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Reaction Mechanism for Olefin Exchange at Chloro Ethene Complexes of Platinum(II)

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Complex equilibria in methanol/chloroform/dichloromethane solutions containing Zeise's anion, $[PtCl_3(C_2H_4)]^-$ (**1**), the solvento species, *trans*-$[PtCl_2(C_2H_4)(MeOH)]$ (**2**), and the dinuclear complex, *trans*-$[PtCl_2(C_2H_4)]_2$ (**3**), have been studied by UV−vis, ^{1}H, and ^{195}Pt NMR spectroscopy, giving average values of $K_{Cl} = (1.6 \pm 0.2)10^3$ M^{-1} and $K_S = (0.16 \pm 0.02)$ M^{-1} for the equilibrium constants between **2** and **1** and **3** and **2**, respectively. The bridged complex **3** is completely split into monomeric solvento complexes **2** in methanol and in chloroform or dichloromethane solutions with $[MeOH] > 0.5$ M. Ethene exchange at the mononuclear complexes **1** and **2** was studied by ^{1}H NMR line-broadening experiments in methanol-d_4. Observed overall exchange rate constants decrease with an increase in free chloride concentration due to the displacement of the rapid equilibrium between **1** and **2** toward the more slowly exchanging parent chloro complex **1**. Ethene exchange rate constants at 298 K for complexes **1** and **2** are $k_{ex1} = (2.1 \pm 0.1)10^3$ M^{-1} $s^{-1}$and $k_{ex2} = (5.0 \pm 0.2)10^5$ M^{-1} s^{-1}, respectively, with corresponding activation parameters $\Delta H_1^‡ = 19.1 \pm 0.3$ kJ mol^{-1}, $\Delta S_1^‡ = -117 \pm 1$ J K^{-1} mol^{-1}, $\Delta H_2^‡ = 10.2 \pm 0.4$ kJ mol^{-1}, and $\Delta S_2^‡ = -102 \pm 2$ J K^{-1} mol^{-1}. The activation process is largely entropy controlled; the enthalpy contributions only amounting to ≈30% of the free energy of activation. Ethene exchange takes place via associative attack by the entering olefin at the labile site trans to the coordinated ethene, which is either occupied by a chloride or a methanol molecule in the ground state. The intimate mechanism might involve a two-step process *via trans*-$[PtCl_2(C_2H_4)_2]$ in steady state or a concerted process via a pentacoordinated transition state with two ethene molecules bound to the platinum(II).

Introduction

Metal-olefin bond breaking and formation are important in catalytic processes involving olefinic substrates.[1−6] Substitution processes trans to olefins are extremely rapid due to the large π trans effect of ethene.[7,8] In some studies on olefin exchange at square−planar complexes, the exchange rate has been reduced by appropriate selection of ancillary ligands and temperature.[9−13]

In the case of the simple ethene complex $[PtCl_3(C_2H_4)]^-$ (**1**), prepared by Zeise in the 1820s,[14] only two studies of the ethene exchange seem to have been published so far.[15,16] In both these investigations, coordinating solvents (i.e., methanol and/or tetrahydrofuran) were used, and there is an obvious risk that rapidly reacting solvento complexes are formed in the solutions, contributing to the observed overall exchange. Thus, it is well-known that Zeise's anion is hydrolyzed in aqueous solution,[17,18] and that the bridged complex *trans*-$[PtCl_2(C_2H_4)]_2$ is split into mononuclear solvento complexes in ethanol[19] and in refluxing acetone.[20]

Reconsidering some earlier results on ethene exchange at **1**,[16] we found that the observed exchange rate is strongly dependent on added chloride concentration, indicating a reaction mechanism in which equilibria between the parent complex **1** and rapidly reacting solvento complexes are important. We have therefore performed a comprehensive UV−vis, and ^{1}H and ^{195}Pt NMR study of equilibria and ethene exchange kinetics in solutions containing Zeise's anion, using methanol and chloroform as solvents.

Experimental Section

General Procedures and Chemicals. All solvents were purified before use, unless otherwise stated. Water was doubly distilled from quartz. Spectrophotometric grade methanol and dichloromethane (Lab-Scan) were distilled over CaH_2 under nitrogen. Methanol-d_4 (99.5+% D, ACROS) and chloroform-d (99.6+% D, ACROS) were used without further purification and stored under dinitrogen over molecular sieves (4 Å) in a MBraun 150 G−I glovebox. *n*-Tetrabutylammonium chloride

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(99+%, Aldrich), tetraethylammonium chloride (99+%, ICN Biomedicals), and silver triflate (99+%, ACROS) were stored and handled under anaerobic conditions in the glovebox. To enable measurements in chloroform/dichloromethane, cation metathesis of potassium for tetrabutylammonium was done in Zeise's salt, K[$PtCl_3(C_2H_4)$]. Ethene was of the highest purity grade available (99.95%). Fast-atom bombardment (FAB) mass spectra were recorded on a JEOL SX-102 spectrometer. Compounds were characterized by elemental analyses (Mikro Kemi AB, Uppsala, Sweden), NMR and UV−vis data (Supporting Information), and FAB mass spectroscopy.

