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Ethene-Exchange Kinetics of Palladium(II) and Platinum(II) Chloro Ethene Complexes

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The ethene-exchange kinetics of $M_2Cl_4(C_2H_4)_2$ and $MCl_3(C_2H_4)^-$ (M = Pd(II), Pt(II)) in thf-d_8 has been studied as a function of temperature by ^{1}H NMR band shape analysis. The exchange is first order with respect to free ethene. The activation parameters and second-order rate constants are as follows (ΔH^*/kJ mol^{-1}, ΔS^*/J K^{-1} mol^{-1}, k_2^{298}/m^{-1} s^{-1}): $PdCl_3(C_2H_4)^-$, 49 ± 5, −17 ± 18, (1.3 ± 0.2) × 10^3; $Pd_2Cl_4(C_2H_4)_2$; 31 ± 4, −11 ± 21, (4.8 ± 0.6) × 10^6; $PtCl_3(C_2H_4)^-$, 43 ± 5, −43 ± 18, (9.0 ± 1.1) × 10^2; $Pt_2Cl_4(C_2H_4)_2$, 30 ± 4, −23 ± 20, (1.7 ± 0.2) × 10^6. Formation of a bis(ethene) complex, $PtCl_2(C_2H_4)_2$, is observed in solutions of $Pt_2Cl_4(C_2H_4)_2$ and ethene in thf-d_8 at low temperatures. The chemical shift parameters and the exchange mechanism are discussed.

Introduction

Ethene exchange in square-planar complexes was first studied by Cramer.[1] He found, by using ^{1}H NMR spectroscopy, that the ethene exchange in Zeise's anion, $PtCl_3(C_2H_4)^-$, in methanol, is rapid on the NMR time scale even at −75 °C. Since then, the ethene exchange in PtCl(acac)(C_2H_4) (acac = acetylacetonate) has also been investigated,[2] but as far as we known, no study has been made on palladium–alkene complexes. This is surprising, considering the many catalytic applications of such compounds.[3] We therefore performed a kinetic NMR study of the ethene exchange on $Pd_2Cl_4(C_2H_4)_2$ (bis(μ-chloro)dichlorobis(η^2-ethene)dipalladium(II)) and $PdCl_3(C_2H_4)^-$ (trichloro(η^2-ethene)palladate(II)) and on the corresponding platinum(II) complexes, $Pt_2Cl_4(C_2H_4)_2$ and $PtCl_3(C_2H_4)^-$. As the palladium complexes are reduced by methanol, the solvent used by Cramer, we chose to run all the kinetic experiments in tetrahydrofuran-d_8 (thf-d_8), where the complexes are stable, as shown earlier.[4] Thf has approximately the same donor properties as methanol (D_S = 17 and 18 for thf and methanol, respective[5]) and a suitable temperature range (−106 to +65 °C). Ethene exchange in $PtCl_3(C_2H_4)^-$ was also measured in methanol-d_4 for comparison with Cramer's result.

Experimental Section

Chemicals and Solutions. Tetrahydrofuran-d_8 (Dr. Glaser AG) and methanol-d_4 (Prochem) were used as received. Ethene (Alfax) was of analytical grade. $Pt_2Cl_4(C_2H_4)_2$ and $Pd_2Cl_4(C_2H_4)_2$ were prepared according to the methods of Chatt and Searle[6] and Kharasch et al.,[7] respectively. The mononuclear complexes were prepared by addition of LiCl (Merck p.a.) in slight excess to the dinuclear complexes in solution.

The complexes were weighed into the NMR tube (typically 2–10 mg) and dissolved in 0.5 mL of thf-d_8 or methanol-d_4. LiCl (dried at 120 °C) was added in a glovebox under nitrogen atmosphere. By means of a syringe, gaseous ethene was added above the solution in the NMR tube. The tube was then sealed with a plastic cap and shaken to dissolve the gas. The ethene concentration was calculated from the amount of complex and the integrated spectrum in the slow-exchange limit. The reaction order with respect to ethene was determined by adding several portions of ethene to the same sample and recording a spectrum for each concentration.

NMR Spectra. NMR spectra were measured at 5.87 T on a Bruker 250 NMR spectrometer equipped with a 5-mm probe for ^{1}H NMR measurements or a 10-mm broad-band tunable probe for ^{195}Pt measurements.

