Hz), −15.6 (septet, J_{PH} = 14 Hz). $^{31}P\{^1H\}$ NMR: −44.8 (s). The solution also contains unreacted *fac*-$H_3Ir(PMe_2Ph)_3$ (33%) and $IrH_4(PMe_2Ph)_3^+$ (33%). The mole percentage composition quoted is based on integration of the PMe proton resonances.

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Solvent-Exchange Mechanisms of Nonaqueous Square-Planar Tetrasolvates: A High-Pressure ^1H NMR Investigation[1]

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Solvent exchange of square-planar PdS_4^{2+} complexes, where S = DMA, DMF, MeCN, MeNC, Me_2S, Et_2S, and $Pt(MeNC)_4^{2+}$, has been studied as a function of temperature (average temperature range of 40 K) and pressure (0.1–200 MPa) by ^1H NMR line-broadening studies in diluents CD_3NO_2 and CD_3CN. The exchange rates span several orders of magnitude—from k_2^{298} = 5 m^{-1} s^{-1} for $Pd(Et_2S)_4^{2+}$ to 1.06 × 10^6 m^{-1} s^{-1} for $Pd(MeNC)_4^{2+}$—as a result of large changes in ligand nucleophilicity and of differing encumbrance of ligand and complex. Nevertheless, the volume of activation remains consistently negative with values ranging from −0.1 to −11.6 cm^3 mol^{-1} for $Pd(MeCN)_4^{2+}$ to $Pd(Et_2S)_4^{2+}$, respectively. In combination with the negative activation entropies obtained, these results indicate that regardless of the nature of the ligand the mechanism of exchange remains associative in nature.

Introduction

Ligand substitution reactions occurring at transition-metal centers have been probed largely by examining concentration and temperature dependence of the reaction rate, substituent effects in the complex, changes of solvent and medium, and changes of the nature of the entering ligands. The study of the pressure dependence of the exchange rate has increasingly found use,[2,3] and it is now firmly established that volumes of activation obtained from pressure dependence studies can make a significant contribution in deciphering the intimate nature of substitution mechanisms.[4] A large quantity of activation volume data exists for solvent exchange reactions of hexasolvento octahedral metal complexes,[5] but exchange reactions of square-planar[6,7] and particularly tetrasolvento square-planar[8,9] complexes have been much less extensively probed by high-pressure techniques. Studies of water exchange on $Pt(H_2O)_4^{2+}$ and $Pd(H_2O)_4^{2+}$, previously performed in this laboratory, give rise to negative entropies and volumes of activation.[8,9] These results supported an associative activation mode. The size of the volumes of activation were, however, small, −4.6 and −2.2 cm^3 mol^{-1}, respectively, and it was not possible therefore to discriminate between an associative interchange I_a and an associative A mechanism. We were thus prompted to extend these studies to nonaqueous solvents where the use of organic diluent would also allow rate laws to be established. A detailed kinetic study of the pressure and temperature effects on the rates of ligand exchange of various MS_4^{2+} complexes was carried out according to eq 1, where S = DMA, DMF, MeCN, MeNC, Me_2S, and Et_2S.

$$MS_4^{2+} + 4S^* \rightleftarrows MS_4^{*2+} + 4S \tag{1}$$

Palladium was chosen as the metal of preference because of the generally observed lability of Pd(II) complexes compared to Pt(II) complexes. For comparison purposes, both metal ions were studied with methyl isocyanide as ligand.