(^{n}Bu$_4$N)[PtCl$_3$(C$_2$H$_4$)]. The tetrabutylammonium salt of [$PtCl_3(C_2H_4)$]$^-$, **1**, was prepared by dissolving $K_2[PtCl_4]$ (0.5 g, 1.2 mmol) in 0.4 mL of concentrated hydrochloric acid (1.3 mmol) plus 10 mL of water and flushing ethene through the solution for ≈4 days, until the color turned light yellow, and adding (^{n}Bu$_4$N)Cl (0.695 g, 2.5 mmol) as a saturated aqueous solution. The yellow precipitate formed was filtered, washed several times with 10 mL of water at room temperature, dried under vacuum in a desiccator over $CaCl_2$, and recrystallized from a mixture of dichloromethane/diethyl ether (1:1 by volume; yield, 0.62 g, 90%).

Anal. Calcd for $C_{18}H_{40}PtCl_3N$: C 37.8; H, 7.05; Cl 18.6; N 2.45. Found: C 37.6; H, 7.2; Cl 18.5; N 2.5.

***trans*-[PtCl$_2$(C$_2$H$_4$)(CH$_3$OH)], 2.** This compound was obtained in situ, in desired concentration, by mixing methanol solutions of $AgCF_3SO_3$ and (^{n}Bu$_4$N)[$PtCl_3(C_2H_4)$] in a molar ratio of Ag:Pt of 1:1.1. The silver chloride precipitate was filtered off on a small column filled with glass-wool fibers and cellulose powder, and the solution was used directly. Complex **2** was also prepared by methanol cleavage of the chloro bridges in the dinuclear compound **3** as described previously.[21]

***trans*-[PtCl$_2$(C$_2$H$_4$)]$_2$, 3.** The dinuclear complex was prepared by a slight modification of the literature procedure.[21] $K_2[PtCl_4]$ (1.0 g, 2.4 mmol) was dissolved in 0.5 mL of concentrated hydrochloric acid (1.6 mmol) in 4.5 mL of water. Ethene was flushed through this solution at room temperature, and the solution was stirred continuously for 5 days. The golden yellow solution was transferred into an evaporating dish and left until dry. The solid orange material was crushed and extracted with a solution of 0.4 mL of concentrated HCl in 10 mL of absolute ethanol, and the undissolved KCl was separated from the solution by filtration. The filtrate was evaporated to dryness under reduced pressure (600 mmHg) and washed with 5 mL of diethyl ether. The orange solid was extracted with chloroform yielding a yellow, water-soluble residue of K[$PtCl_3(C_2H_4)$]·H_2O as characterized by mass spectroscopy and ^{1}H and ^{195}Pt NMR in deuterium oxide: δ (^{1}H): 4.60 ppm ($^2J_{PtH}$ = 67.3 Hz); δ (^{195}Pt): −2824 ppm.

Anal. Calcd for $KPtC_2H_4Cl_3{\cdot}H_2O$: C, 6.21; H, 1.56; Cl, 27.5; K, 10.1. Found: C, 5.5; H, 1.6; Cl, 28.1; K, 10.6.

FAB-MS (M^+, *m/z* (amu)): 368, 386 (calcd); 368, 386 (found). Evaporation of the resulting chloroform solution gave an orange solid of **3** that was recrystallized from a mixture of dichloromethane/diethyl ether (1:1 by volume) at −35 °C and was handled and stored under dinitrogen in the glovebox (yield: 0.60 g, 85%).

Anal. Calcd for $C_4H_8Pt_2Cl_4$: C, 8.17; H, 1.37; Cl, 24.1; Pt, 66.4. Found: C, 8.1; H, 1.4; Cl, 24.4; Pt, 66.7.

***trans*-[PtCl$_2$(C$_2$H$_4$)$_2$], 4.** The mononuclear bis-olefin complex was separated by bridge-splitting of **3** with ethene in a noncoordinating solvent. Ethene gas was flushed for ≈24 h through a suspension of *trans*-[$PtCl_2(C_2H_4)$]$_2$ (50 mg, 0.085 mmol) in 3 mL of chloroform-*d* at room temperature, until the orange solid turned pale yellow. The solid was separated by decanting and washed three times with 1 mL of chloroform-*d*. The compound decomposes slowly with time. Newly prepared samples were characterized by mass spectroscopy and NMR (see Supporting Information). FAB-MS (M+, *m/z* (amu)): 322 (calcd), 322 (found).

NMR Measurements. NMR spectra were recorded on a Varian Unity 300 spectrometer working at 299.78 and 64.27 MHz for the ^{1}H and ^{195}Pt nuclei, respectively. The probe temperature was calibrated with a Pt-resistor. The ^{1}H chemical shifts are reported in ppm downfield from TMS (δ = 0 ppm) as internal standard. The ^{195}Pt spectra were recorded with a WALTZ-16 proton decoupling sequence and the ^{195}Pt resonances are reported in ppm relative to K_2PtCl_6 (δ = 0 ppm), using a sample of K_2PtCl_4 (δ = −1639 ppm) as external reference. All solutions for NMR were prepared under dinitrogen in a glovebox. A weighed sample of the platinum complex in CD_3OD was introduced in a 5- or 10-mm NMR tube that was capped with a rubber septum. For the exchange studies, ethene was added to the deuterated solutions into the sealed NMR tube by use of a microsyringe, and the solution was shaken to dissolve the gas. The ethene concentration was calculated by integration of the signals for bound and free ethene, or, at the end of an experiment (if in fast exchange), by addition of an excess of chloride to the reaction mixture, forcing the system into the slow exchange regime.