^{1}H chemical shifts (δ) are reported in ppm relative to tetramethylsilan (TMS, δ = 0). ^{195}Pt chemical shifts (δ) are reported relative to an external sample of K_2PtCl_4 in 1 M HCl(aq) (δ = 2896 ppm), using replacement of the sample.

Results and Data Treatment

The ^{1}H resonance frequency of ethene which is coordinated to Pd(II) or Pt(II) is 0.3–1.2 ppm lower than that of free ethene (Table I). At slow exchange between free ethene and coordinated ethene, the ^{1}H NMR spectrum therefore shows two separate resonance signals. With increasing exchange rates, the ^{1}H NMR signals become broader, and at high exchange rates only a single average signal is seen.

Table I. ^{1}H NMR Data for Free and Coordinated Ethenes in thf-d_8[a]

species	T/K	δ/ppm	J_{HM}/Hz[b]
C_2H_4	280	5.36	
$PdCl_3(C_2H_4)^-$	260	5.09	nr
$Pd_2Cl_4(C_2H_4)_2$	170	5.11	nr
$PtCl_3(C_2H_4)^-$	280	4.14	64.2
$PtCl_3(C_2H_4)^-$	280	4.36	65.2[c]
$Pt_2Cl_4(C_2H_4)_2$	260	4.39	71.5
$PtCl_2(C_2H_4)_2$	172	4.68	nr

[a] Chemical shifts are reported relative to TMS. All resonance frequencies are temperature dependent. nr = not resolved due to fast relaxation of the metal nucleus. [b] M = ^{195}Pt (I = $^1/_2$) or ^{105}Pd (I = $^5/_2$). [c] In methanol-d_4.

By varying the temperature, one can observe all stages of the signal averaging for the two Pd(II) complexes and $Pt_2Cl_4(C_2H_4)_2$ in thf-d_8 (Figure 2). The temperature intervals are shown in Table II. The resonance frequencies of free ethene and $PtCl_3(C_2H_4)^-$ in thf-d_8, however, do not coalesce even at 330 K, the upper limit set by the solvent (Figure 3). From the line shape an exchange rate can be calculated. All exchange rates reported here were calculated using the computer program DNMR 5,[8] and the computer-calculated spectra were visually compared to the experimental spectra.

Effective relaxation times, T_2^*, were determined by recording spectra of samples containing only ethene or complex dissolved in thf-d_8 and, in some cases, also by direct fitting of T_2^* to the experimental spectra. The results from the two methods agreed well.

All resonance frequencies are temperature dependent. The shielding of free ethene (relative to TMS) decreases upon decreasing temperature, while the shielding of coordinated ethene increases upon decreasing temperature.

Ligand substitution reactions in square-planar complexes usually follow the two-term rate law

$$R = nk_1[AL_n] + nk_2[AL_n][L] \qquad (1)$$

where the first term on the right-hand side represents the solvolytic pathway and the second term corresponds to direct attack of the

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(2) Holloway, C. E., Fogelman, J. *Can. J. Chem.* **1970**, *48*, 3802.
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Table II. Activation Parameters and Rate Constants for Ethene Exchange in Square-Planar Complexes[a]

species	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}	k_2^{298}/m^{-1} s^{-1}	temp interval/K	ref
$PtCl_3(C_2H_4)^-$	31 ± 1	−69 ± 4	(6.4 ± 0.2) × 10^3	250–300	this work[b]
$PtCl_3(C_2H_4)^-$	43 ± 5	−43 ± 18	(9.0 ± 1.1) × 10^2	270–330	this work[c]
$PdCl_3(C_2H_4)^-$	49 ± 5	−20 ± 18	(1.3 ± 0.2) × 10^3	260–310	this work[c]
$Pt_2Cl_4(C_2H_4)_2$	30 ± 4	−23 ± 20	(1.7 ± 0.2) × 10^6	172–260	this work[c]
$Pd_2Cl_4(C_2H_4)_2$	31 ± 4	−11 ± 21	(4.8 ± 0.6) × 10^6	170–230	this work[c]
$PtCl_2(C_2H_4)_2$	42 ± 10	64 ± 54	(6.0 ± 1.3) × 10^8	172–190	this work[c]
$PtCl(acac)(C_2H_4)$	8.8	−150	2.6 × 10^3	218–267	2[d]
$Rh(acac)(C_2H_4)_2$	9.7 ± 1.5	−145 ± 20	(3.0 ± 0.3) × 10^3	253–298	12[e]

[a] Errors quoted are standard errors with a confidence level of 95%. [b] In methanol-d_4. [c] In thf-d_8. [d] In $CDCl_3$ and benzene. [e] In $CDCl_3$, CD_2Cl_2, and acetone-d_6.