Experimental Section

Materials and Preparation of Solutions. $[Pd(MeCN)_4](BF_4)_2$ was prepared according to the method described in the literature[10] or was obtained commercially (Fluka, purum). The new complexes, $[Pd(DMA)_4](BF_4)_2$, $[Pd(DMF)_4](BF_4)_2$, $[Pd(Me_2S)_4](BF_4)_2$, and $[Pd(Et_2S)_4](BF_4)_2$, were prepared by dissolution of $[Pd(MeCN)_4](BF_4)_2$ in an excess of dimethylacetamide (DMA) (Fluka, p.a.), dimethylformamide (DMF) (Fluka, p.a.), dimethyl sulfide (Me_2S) (Fluka, purum), and diethyl sulfide (Et_2S) (Fluka, purum), respectively, followed by precipitation with ether. $[Pd(MeNC)_4](BF_4)_2$ was prepared by adding a slight excess of MeNC (methyl isocyanide)[11] to a solution of $[Pd(MeCN)_4](BF_4)_2$ in acetonitrile; after the solvent and excess ligand were pumped off, the residue was redissolved in a small volume of acetonitrile, the solution was filtered, and $[Pd(MeNC)_4](BF_4)_2$ was obtained as white crystals on cooling. $[Pt(MeNC)_4](PF_6)_2$ was prepared by the literature method.[12]

The complexes were dried under vacuum for several hours, and the purity was checked by ^1H NMR spectroscopy. The coordination number, n_c, was obtained by integration of the free and bound NMR signals, except in the case of MeNC in which fast exchange precluded this me-

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Table I. Exchange Rate Constants and Activation Parameters for Solvent Exchange on PdS_4^{2+} and PtS_4^{2+} Complexes[a]

complex	$k_2^{298}/m^{-1}\ s^{-1}$	ΔH^*/kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1} (T range/K)	ΔV^*/cm^3 mol^{-1} (T/K)	n_c[b]
$Pd(NH_3)_4^{2+}$[h,j]	1.6×10^{-2}[i]	67.3	−54.1 (273–298)		
$Pd(Et_2S)_4^{2+}$[c]	5.0 ± 0.6	50.4 ± 2.4	−62.8 ± 6.9 (323–369)	−11.6 ± 0.4 (358)	3.99
$Pd(H_2O)_4^{2+}$[e,f]	10.2 ± 0.7	49.5 ± 1.9	−60 ± 6 (239–345)	−2.2 ± 0.2 (324)	
$Pd(DMA)_4^{2+}$[c]	34.8 ± 1.0	43.2 ± 1.3	−76.2 ± 4.2 (275–332)	−2.8 ± 0.2 (303)	3.99
$Pd(MeCN)_4^{2+}$[c]	48.8 ± 1.3	45.4 ± 0.8	−60.1 ± 2.4 (285–368)	−0.1 ± 0.4 (336)	3.93
$Pd(DMF)_4^{2+}$[c]	153 ± 6	41.9 ± 1.0	−62.3 ± 3.4 (272–345)	−0.2 ± 0.6 (305)	3.96
$Pd(Me_2S)_4^{2+}$[c]	2140 ± 53	31.9 ± 0.6	−112.6 ± 2.0 (248–355)	−9.4 ± 0.3 (303)	4.02
$Pd(MeNC)_4^{2+}$[d]	$(10.6 \pm 0.7) \times 10^5$	16.4 ± 1.1	−74.5 ± 4.1 (234–314)	−3.1 ± 0.1 (264)	3.93
$Pt(H_2O)_4^{2+}$[e,g]	$(7.1 \pm 0.5) \times 10^{-6}$	89.7 ± 2.4	−43 ± 8 (273–334)	−4.6 ± 0.2 (297)	
$Pt(MeNC)_4^{2+}$[d]	$(6.2 \pm 0.4) \times 10^5$	13.8 ± 1.1	−87.9 ± 3.9 (231–316)	−3.7 ± 0.1 (264)	4.08

[a] Quoted errors are one standard deviation. [b] Coordination number. [c] In diluent CD_3NO_2. [d] In diluent CD_3CN. [e] Rate constant and ΔS^* for the exchange of a particular water molecule recalculated to second-order units, i.e.: $k_{ex}^{298}/55$. [f] Reference 8. [g] Reference 9. [h] In diluent H_2O. [i] k_2 in L mol^{-1} s^{-1}. [j] Reference 28.