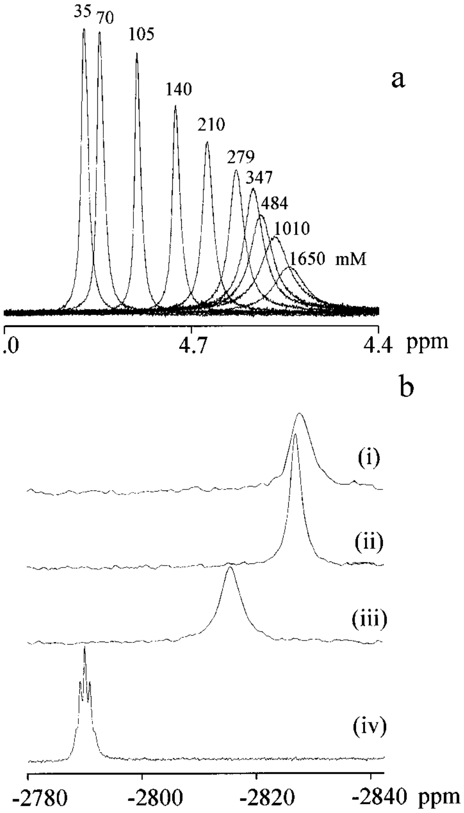

Figure 1. NMR spectra of complexes **2** and **3** at 298.2 K. (a) ^{1}H chemical shifts for a 4.74 mM chloroform-*d* solution of complex **3** as a function of the CD_3OD concentration showing the effect of bridge splitting on **2**. (b) ^{195}Pt NMR spectra of (*i*): complex **2**; (*ii*): (*i*) + 10 mM ethene; (*iii*): (*ii*) + 20 mM chloride; and (*iv*): (*iii*) + 100 mM chloride (methanol-d_4; 298.2 K; C_{Pt} = 30 mM).

Equilibrium Measurements. UV−Vis spectra were recorded at 298.2 K on a Milton Roy 3000 Diode Array spectrophotometer, after mixing pre-thermostated solutions of the platinum complex and ligand (methanol or chloride) in a 1-cm quartz cell in the thermostated cell compartment. The equilibrium constant K_S for reaction 1

$$\underset{(\mathbf{3})}{[PtCl_2(C_2H_4)]_2} + 2S \xrightleftharpoons{K_S} \underset{(\mathbf{2})}{2[PtCl_2(C_2H_4)(S)]} \tag{1}$$

(S = MeOH) was determined from the absorbance changes at 244 nm for solutions of **3** in dichloromethane containing different concentrations of added methanol.

Similarly, K_S was calculated from the ^{1}H NMR chemical shifts measured in chloroform-*d* between 4.88 and 4.54 ppm, and from the ^{195}Pt resonances from −2524 to −2808 ppm. Because the ^{195}Pt chemical shifts are significantly influenced by the environment, the methanol concentration was only varied up to ≈0.5 M in these experiments.

The equilibrium constant for reaction 2, K_{Cl}, was determined from the absorbance changes at 260 nm and the ^{195}Pt NMR resonances from −2791 to −2828 ppm, for methanol solutions of complex **2** containing different concentrations of added chloride.

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$$\underset{\mathbf{(2)}}{[PtCl_2(C_2H_4)(S)]} + Cl^- \overset{K_{Cl}}{\rightleftharpoons} \underset{\mathbf{(1)}}{[PtCl_3(C_2H_4)]^-} + S \qquad (2)$$

Complete absorbance and NMR data are given as Supporting Information.

Exchange Kinetics. The ethene exchange reactions on complexes **1** and **2**, eqs 3 and 4, were determined by ^1H NMR line-broadening experiments in methanol-d_4 solutions containing variable concentrations of free chloride. The rate constants

$$\underset{\mathbf{(1)}}{[PtCl_3(C_2H_4)]^-} + C_2H_4{}^* \overset{k_{ex1}}{\rightleftharpoons} [PtCl_3(C_2H_4{}^*)]^- + C_2H_4 \qquad (3)$$

$$\underset{\mathbf{(2)}}{[PtCl_2(C_2H_4)(S)]} + C_2H_4{}^* \overset{k_{ex2}}{\rightleftharpoons} [PtCl_2(C_2H_4)^*(S)] + C_2H_4 \qquad (4)$$

for the intermolecular ethene exchange between the bound and free sites in reactions 3 and 4 were determined by line-shape analysis using the known equations in the slow,[22] intermediate,[22] and fast exchange[23] regions. The exchange rate was also evaluated by visual comparison of computer-calculated and experimental spectra using the computer simulation program DNMR5.[24] The two methods were in good agreement (see *Results*). Complete data are given as Supporting Information.

Results

Bridge Cleavage of 3. Addition of different concentrations of methanol (S = MeOH and/or CD_3OD) to a dichloromethane and/or a chloroform-*d* solution of the dinuclear complex **3** enabled the determination of the equilibrium constant K_S for the bridge-splitting reaction eq 1 from UV−vis, and ^1H and ^{195}Pt NMR spectroscopic data. Typical ^1H NMR shifts as observed upon addition of methanol to solutions of complex **3** are depicted in Figure 1a.