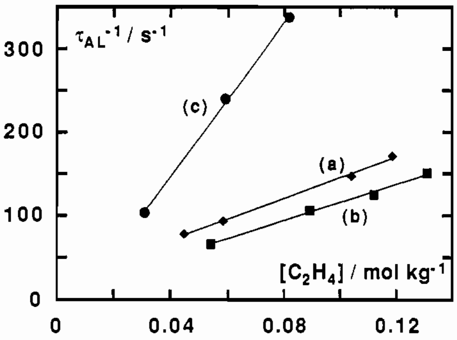

Figure 1. Influence of the concentration of free ethene on the mean lifetimes of $MCl_3(C_2H_4)^-$ (M = Pd(II), Pt(II)): (a) $PdCl_3(C_2H_4)^-$ in thf-d_8 at 300 K; (b) $PtCl_3(C_2H_4)^-$ in thf-d_8 at 300 K; (c) $PtCl_3(C_2H_4)^-$ in methanol-d_4 at 290 K.

entering ligand on the complex,[9] which in our case corresponds to reactions 2 and 3, respectively. AL_n is a complex with n

$$AL_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AL_{n-1} + L \qquad (2)$$

$$AL_n + L^* \overset{k_2}{\rightleftharpoons} AL_{n-1}L^* + L \qquad (3)$$

identical ligands L, which independently exchange with the free ligand with equal exchange rates. In eq 1 R is given in units of moles of ligand per kilogram of solvent per second.

If τ_L is the mean lifetime of the free ligand and τ_{AL_n} is the mean lifetime of a particular coordinated ligand, the exchange rate, R, is given by

$$R = n[AL_n]\tau_{AL_n}^{-1} = [L]\tau_L^{-1} \qquad (4)$$

Combining eqs 1 and 4, we obtain the expression

$$\tau_{AL_n} = k_1 + k_2[L] \qquad (5)$$

which is used to determine the reaction order with respect to ethene.

Palladium Complexes. The ^1H NMR spectra of $PdCl_3(C_2H_4)^-$ in thf-d_8 (without added ethene) show dissociation of ethene from the complex. $PdCl_3(C_2H_4)^-$ is in equilibrium with C_2H_4 and some other palladium(II) complex, presumably $PdCl_3(thf)^-$ or $Pd_2Cl_6^{2-}$. The equilibrium is temperature dependent, and low temperature favors the Pd(II)–ethene complex. This is probably why $Pd_2Cl_4(C_2H_4)_2$ does not show this dissociation, since the useful temperature range appears at much lower temperature for this complex than for $PdCl_3(C_2H_4)^-$ (Table II). We cannot be sure that solvolysis of the dinuclear Pd(II) complex does not occur, but this will not affect the calculated exchange rates and second-order rate constants, as these are measured per mole of ligand.

The ethene exchange of $PdCl_3(C_2H_4)^-$ takes place according to reactions 2 and 3 (n = 1), giving a two-site exchange scheme. A plot of eq 5 for $PdCl_3(C_2H_4)^-$ + ethene is shown in Figure 1. The straight line confirms that the rate law (1) is valid and gives k_1 = 22 ± 18 s^{-1} and k_2 = (12 ± 2) × 10^2 m^{-1} s^{-1}. During the temperature variation, the concentration of free ethene is about 0.05 m, giving a k_1 contribution to the total exchange rate of 27% at 300 K. If we assume this percentage to be constant over the temperature interval studied, we can use $k_2 = 0.73\tau_{AL_n}^{-1}/[L]$ in the Eyring plot (Figure 4) for $PdCl_3(C_2H_4)^-$. This correction does not affect the activation parameters to any greater extent; ΔS^* increases with a mere 3 J K^{-1} mol^{-1}.