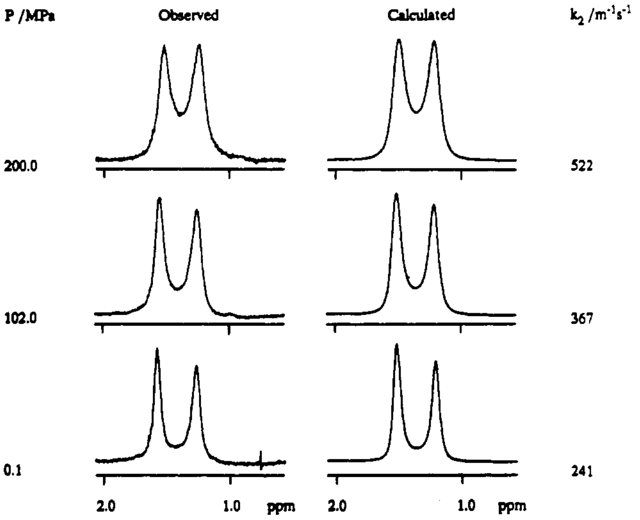

Figure 1. Observed and calculated 400-MHz ^1H NMR spectra for Et_2S exchange on $Pd(Et_2S)_4(BF_4)_2$ at different pressures ($[Pd(Et_2S)_4(BF_4)_2]$ = 0.062 m, $[Et_2S]$ = 0.234 m, T = 357.8 K). The signals correspond to the methyl group: δ_C = 1.53 ppm, δ_F = 1.21 ppm, and $J(^1H-^1H)$ = 7.3 Hz.

thod. Instead, n_c was calculated from the chemical shift of the coalesced signal. In all cases n_c was found to be 4. All solvents were used as received but were stored over 4-Å molecular sieves for 48 h before use. The solutions used for NMR measurements were freshly prepared in a nitrogen-filled glovebox. Deuterated nitromethane (CD_3NO_2, Ciba-Geigy) or acetonitrile (CD_3CN, Glaser) was added to the solutions as inert diluent as well as internal lock substance. 2% CH_2Cl_2 or $CHCl_3$ was used as internal line width and chemical shift references. TMS could not be used because it reacts with the Pd^{2+} solvates, inducing precipitation of palladium metal. All concentrations are expressed in moles per kilogram of solvent (m = mol kg^{-1}).

NMR Measurements. Ambient-pressure spectra were recorded on a Bruker WP-60 spectrometer working at 60 MHz, a Bruker CXP-200 spectrometer (cryomagnet 4.7 T) working at 200 MHz, or a Bruker AM-400 spectrometer (cryomagnet 9.4 T) working at 400 MHz. The temperature was measured before and after spectral accumulation by substituting the sample with a Pt-100 resistance[13] and was constant within ±0.2 K.

Spectra at variable pressure were recorded by using a Bruker AM-400 (CXP-200) spectrometer working at 400 MHz (200 MHz). Measurements were made up to 200 MPa by using home-built high-pressure probes, which have previously been described.[14,15] A built-in platinum resistor allows temperature measurements with an accuracy of 1 K after all corrections.[16] By pumping thermostated synthetic oil through the bomb, the temperature was stabilized to ±0.2 K.

Computation Method. The rate constants reported were calculated from line-broadened spectra and were treated by a complete line shape analysis based on the Kubo-Sack formalism, using modified Block equations.[17] The analysis of the experimental data using the required equations was done by a nonlinear least-squares program fitting the desired parameter values. Reported errors are one standard deviation.

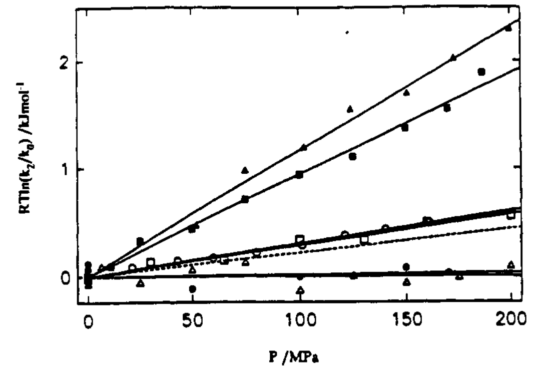

Figure 2. Pressure effect on the normalized natural logarithm of the second-order rate constant for solvent exchange on PdS_4^{2+} (Et_2S = ▲, DMA = □, MeCN = △, DMF = ●, Me_2S = ■, MeNC = ○, H_2O = dashed line[8]). The equation $\ln k_2 = \ln k_0 - (\Delta V^* P/RT)$, where k_0 and ΔV^* are adjustable parameters, was fitted to the data, by using a least-squares routine.