Measured absorbances and chemical shifts ($\delta(^1H)$, $\delta(^{195}Pt)$) versus the methanol concentration were fitted to eqs 5−7 with the SCIENTIST nonlinear least-squares minimizing program.[25] Examples of these fits are given as Supporting Information, and the derived equilibrium constants are reported in Table 1.

$$K_S = [\mathbf{2}]^2/([\mathbf{3}]\,[S]^2) \qquad (5)$$

$$A_{obs} = (A_3[\mathbf{3}] + A_2[\mathbf{2}]/2)/C_{PtD} \qquad (6)$$

$$\delta_{obs} = (\delta_3[\mathbf{3}] + \delta_2[\mathbf{2}])/(C_{PtD} + [\mathbf{2}]/2) \qquad (7)$$

$$-[\mathbf{2}]^3K_S + 2[\mathbf{2}]^2(C_{PtD}K_S + K_SC_S - 1) - [\mathbf{2}](4C_{PtD}C_SK_S + K_SC_S{}^2) + 2K_SC_{PtD}C_S{}^2 = 0 \qquad (8)$$

In eqs 5−8, C_{PtD}, δ, and A denote the total starting concentration of **3** (as Pt_2), the chemical shift, and the absorbance, respectively. The equilibrium concentrations of $[\mathbf{3}] = C_{PtD} - [\mathbf{2}]/2$, [**2**] and [S] in eqs 5−7 were calculated each time a new aliquot of methanol was added using eq 8 (derived from eq 5), where C_S = [S] + [**2**] denotes the concentration of methanol added.

Table 1. Equilibrium Constants for Reactions 1 and 2, and Second-Order Exchange Rate Constants for Reactions 3 and 4

constant	T, K	value
K_S, M^{-1}	298	0.13 ± 0.01[a]
		0.174 ± 0.005[b]
		0.17 ± 0.01[c]
$10^{-3}K_{Cl}$, M^{-1}	298	1.5 ± 0.1[d]
		1.8 ± 0.2[e]
$10^{-3}k_{ex1}$, $M^{-1}\ s^{-1}$ [f]	288	1.3 ± 0.2[g]
		1.7 ± 0.2[h]
$10^{-5}k_{ex2}$, $M^{-1}\ s^{-1}$	204	0.38 ± 0.03[i]
	243	0.81 ± 0.05[i]
	267	2.3 ± 0.4[i]
	288	4.6 ± 0.2[i]
		3.35 ± 0.04[g,f]
		3.2 ± 0.1[h,f]
	291	5.2 ± 0.2[i]

[a] CH_2Cl_2, UV−vis, eqs 6 and 8. [b] ^{195}Pt NMR, $CHCl_3$, eqs 7 and 8. [c] ^1H NMR, $CDCl_3$, eqs 7 and 8. [d] **1**, **2** (prepared by halide abstraction and bridge splitting), CH_3OH, UV−vis, eqs 9−11. [e] **1**, **2** (prepared by halide abstraction and bridge splitting), CH_3OH, ^{195}Pt NMR, eqs 9−11. [f] ^1H NMR, CD_3OD. [g] Global fitting of data (Supporting Information), K_{Cl} fixed at $1.8 \times 10^3\ M^{-1}$, eqs 10 and 13. [h] Global fitting of data in Figure 3, K_{Cl} fixed at $1.8 \times 10^3\ M^{-1}$, eq 16. [i] ^1H NMR, CD_3OD, eq 14.

Formation Constant of 1. For equilibrium 2, the dependence of the measured absorbance or population-weighted chemical shift $\delta(^{195}Pt)$ on chloride concentration in methanol solvent is given by eq 10, where Y denotes $\delta(^{195}Pt)$ or absorbance, and subscripts denote the complexes **1** and **2**. Methanol solutions of **2**, prepared by bridge-splitting reactions of **3**, never contained >0.09% of the Pt as dinuclear complex in the concentration range used (0.155 < [**3**] < 40.8 mM). The equilibrium concentrations [**1**], [**2**], and $[Cl^-]$ in eqs 9 and 10 were calculated for each concentration

$$K_{Cl} = [\mathbf{1}]/([\mathbf{2}]\,[Cl^-]) \qquad (9)$$

$$Y_{obs} = (Y_2 + Y_1K_{Cl}[Cl^-])/(1 + K_{Cl}[Cl^-]) \qquad (10)$$

$$K_{Cl}[Cl^-]^2 + (K_{Cl}C_{Pt} - K_{Cl}[Cl^-]_{add} + 1)[Cl^-] - [Cl^-]_{add} = 0 \qquad (11)$$

of added chloride using eq 11, where C_{Pt} and $[Cl^-]_{add}$ represent the total concentration of mononuclear platinum complexes (i.e., C_{Pt} = [**1**] + [**2**]) and the concentration of added chloride, respectively. The UV−vis absorbances were measured at 260 nm, where the spectral changes are large. Computer fits of the molar absorptivity ($\epsilon = A/C_{Pt}$ or Y/C_{Pt}) and ^{195}Pt NMR shifts at 298.2 K according to eqs 9−11 are given as Supporting Information, and the values of K_{Cl} obtained from these fits are reported in Table 2.