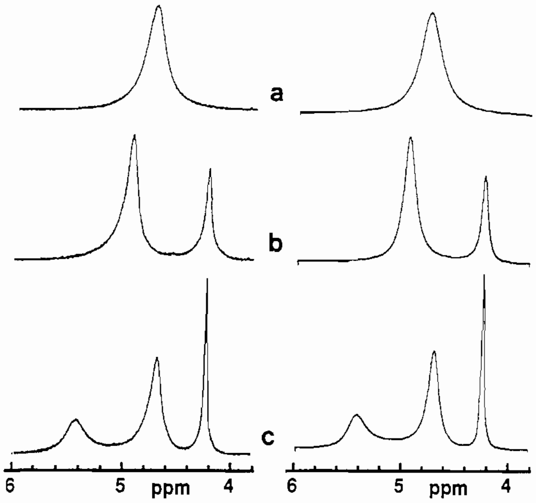

Figure 2. Experimental (left) and calculated (right) ^1H NMR spectra of $Pt_2Cl_4(C_2H_4)_2$ + ethene in thf-d_8 (see text). C_{Pt} = 0.103 m. Temperatures: (a) 220 K; (b) 190 K; (c) 172 K.

The ethene exchange of $Pd_2Cl_4(C_2H_4)_2$ also follows this two-site exchange scheme, provided that exchanges of the two ethene molecules are equal and independent. Neglecting solvolysis, only reaction 3 (n = 2) needs to be considered. Assuming that the exchange rate for $Pd_2Cl_4(C_2H_4)_2$ is first order in both reactants, the second-order rate constant k_2 can be calculated from eq 5 with k_1 = 0. Figure 4 shows an Eyring plot of the calculated rate constants. A least-squares fit gives the activation parameters presented in Table II.

$PdCl_3(C_2H_4)^-$ is decomposed to some extent through the reaction

$$PdCl_3(C_2H_4)^- + H_2O \rightarrow Pd(0) + CH_3CHO + 3Cl^- + 2H^+$$

the water probably being added with the LiCl, which is very hygroscopic. Resonance frequencies of CH_3CHO appear in the ^1H NMR spectrum ($\delta(CH_3$, doublet) = 2.08 ppm, δ(CHO, quartet) = 9.67 ppm).

Platinum Complexes. The two platinum(II) complexes are both stable in solution in the absence of added ligand; i.e., no free ethene can be observed in the ^1H NMR spectrum. Both complexes show resolved spin–spin coupling to ^{195}Pt (I = $^1/_2$, 33.8% natural abundance) in the absence of free ethene. For $Pt_2Cl_4(C_2H_4)_2$ in thf-d_8 $^2J(^1H^{195}Pt)$ = 68 Hz. No splitting of the ^1H resonance signals of $Pt_2Cl_4(C_2H_4)_2$ is observed, not even at low temperatures, which means that all the protons are equivalent. Whether this is due to fast rotation of ethene around the Pt–ethene axis or is due to a very small chemical shift difference between protons facing a terminal chloride compared to protons facing a bridging

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(9) Katakis, D.; Gordon, G. *Mechanisms of Inorganic Reactions*; Wiley-Interscience: New York, 1987; pp 191–199.

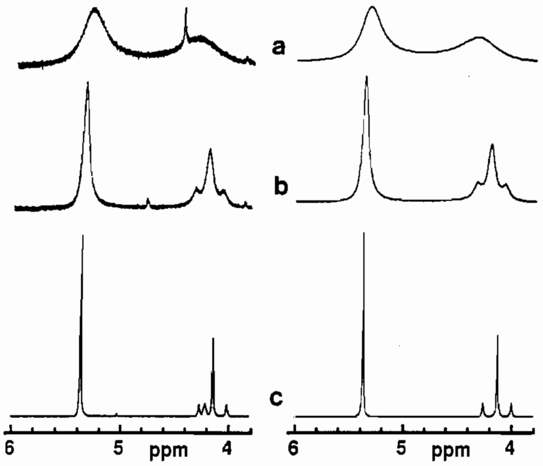

Figure 3. Experimental (left) and calculated (right) ^1H NMR spectra of $PtCl_3(C_2H_4)^-$ + ethene in thf-d_8. $C_{Pt} = 0.042$ *m*. Some temperature-dependent signals from unknown compounds (probably water) in thf-d_8 appear in the spectrum. Temperatures: (a) 330 K; (b) 300 K; (c) 270 K.

