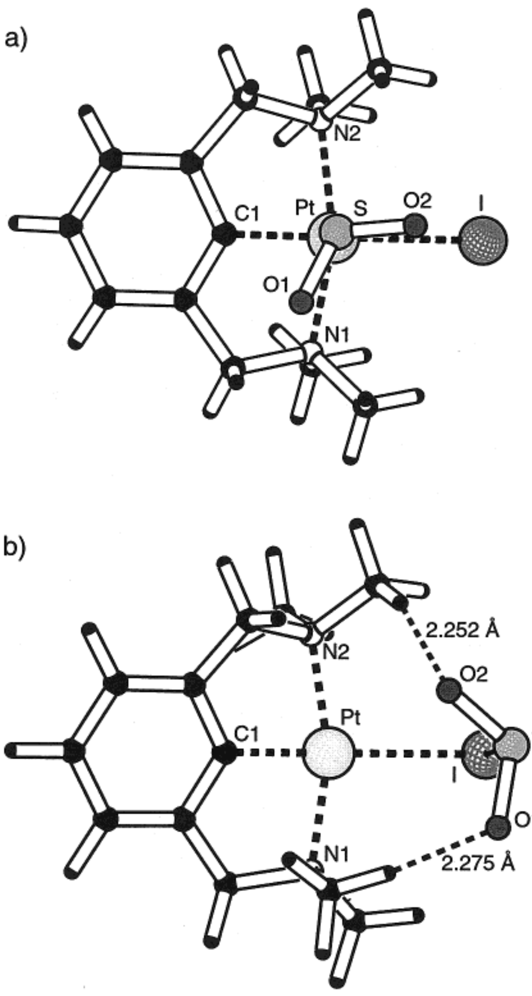

Figure 3. (a) Solid-state structure of the SO_2 adduct **2** (from X-ray); (b) geometry-optimized structure of complex **3**.

Nevertheless, a good qualitative estimate of the SO_2 binding and exchange has been obtained that corresponds well with the experimental results.

1. Spectroscopic and DFT investigations are both in agreement with a dissociative mechanism (D; Scheme 3) involving rapid decoordination and coordination of an SO_2 molecule on a platinum(II) metal center. A tentatively proposed associative interchange, I_a, including a transition state with an octahedrally coordinated metal center containing two platinum-bound SO_2 molecules,[6] may be discarded, particularly because of the decisive NMR experiments (cf., zero-order dependence of k on the concentration of SO_2 and positive activation entropy $\Delta S^{\ddagger}$).[14]

2. No experimental evidence has been obtained for an intermediate structure similar to **3** containing the SO_2 molecule bound to iodide. Such an intermediate does not seem very likely, although its existence, particularly as a thermodynamically unstable but kinetically crucial intermediate, cannot be fully ruled out based on the data presented here.

3. According to the DFT calculations, an exclusively intramolecular exchange of the binding site of the SO_2 molecule (via **3**$-$***C*₂**, i.e., a reversible SO_2 migration along the Pt$-$I bond following a C_2 type pathway; Scheme 4) seems kinetically competitive compared with a dissociative exchange mechanism, but no experimental evidence for its occurrence was obtained.

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(17) Intuitively, a binding route involving prior amine rearrangement in a C_s conformation and subsequent SO_2 bonding on iodide can be discarded because such a conformation creates a favorable coordination site for direct SO_2 coordination on the platinum center (see Supporting Information for further details).

Conclusions

The mechanistic studies presented here show that the platinum-bound iodide in **1** is not directly involved in the SO_2 binding process and that the nature of the metal-bound halide in organoplatinum(II) complexes of the general type [PtX(NCN−R)] does not influence the mechanism of SO_2 bonding. Formation of the corresponding adduct [PtX(NCN−R)(SO_2)] invokes direct bonding of the SO_2 molecule on the platinum center. This is in agreement with the fact that variation of the platinum-bound halide does not have a significant influence on the equilibrium constant K. However, previous investigations revealed that the metal−halide bond is essential for tuning the nucleophilic character of the metal center and for ensuring full reversibility of the SO_2 bonding. The dissociative SO_2 exchange on the adduct is very fast at ambient temperature, with an extrapolated rate constant $k_{298} = 1.5\ (\pm 0.5) \times 10^8\ s^{-1}$. This signal transmission is suitably fast for most common sensor applications based on such organoplatinum(II) complexes. Hence, this nearly ideal sensor response in the presence of SO_2 demonstrates the potential of these platinum materials for the instantaneous detection and the quantitative on-line monitoring of this gas.

Experimental and Methods

General. All solvents, including SO_2 (99.9%, Aldrich), were commercially available and were used without further purification. The platinum complexes **1** and **2** were prepared according to published procedures.[1,3] Stopped-flow UV−vis spectroscopic studies were performed in toluene on a Hi-Tech Scientific (Salisbury, U.K.) SF-40 apparatus that was modified in house for low-temperature stoichiometric measurements.[18]

NMR Spectroscopy. All ^1H NMR spectra were recorded on a Bruker ARX400 spectrometer operating at 400 MHz. Chemical shift values (δ in ppm) were referenced to $SiMe_4$ and measured with respect to residual protons of added CD_2Cl_2 (5%; $\delta_H = 5.29$). The temperature was determined by substituting the sample with a Pt-100 resistor.[19] Samples containing an excess of SO_2 (relative to the arylplatinum compound) were prepared by dissolving complex **1** in a mixture of $C_2F_4Br_2$ (95%) and CD_2Cl_2 (5% v/v), which was previously saturated with SO_2. Solutions for the thermodynamic and kinetic studies were obtained by dissolving complex **1** in a mixture of $C_2F_4Br_2$ (95%) and CD_2Cl_2 (5% v/v) and adding the appropriate amount of SO_2 (0.83 M stock solution in $C_2F_4Br_2$). The observed rate constants were obtained by ^1H NMR line-shape analysis using the program ECHANGE.[20] The analyses of the equilibrium and rate constants using the required equations were accomplished with a nonlinear least-squares fitting program. The reported errors correspond to 1 standard deviation.

Density Functional Calculations. The calculations were carried out using the Amsterdam-Density-Functional (ADF) program developed by Baerends et al.[21] The MOs were expanded in an uncontracted set of Slater type orbitals (STOs). The used basis sets were of triple-ζ with one set of polarization functions on each element.[22,23] The 1s core shell of carbon, nitrogen, and oxygen, the 1s2s2p core shell of S, and the 1s2s2p3s3p4s4p core shell of platinum were treated by the frozen-core (FC) approximation.[24] An auxiliary set of s, p, d, f, and g STOs, centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent-field (SCF) cycle.[25] The numerical integration was done using the scheme developed by te Velde et al.[26] All calculations were performed at the NL-SCF level using the local density approximation (LDA) in the Vosko−Wilk−Nusair parametrization[27] with nonlocal corrections for exchange (Becke88)[28] and correlation (Perdew86)[29] including relativistic effects by the Pauli approximation.[30] Geometries were optimized by using the analytical gradient method implemented by Versluis and Ziegler.[31]

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Supporting Information Available: Listing of the measured data in $C_2F_4Br_2$ solution and details on calculations of an indirect SO_2 binding via a C_s type pincer conformation. This material is available free of charge via the Internet at http://pubs.acs.org.

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