Kinetics. No signal from coordinated methanol in **2** is observed (Supporting Information). All NMR spectra of solutions containing **1**, **2**, and **3** in equilibrium (eqs 1 and 2) display only one single average signal from bound ethene. It is therefore concluded that methanol exchange of **2** is rapid in the NMR time scale and compared with ethene exchange, and that displacement of the equilibria of eqs 1 and 2 is rapid in the time scale of the ethene exchange on complex **1** and **2**. This result is in agreement with the nucleophilicity sequence $Cl^- >$ ethene $\gg$ MeOH $\approx 1:0.4:10^{-3}$.[26,27] In the range of concentrations used, this sequence results in relative rates $Cl^- >$ MeOH > ethene in all cases studied.

Based on these conditions, the overall rate of ethene exchange on species **1** and **2** in rapid equilibrium determined by the excess

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Table 2. Second-Order Rate Constants at 298 K and Activation Parameters for Exchange Reactions at Square-Planar Metal Complexes

complex	$10^{-3}k^{298}$, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J $K^{-1}\ mol^{-1}$	ref
$[PtCl_3(C_2H_4)]^-$	2.1 ± 0.1	19.1 ± 0.3	-117 ± 1	this work[a]
trans-$[PtCl_2(C_2H_4)(MeOH)]$	500 ± 20[b]	10.2 ± 0.4	-102 ± 2	this work[a]
	440 ± 20[b]	10.4 ± 0.3	-102 ± 1	this work[a,c]
trans-$[PtCl_2(C_2H_4)(imidazole)]$	0.148 ± 0.009	29.3 ± 0.6	-105 ± 2	28[d]
$[PtCl(C_2H_4)(acac)]$	2.6 ± 0.2	8.8 ± 0.7	-150 ± 20	9[e]
$[Rh(C_2H_4)_2(acac)]$	3.0 ± 0.3	9.7 ± 1.5	-145 ± 20	4[f]
trans-$[PtCl_2(ol)(py)]$	4.3 ± 0.4	45 ± 8	-140 ± 20	12[g]

[a] Methanol-d_4. [b] Exchange constants are calculated from the activation parameters. [c] Prepared by bridge splitting of **3**. [d] Acetone-d_6; k_{ex} for imidazole exchange recalculated to 298.2 K. [e] Chloroform-*d*; k_{ex} recalculated to 298.2 K. [f] Chloroform-*d*. [g] Chloroform-*d*; k_{ex} refers to styrene substitution (ol = 3,3-dimethylbut-1-ene; py = 3-(2′,4′-dimethyl-6′-pyridyl)propan-1-ol).

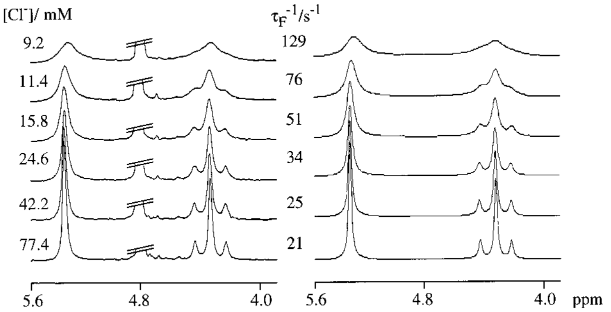


Figure 2. Experimental (left) and calculated (right) ^1H NMR spectra showing the decreasing overall ethene exchange rate in an equilibrium mixture of complex **1** and **2** with increasing concentrations of free chloride (methanol-d_4; C_{Pt} = 7.0 mM; $[C_2H_4]$ = 9.0 mM; 288.2 K).

concentration of free chloride can be defined according to eq 12, where [L] represents the concentration of free ethene.

$$rate = k_{ex1}[\mathbf{1}][L] + k_{ex2}[\mathbf{2}][L] \qquad (12)$$

The mean lifetime of a specific site (τ_B or τ_F) was calculated from the line broadening of the NMR signal of either site B or F. It is obvious from the decrease in line widths of the signals for free and coordinated ethene shown in Figure 2 that the exchange rate decreases with an increase in chloride concentration, due to the rapid displacement of the equilibrium of eq 2 toward the more slowly exchanging complex **1**.

Incorporating the equilibrium constant of eq 9, the rate of the overall exchange process is described by eq 13. The observed exchange rate constant as derived

$$rate = [L]C_{Pt}(k_{ex1}K_{Cl}[Cl^-] + k_{ex2})/(1 + K_{Cl}[Cl^-]) \qquad (13)$$

from the line broadening of the bound or free signal (X = B or F; $[X]$ = C_{Pt} or [L]) is given by eq 14. The observed rate constants for the ethene exchange on complexes **1** and **2**

$$(k_{obs})_X = \tau_x^{\ -1} = (d[X]/dt)\ [X]^{-1} \qquad (14)$$

as a function of the chloride concentration for different concentrations of ethene and platinum, as well as the least-squares fits of the data to eqs 13−15, are shown in Figure 3. Derived rate constants are reported in Table 1.