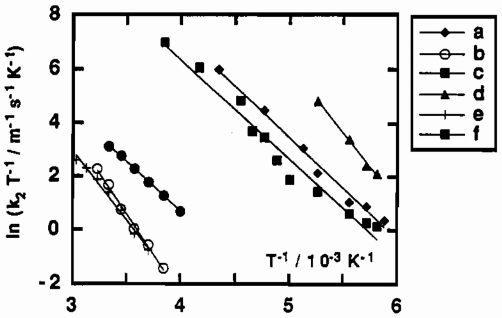

Figure 4. Eyring plots of the temperature dependence of the second-order rate constants, $k_2/m^{-1}\ s^{-1}$, for ethene exchange in $M_2Cl_4(C_2H_4)_2$ and $MCl_3(C_2H_4)^-$ (M = Pd(II), Pt(II): (a) $Pd_2Cl_4(C_2H_4)_2$; (b) $PdCl_3(C_2H_4)^-$; (c) $Pt_2Cl_4(C_2H_4)_2$; (d) $PtCl_2(C_2H_4)_2$; (e) $PtCl_3(C_2H_4)^-$; (f) $PtCl_3(C_2H_4)^-$ (in methanol-d_4; all others in thf-d_8).

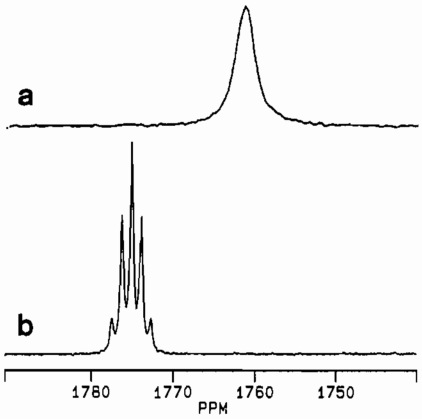

Figure 5. ^{195}Pt NMR spectra of (a) $Pt_2Cl_4(C_2H_4)_2$ and (b) $PtCl_3(C_2H_4)^-$ in thf-d_8 at 300 K.

chloride cannot be determined from the present study.

At room temperature the ^1H NMR spectrum of a solution of $Pt_2Cl_4(C_2H_4)_2$ + ethene in thf-d_8 shows a single ^1H resonance signal from ethene due to fast exchange between coordinated and free ethene. When the solution is cooled, the signal gradually broadens, and at 210 K, two separate resonance signals can be seen (Figure 2). At 180 K, a third resonance signal emerges, which separates clearly from free ethene at 175 K. The third signal is most probably due to formation of a bis(ethene) complex, according to reaction 6.

$$Pt_2Cl_4(C_2H_4)_2 + 2C_2H_4 \rightleftarrows 2\,\textit{trans}\text{-}PtCl_2(C_2H_4)_2 \qquad (6)$$

This complex was reported by Chatt and Wilkins in 1952.[10] The spin–spin coupling to ^{195}Pt is not resolved due to the fast relaxation of this nucleus at low temperatures. The equilibrium constant for reaction 6 can be calculated at low temperatures, and at 175 K equals 27 m^{-1}.

We then have two coupled equilibria, namely

$$Pt_2Cl_4(C_2H_4)_2 + C_2H_4^* \rightleftarrows Pt_2Cl_4(C_2H_4)(C_2H_4^*) + C_2H_4 \qquad (7)$$

$$PtCl_2(C_2H_4)_2 + C_2H_4^* \rightleftarrows PtCl_2(C_2H_4)(C_2H_4^*) + C_2H_4 \qquad (8)$$

The ^1H NMR spectra show that the ligand exchange in the equilibrium mixture occurs via the free ligand, as no rate constants for the direct exchange between the two complexes are needed to describe the spectra. If the lifetime, τ_L, of the free ligand is long, i.e. at slow exchange, the two exchange rates are independent of each other. The lifetimes were obtained by calculating the line shape according to a three-site exchange scheme, yielding two independent mean lifetimes, τ_{AL_n} and τ_{BL_n}, for $Pt_2Cl_4(C_2H_4)_2$ and $PtCl_2(C_2H_4)_2$, respectively, and the two exchange rates were each calculated from eq 4 with $n = 2$. Assuming that the exchange rates are first order in both reactants and that solvolysis is negligible, the second-order rate constant k_2 can be calculated. Figure 4 shows an Eyring plot of the calculated rate constants for the two exchange reactions. A least-squares fit gives the activation parameters presented in Table II.