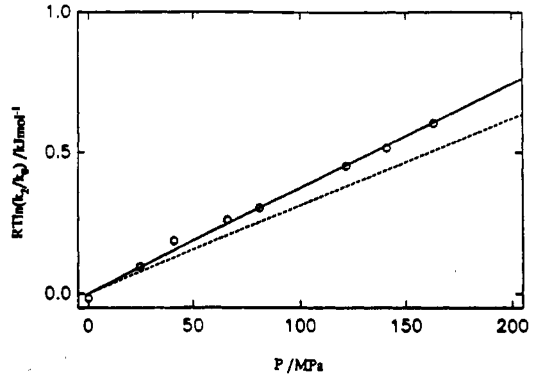

Figure 3. Pressure effect on the normalized natural logarithm of the second-order rate constant for solvent exchange on PtS_4^{2+} (MeNC = ○, H_2O = dashed line[9]). The equation $\ln k_2 = \ln k_0 - (\Delta V^* P/RT)$, where k_0 and ΔV^* are adjustable parameters, was fitted to the data, by using a least-squares routine.

Results and Discussion

The rates of solvent exchange on the square-planar palladium(II) and platinum(II) tetrasolvates, shown in Table I, span several orders of magnitude. Because the exchanges were followed in an organic diluent (nitromethane or acetonitrile) the ligand concentration could be varied, thus allowing the rate law to be established. In all cases the exchange is first order with respect to free ligand concentration with negligible intercepts in k_{obs} versus [S] linear plots. The rate law therefore follows the form shown

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in eq 2, where k_{obs} is the observed first-order rate constant (s^{-1})

$$k_{obs} = k_2[S] \qquad (2)$$

for the exchange of a particular solvent molecule S in MS_4^{2+} according to eq 1. The temperature influence on the rate constants was measured over an average temperature range of at least 40 K. The data were fitted to the Eyring equation with ΔH^* and ΔS^* as adjustable parameters. Figure 1 shows the effect of pressure on the NMR spectra for the Et_2S exchange. As the pressure is increased from 0.1 to 200 MPa, the signals merge together toward a coalescence. This acceleration of the exchange rate with pressure was observed for all the ligands studied and gives negative volumes of activation. Figures 2 and 3 present the pressure dependences of the normalized second-order rate constants. Using a diluent of high dielectric constant such as CD_3NO_2 or CD_3CN and uncharged ligands should minimize changes in electrostriction along the reaction path. The volumes of activation reported in Table I thus reflect primarily the changes of molecular volumes on going to the transition state. These values will be discussed below.

The effect of ligand size on substitution rate is evident from Table I. The soft, polarizable Me_2S and Et_2S ligands are of approximately equal basicity,[18] but the less sterically encumbered Me_2S complex reacts 10^3 times faster than the Et_2S complex. Clearly, the bulkiness of the ligand and the substrate combined determine whether the rate of the substitution is under electronic or steric control. This is further evidenced by the fact that DMA (donor number[19] DN = 27.8), though a stronger nucleophile than DMF (DN = 27.0), reacts more slowly. It appears that the extra methyl group of DMA compared to DMF creates enough steric encumbrance to reverse the order of reactivity expected on purely electronic grounds. These observations are strong support for an associative activation mode.