For $[Cl^-] \geq 10$ mM and $K_{Cl}[Cl^-] \gg 1$ (Table 1), eq 13 simplifies to eq 15, expressed in terms of either the bound or free site.

$$rate = [L]\ C_{Pt}(k_{ex1} + k_{ex2}/K_{Cl}[Cl^-]) \qquad (15)$$

The most accurate determinations of the observed rate constants were obtained by line-broadening on the free site according to eq 16. Figure 3 shows computer fits of the exchange data at 288 K to eqs 13 and 16, yielding the exchange rate constants k_{ex1} and k_{ex2}, with the 298 K value of $K_{Cl} = 1.8 \times 10^3\ M^{-1}$ as a fixed parameter (variation of K_{Cl} between 288 and 298 K being neglected). The nonzero intercept confirms the proposed stoichiometric mechanism as presented in Scheme 1. The data in Figure 3 also illustrate that virtually identical reactivity is observed for the solvento complex **2** prepared in situ by halide abstraction or by dissolving the dinuclear species **3** in methanol. This result is further confirmation that bridge cleavage in **3** by methanol is complete. Several measurements where done at different temperatures and concentrations of ethene and platinum(II) mononuclear complex and chloride. The values of the rate constants derived from the different experiments are in good agreement (cf. Table 1). Complete data are available as Supporting Information.

$$(k_{obsd})_F = C_{Pt}(k_{ex1} + k_{ex2}/K_{Cl}[Cl^-]) \qquad (16)$$

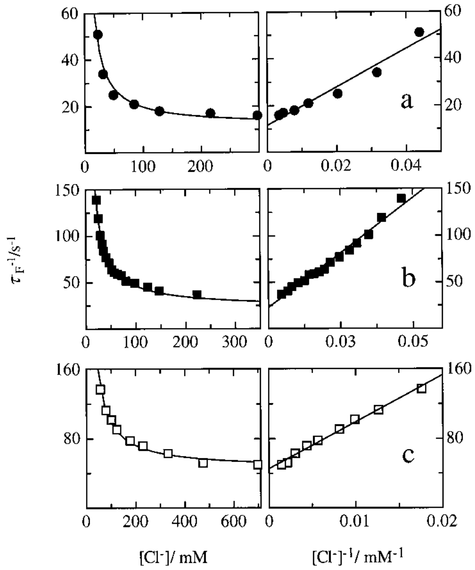
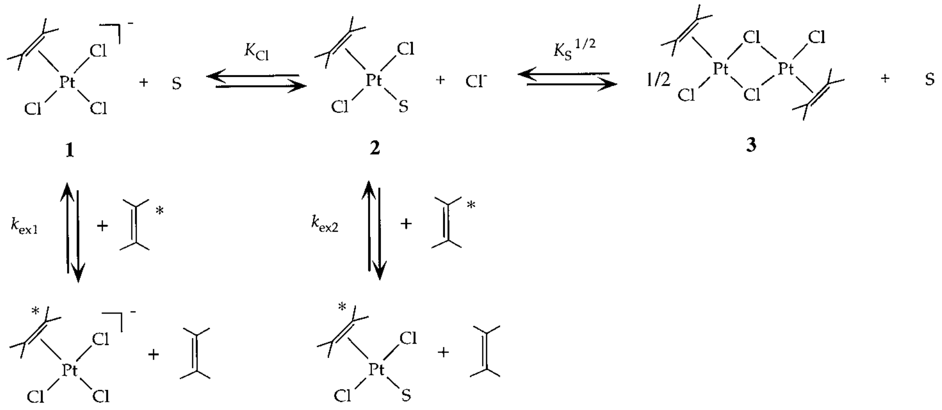


Figure 3. Observed rate constants τ_F^{-1} at 288.2 K, according to eq 13, as a function of concentration of free chloride (left) and reciprocal plots (right) for ethene exchange in methanol-d_4 solutions of (a) complex **1** (●), (b) complex **2** prepared by halide abstraction (■), and (c) complex **2** (□) prepared by bridge splitting ((●): C_{Pt} = 7 mM, $[C_2H_4]$ = 9 mM; (■) C_{Pt} = 14 mM, $[C_2H_4]$ = 8.2 mM; and (□) C_{Pt} = 28 mM, $[C_2H_4]$ = 5.4 mM).

The temperature dependence of the observed and calculated ^1H NMR spectra for exchange on **1** and **2** (Figure 4) shows that the process is in slow exchange for **1** and in fast exchange for **2**, even at 214 K, illustrating the high reactivity of the solvento complex. Both reactions display an unusually small temperature dependence (i.e., only 1 order of magnitude increase in rate over a ∼70 K temperature change). Derived activation parameters are summarized in Table 2, and complete data are given as Supporting Information.

Scheme 1. Reaction Mechanism for the Ethene Exchange on Species **1** and **2**, and Equilibria (K_{Cl}, K_s) between Species **1**−**3** in Methanol Solutions