The ^1H NMR spectrum of a solution of $PtCl_3(C_2H_4)^-$ + ethene in thf-d_8 in the slow-exchange limit shows resolved spin–spin coupling to ^{195}Pt (Figure 3). The ^1H spectra of $PtCl_3(C_2H_4)^-$ + ethene in methanol-d_4 are similar to those in thf-d_8 except that the exchange rates are slightly higher in methanol (Table II). Eyring plots are shown in Figure 4.

The order of reaction with respect to ethene was investigated by injecting various volumes of ethene into the same samples of $PtCl_3(C_2H_4)^-$ in thf-d_8 and methanol-d_4, respectively. The result is shown in Figure 1. The straight lines show that the exchange reactions are first order in ethene, and the small *y* intercepts show that the solvent path is negligible.

The ^{195}Pt NMR spectrum of $Pt_2Cl_4(C_2H_4)_2$ in thf at 300 K (Figure 5a) shows a single resonance signal due to fast exchange of ethene at this temperature. Couplings to ethene protons are resolved in the ^{195}Pt NMR spectrum of $PtCl_3(C_2H_4)^-$ in thf (Figure 5b), giving the expected quintet. The almost identical chemical shifts of the two platinum complexes, 1761 and 1775 ppm, respectively, indicate that Pt(II) coordinates three chloride ions and one ethene molecule in both cases. This means that solvolysis of the dinuclear Pt(II) complex is unlikely to occur in thf.

Discussion

The ^1H chemical shift and ^1H–^{195}Pt coupling constant of $PtCl_3(C_2H_4)^-$ in CD_3OD (Table I) are in good agreement with the results of Kaplan and Orchin (4.41 ppm, 66.0 Hz)[11] but not with those of Cramer (4.83 ppm, 34 Hz).[1] Cramer's NMR parameters for $PtCl_3(C_2H_4)^-$ therefore seem to be in error, although the use of 1 M methanolic HCl might affect the chemical shift. He does not claim to have observed the ^{195}Pt satellites himself but refers to Powell and Sheppard.[12] Cramer found only a broadening of the single, average signal from ethene + $PtCl_3(C_2H_4)^-$ at temperatures as low as −75 °C, while in our study the same signals were completely separated at −25 °C. It must be pointed out, however, that Cramer used a lower magnetic field (a ^1H resonance frequency of 60 MHz), and furthermore there might very well be a difference in using H^+ as a cation compared to Li^+. Because of the different chemical systems studied, it is not possible to directly compare our results with those of Cramer.

The ^1H chemical shifts of $PtCl_3(C_2H_4)^-$ (4.14 ppm) and $Pt_2Cl_4(C_2H_4)_2$ (4.39 ppm), both in thf-d_8 (Table I), show that coordinated ethene is slightly more shielded in the mononuclear

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(10) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 2622.

(11) Kaplan, P. D.; Orchin, M. *Inorg. Chem.* **1965**, *4*, 1393.

(12) Powell, B. D.; Sheppard, N. *J. Chem. Soc.* **1960**, 2519.

complex than in the dinuclear complex. This can be attributed to the different ligands trans to ethene, terminal vs bridging chloride, since the former is expected to be a better donor than the latter. A good donor trans to ethene increases the electron density on ethene in two ways: increased back-bonding from the metal ion to ethene and reduced σ-donation from ethene to the metal. Since the ^{1}H resonance frequency of ethene upon coordination is shifted more to lower frequency for platinum(II) than for palladium(II), it is confirmed that Pt(II) is a more efficient π-back-donor toward ethene than Pd(II) is. This is also reflected in the higher stability of Pt(II)–alkene complexes, compared to Pd(II)–alkene complexes.[13] The chemical shift for $PtCl_2(C_2H_4)_2$ supports Chatt's hypothesis of a trans configuration, since this requires the two ligands to share the same d orbital for back-donation, and hence will recieve less electron density than two ethenes coordinated in cis positions, where two d orbitals would be involved.