Ligands with hard donor atoms such as H_2O, MeCN, and amides have similar exchange rates. The much softer Me_2S and MeNC ligands undergo substitution more rapidly, indicating that in the absence of steric effects, ligand nucleophilicity and the trans effect determine reactivity. The enhanced reactivity of the MeNC complexes (approximately 10^3 times more rapid than Me_2S) may be due to a stabilization of a five-coordinate transition state or intermediate by π back-bonding from the metal to the ligand. A five-coordinate intermediate has been isolated in the substitution of coordinated methyl isocyanide by iodide in $[Pt(PPh_3)_2(MeNC)_2](BF_4)_2$.[20] It can be added that IR studies[21] have shown that the C≡N stretching vibration of the complex $M(MeNC)_4^{2+}$ has a higher value than that found for free methyl isocyanide,[22] indicating that insignificant back-donation from the metal to the ligand is occurring in the ground state. It is interesting to compare the discriminating ability of Pd^{2+} and Pt^{2+}. With a relatively hard ligand such as H_2O, $Pd(H_2O)_4^{2+}$ undergoes exchange 10^6 times more rapidly than $Pt(H_2O)_4^{2+}$. In contrast, with soft ligands such as CN^- or MeNC the rates of exchange are virtually the same ($M(CN)_4^{2-}$: $k_{Pd} = 120\ M^{-1}\ s^{-1}$, $k_{Pt} = 26\ M^{-1}\ s^{-1}$).[23]

From Table I it is clear that with the exception of the sulfide ligands, Me_2S and Et_2S, the volumes of activation for the solvent exchange on Pt^{2+} and Pd^{2+} tetrasolvates are invariably small and negative, being within the range −0.1 to −3.1 $cm^3\ mol^{-1}$ in all cases.[24] The interpretation of these values in molecular terms is not trivial, as these solvates are subject to large changes in coordination geometry on going from ground state to transition state. Tetrasolvate species may have their axial sites occupied by loosely bound solvent molecules. The loss of these two axially bound solvent molecules together with formation of a new bond in going to a five-coordinate transition state or intermediate involving concerted exchange of ligand may mean that through compensation, the overall volume change is small or negligible, making it difficult to distinguish between an associative interchange I_a and a limiting A mechanism. The consistently negative values together with the previously discussed observations, do however allow an unambiguous assignment of an associative activation mode. The magnitudes of the ΔV^* values for Me_2S and Et_2S are worthy of comment. The values of −9.4 and −11.6 $cm^3\ mol^{-1}$ are by far the largest obtained in the series of tetrasolvates studied. The largest value for Et_2S may be explained in terms of steric encumbrance. It is unlikely in the case of $Pd(Et_2S)_4^{2+}$ that two molecules of solvent will occupy sites above and below the plane defined by the complex. Formation of a pentacoordinate transition state in this case will lead to a significant decrease in volume. A similar observation has been noted for water exchange on $Pd(dien)H_2O^{2+}$ complexes.[26,27] The parent complex has an activation volume of −2.8 $cm^3\ mol^{-1}$, but the value for the much more sterically encumbered $Pd(Et_5dien)H_2O^{2+}$ complex is −7.7 $cm^3\ mol^{-1}$.

In conclusion, it is difficult to distinguish the type of associative mechanism involved, A or I_a, but it is clear from the ΔV^* and ΔS^* data (note that there is no direct relationship between the two), from steric, nucleophilic, and trans effects, and from the rate law, that square-planar tetrasolvate species undergo exchange via an associative activation mode.

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Registry No. $Pd(Et_2S)_4(BF_4)_2$, 131832-53-6; $Pd(DMA)_4(BF_4)_2$, 131832-54-7; $Pd(MeCN)_4(BF_4)_2$, 21797-13-7; $Pd(DMF)_4(BF_4)_2$, 52304-88-8; $Pd(Me_2S)_4(BF_4)_2$, 131832-56-9; $Pt(MeNC)_4(PF_6)_2$, 38317-61-2; $Pd(MeNC)_4(BF_4)_2$, 131832-57-0.

Supplementary Material Available: Tables of second-order rate constants and chemical shifts for the solvent exchange on MS_4^{2+} as a function of temperature (Tables SI–SVII) and pressure (Tables SVIII–SXIV) and observed and second-order rate constants as a function of concentration of free ligand (Tables SXV–SXIX) (10 pages). Ordering information is given on any current masthead page.

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