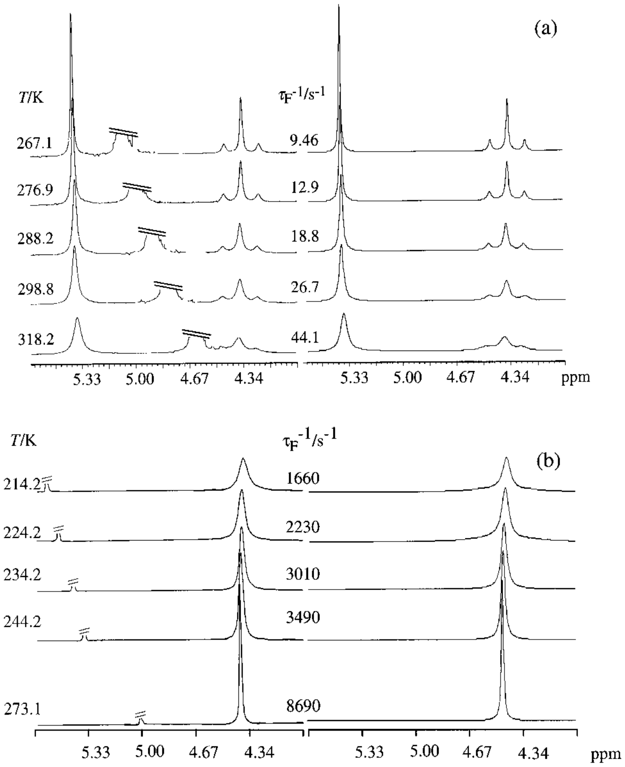


Figure 4. Experimental (left) and calculated (right) ^1H NMR spectra for ethene exchange in methanol-d_4 solutions as a function of temperature. (a) Complex **1**, with C_{Pt} = 12 mM, $[C_2H_4]$ = 17 mM, and $[Cl^-]$ = 225 mM. (b) Complex **2**, with C_{Pt} = 30 mM and $[C_2H_4]$ = 0.7 mM, prepared in situ by bridge splitting of **3**.

Discussion

NMR Spectra. In methanol-d_4, the ^1H NMR spectrum of Zeise's anion **1** shows a triplet at δ = 4.36 ppm with ^{195}Pt (34%) coupling constant $^2J_{PtH}$ = 64.9 Hz in the low field region. The olefin proton resonance for the solvento complex **2** appears as a triplet at δ = 4.37 ppm with $^2J_{PtH}$ = 71.0 Hz, whereas the free ethene signal lies at 5.37 ppm. Magnetic equivalence of the four ethene protons is observed. The proton chemical shifts for the chloride and methanol derivatives are very similar (4.36 ppm versus 4.37 ppm) and therefore not very informative, whereas the coupling constants and ^{195}Pt resonances can be used to rationalize the donor properties of the ligand trans to ethene.

The $^2J_{PtH}$ coupling constants in chloroform-*d* of 66.0, 71.8, and 74.5 Hz for complexes **1**, **3**, and **2**, respectively, are in agreement with the methanol data and indicate, as expected, that the platinum−ethene bond (trans to a bridging chloride) in the dinuclear complex **3** is intermediate in length between that trans to a nonbridging chloride in **1** and that trans to a methanol molecule in **2**. Furthermore, the $^2J_{PtH}$ constant for the trans bis ethene complex **4** of 55.8 Hz indicates that the platinum−ethene bonds in **4** are much weaker than those in **1**−**3**. Cleavage of a platinum−ethene bond in **4** is therefore expected to be easy compared with cleavage of the platinum−methanol or −chloride bonds in complexes **1**−**3**. Chloride, being a more efficient σ donor than methanol, weakens the metal−ethene σ bond trans to itself and increases the π back-donation from platinum to ethene, resulting in a shorter platinum−ethene bond, and a corresponding increase in the $^{195}Pt-^1H$ coupling constant.[28]

The ^{195}Pt NMR signals of **1** and **2** are well separated in methanol. Complex **1** shows an expected quintuplet at −2791 ppm due to $^{195}Pt-^1H$ coupling, whereas **2** is characterized by a broad signal at −2828 ppm (Figure 1b). The small difference in ^{195}Pt chemical shifts between the solvento complex **2** prepared in situ by halide abstraction or from **3** by bridge splitting (−2828 versus −2832 ppm, respectively) could be ascribed to the high sensitivity of these chemical shifts to changes in the ionic medium because the methanol solutions of **2** (prepared in situ by halide abstraction) also contain tetrabutylammonium and triflate. Because of the nature and the strength of the platinum−olefin bond, it is expected that the ^{195}Pt chemical shift of the solvento complex will be observed at a lower frequency than that of the analogous parent chloro complex (less shielding and more π-back-donation). Indeed, the signals at −2791 ppm for **1** and −2828 ppm for **2** show that the platinum(II) center is more deshielded due to the lengthening of the platinum−olefin bond in complex **1** compared with **2**. A quantitative comparison between the ^{195}Pt chemical shifts for complexes **3** (−2525 ppm, 298 K) and **4** (−2994 ppm, 203 K) is more difficult because these spectra refer to different temperatures.

Reaction Mechanism. The equilibrium and exchange results just reported are consistent with the stoichiometric mechanism depicted in Scheme 1. Each of the complexes **1** and **2**, in rapid equilibrium according to eq 2, exchange with free ethene (eqs 3 and 4). Equilibrium 2 is displaced from **2** toward **1** upon addition of free chloride to the reaction mixture. Only for a large excess of free chloride ($[Cl^-]$ > 150 mM), complex **1** will be the primary exchanging species in methanol solution. For lower concentrations, the contribution from the solvento complex **2** will be increasingly important. This inverse dependence

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[28] Steyn, G. J. J.; Roodt, A.; Poletaeva, I.; Varshavsky, Y. S. *J. Organomet. Chem.* **1997**, *536*−*537*, 197−205.

of the overall exchange rate on the concentration of free chloride provides strong evidence that equilibrium 2 is involved in the mechanism.