Activation parameters and rate constants for the reactions studied are shown in Table II. Results for $PtCl(acac)(C_2H_4)$[2] and $Rh(acac)(C_2H_4)_2$[14] are added for comparison. The results in Table II show that there is only a small difference in the second-order rate constants for ethene exchange in thf-d_8 between Pd(II) and Pt(II), for both $M_2Cl_4(C_2H_4)_2$ ($k_{Pd}/k_{Pt} = 2.8$) and $MCl_3(C_2H_4)^-$ ($k_{Pd}/k_{Pt} = 1.4$). This has also been observed in the exchange of cyanide ion in $M(CN)_4^{2-}$ ($k_{Pd} = 120$ M^{-1} s^{-1}, $k_{Pt} =$ 26 M^{-1} s^{-1})[15] and methyl isocyanide, CH_3NC, in $M(CH_3NC)_4^{2+}$ ($k_{Pd} = (10.6 \pm 0.7) \times 10^5$ m^{-1} s^{-1}, $k_{Pt} = (6.2 \pm 0.4) \times 10^5$ m^{-1} s^{-1})[16] (M = Pd(II) and Pt(II)). It seems that the ratio k_{Pd}/k_{Pt} decreases with increasing π-accepting ability of the entering ligand, from 5×10^6 for H_2O[17,18] to 4.6 for CN^- and 1.7 for CH_3NC.

It is interesting to note that the ethene exchange is about 10^3 times faster in the dinuclear complexes than in the corresponding mononuclear complexes. This might be an effect of the different ligand trans to ethene, bridging chloride vs terminal, but the magnitude of this effect is hard to estimate. Saito and co-workers[19] studied the trans effect in the system *trans*-$PtCl_2$(olefin)(4-X-pyridine), by varying the substituent X and following the rate of olefin exchange. They found that a decrease in the σ-donating ability of the ligand trans to the olefin (as expressed by the pK_a value of the substituted pyridine) caused an increase in olefin-exchange rate, an observation which is in qualitative agreement with our results. Elding and Gröning[20] studied the reactions between ethene and a series of aquachloroplatinates(II). They found that ethene is a poor entering ligand in these complexes, with second-order rate constants in the interval 1.1×10^{-3}–3.6×10^{-2} M^{-1} s^{-1} at 25 °C and that the reaction rates were independent of the ionic charges of the substrate complexes. Thus it is clear that the difference in ethene-exchange rate between mono- and dinuclear complexes cannot be a charge effect, as has been suggested earlier.[2] It is obvious, however, that the substrate complex plays an important role in determining the reaction rate, since ethene readily enters the (ethene)chloroplatinates in this study.

$PdCl_3(C_2H_4)^-$ and $PtCl_3(C_2H_4)^-$ have about the same exchange rates as the acetylacetonato complexes, but the relative importance of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ differs. The acac complexes have a large entropy term and a relatively small enthalpy term, while the opposite is true for the the complexes in this study. Thus, the ethene exchange seems to be entropy-controlled for the acac complexes but enthalpy-controlled for the chloro complexes. The activation entropy for $PtCl_2(C_2H_4)_2$ is based on experiments obtained from a narrow temperature interval and should be interpreted with great care, since any systematic errors will introduce a large error in $\Delta S^\ddagger$. For the other complexes, the values are more reliable and are all negative, which supports an associative reaction mechanism.

Cramer discusses two possible reaction mechanisms for the second-order ethene exchange in $PtCl_3(C_2H_4)^-$: (a) displacement of the trans chloride by ethene, to form $PtCl_2(C_2H_4)_2$ as an intermediate, which subsequently reacts with chloride to form $PtCl_3(C_2H_4)^-$ again; (b) formation of a trigonal-bipyramidal activated complex of composition $PtCl_3(C_2H_4)_2^-$, with the entering and leaving ethene ligands and the trans chloride in the equatorial plane. This activated complex then loses one ethene to form $PtCl_3(C_2H_4)^-$. These mechanisms are also applicable to $PdCl_3(C_2H_4)^-$, but the ethene exchange in the dinuclear complexes probably follows scheme b, since scheme a would require breaking the chloride bridges. Mechanism a is not very likely for the mononuclear complexes either, since no evidence of formation of $PtCl_2(C_2H_4)_2$ has been found in the NMR spectra of solutions containing $PtCl_3(C_2H_4)^-$.

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Registry No. $Pt_2Cl_4(C_2H_4)_2$, 12073-36-8; $Pd_2Cl_4(C_2H_4)_2$, 12122-75-7; $PdCl_3(C_2H_4)^-$, 34664-23-8; $PtCl_3(C_2H_4)^-$, 12275-00-2; $PtCl_2(C_2H_4)_2$, 31781-68-7.

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