Participation of rapidly exchanging solvento complexes has been neglected in previous studies of ethene exchange,[9,15,16] which might have resulted in erroneous assignments of observed rate constants and activation parameters in some cases. For instance, in a study of exchange at some platinum(II) and palladium(II) chloro ethene complexes in methanol and tetrahydrofuran solvent without added extra chloride, the observed rate constants and derived activation parameters were referred to the exchange of the parent chloro complexes, exclusively.[16]

The bridged complex **3** is easily split into monomeric complexes in coordinating solvents or in the presence of coordinating ligands. Thus, addition of methanol to chloroform or dichloromethane solutions of **3** results in complete bridge splitting to the mononuclear solvento complex **2** for [MeOH] $> \approx 0.5$ M, and the trans complex **4** is formed by bridge splitting with ethene. This result is in agreement with early observations of bridge splitting in ethanol.[19] Current experiments indicate that cleavage of **3** into solvento complexes takes place in tetrahydrofuran solution, too.[29] In this respect, a previous study[16] claiming observation of ethene exchange only at the dinuclear complex **3** and its palladium(II) analogue in tetrahydrofuran solution, neglecting possible contributions from rapidly exchanging solvento complexes, is therefore questionable.

Rate constants and activation parameters are summarized in Tables 1 and 2. The high reactivity of complexes **1** and **2** is due to the large trans effect of ethene, labilizing the coordination position trans to itself. The ≈200 times higher reactivity of **2** compared with **1** corresponds to what is expected when the reactivity of a solvento complex is compared with its corresponding parent chloro complex.[30]

The activation entropies are negative, as expected for associative processes. Noteworthy, the $T\Delta S^\ddagger$ contribution to the free energy of activation is unusually large, amounting to 67% for **1** and 75% for **2**, whereas the enthalpy terms are correspondingly small. This situation is also the case for the few other known substitution or exchange reactions taking place trans to an olefin[7,9,12,31] (cf. Table 2). The activation process is primarily entropy controlled, involving formation of a well-ordered, stable transition state, whereas bond weakening in the ground state trans to the olefin is less important. These observations fit very well with the general view that olefins exert their high π-trans effect mainly through facilitating formation and stabilization of the transition state, whereas the ground-state destabilization is of minor importance.

A comparison with activation parameters for very fast associative square-planar substitution processes trans to ligands having a strong σ trans effect is worthwhile. Substitution reactions at arylchlorobis(dialkylsulfide)platinum(II) complexes of the type *trans*-$[PtRCl(SR'_2)_2]$, where R denotes phenyl, methyl, or *p*-anisyl and SR'_2 denotes an alkylthioether, respectively, take place with a free energy of activation that is ≈20 kJ/mol higher than the reactions of the olefin complexes studied here, and with a $-T\Delta S^\ddagger$ term that amounts only to between 20 and 40% of the overall $\Delta G^\ddagger$.[32] This result is a clear indication that for this class of ligands, ground-state destabilization in terms of Pt−Cl bond weakening is the main reason for their large trans effect, in contrast to the situation for the olefin complexes.

The mechanism for olefin exchange at *trans*-$[PtCl_2(C_2H_4)(S)]$ and $[PtCl_3(C_2H_4)]^-$, where S denotes a coordinating solvent molecule, thus involves rate-determining associative attack by the entering olefin at the labile site trans to the coordinated olefin, which is occupied by either a chloride or a solvent molecule. As pointed out before,[9,15] there are two possible intimate mechanisms for substitution-controlled olefin exchange processes; either a concerted reaction via a five-coordinate transition state with two olefins coordinated, or a two-step process, involving rate-determining formation of *trans*-$[PtCl_2(C_2H_4)_2]$, **4**, as a steady-state intermediate, followed by rapid reaction between **4** and a solvent molecule or a chloride ion. The expected high reactivity of **4** as already discussed is compatible with the second mechanism. However, the present experimental evidence is not sufficient to differentiate between these two possibilities. Further studies of exchange and substitution processes at olefin complexes have recently been initiated[33] and are in progress.

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Supporting Information Available: ^{1}H and ^{195}Pt NMR Chemical Shifts and UV Molar Absorptivities at 298 K (Table S1); absorbance at 244 nm of dichloromethane solutions of complex **3** at 298.2 K as a function of methanol concentration (Table S2); ^{195}Pt and ^{1}H chemical shifts of chloroform-*d* solutions of complex **3** at 298.2 K as a function of methanol-d_4 concentration (Table S3); absorbance at 260 nm as a function of chloride concentration for compounds **1**−**3** in methanol at 298.2 K (Table S4); ^{195}Pt chemical shifts as a function of chloride concentration for compounds **1**−**3** in methanol-d_4 at 298.2 K (Table S5); observed rate constants for ethene exchange in methanol-d_4 on complex **1** at 288.2 K (Table S6), and on complex **2**, as prepared by chloride abstraction (Table S7), and by bridge-splitting (Table S8); temperature dependence of the calculated exchange rate constants for the platinum(II) complexes **1** and **2** in methanol-d_4 (Table S9); spectral changes relative to the methanol bridge splitting reaction of complex **3** in dichloromethane at 298.2 K (Figure S1); determination of K_s, defined by eq 5, for the equilibrium between complexes **2** and **3** by use of eqs 6−8 at 298.2 K (Figure S2); determination of K_{Cl}, defined by eq 9, for equilibrium between complexes **1** and **2** by use of eqs 10 and 11 at 298.2 K (Figure S3); Eyring plots for ethene exchange at platinum(II) complexes **1** and **2** in methanol-d_4 (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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