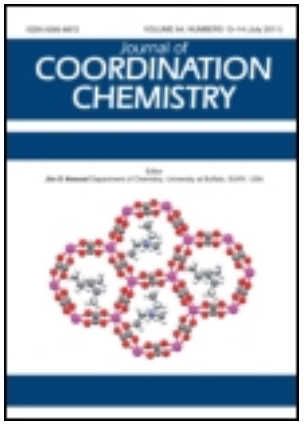

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Effect of solvent on the exchange of ethylene for propylene on cis-$PtCl_2(C_3H_6)(TPPTS)$, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$

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Published online: 18 Oct 2011.

To cite this article: Jeffrey Dudziak & Jim D. Atwood (2011) Effect of solvent on the exchange of ethylene for propylene on cis-$PtCl_2(C_3H_6)(TPPTS)$, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$, Journal of Coordination Chemistry, 64:20, 3575-3584, DOI: 10.1080/00958972.2011.624597

To link to this article: http://dx.doi.org/10.1080/00958972.2011.624597

Journal of Coordination Chemistry
Vol. 64, No. 20, 20 October 2011, 3575–3584

Effect of solvent on the exchange of ethylene for propylene on *cis*-$PtCl_2(C_3H_6)$(TPPTS), TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$

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(*Received 31 August 2011; in final form 2 September 2011*)

To further understand the effect of water as a solvent in organometallic reactions, the lability of η^2-alkenes coordinated to platinum(II) phosphine complexes has been studied in water and chloroform as a comparison of solvent effects on the exchange kinetics and alkene complex stability. ^{1}H NMR techniques with both deuterated chloroform and a deuterium oxide/deuterated methanol mixture as solvent systems were used at temperatures as low as −50°C. Reaction of *cis*-$PtCl_2L(\eta^2\text{-}C_3H_6)$ [L = PPh_3 (triphenylphosphine) (**1a**), TPPTS (tris(*m*-sulfonatophenyl)phosphine) **1b**] with ethylene to form *cis*-$PtCl_2L(\eta^2\text{-}C_2H_4)$ (**2 a, b**) was observed with dependence on the rate by starting platinum complex and ethylene. The role of water on this reaction, as well as its effect on the equilibrium, will be discussed. The equilibrium constant shows preference for coordination of ethylene and the temperature dependence indicates the reaction is entropy controlled.

Keywords: Exchange kinetics; Platinum; Water as solvent

1. Introduction

One of the most sought after goals of modern synthesis and catalysis is to employ ''green'' chemical methods to minimize hazardous waste production, increase atom efficiency and catalyst activity, and decrease the likelihood of chemical accidents [1]. While not the only way to accomplish these goals, one of the most discussed methods is to use solvents that are relatively environmentally benign and minimize the risk of incidents, the ideal solvent for this being water [2].

In recent years, our group has taken interest in the chemistry of water soluble TPPTS complexes of platinum, with their synthesis, reactivity, and catalytic viability having been studied [3–9]. These studies included the use of Pt(TPPTS) complexes as Wacker oxidation-type catalysts and also to catalyze the hydration of alkynes. With this in mind, we wanted to compare complexes of triphenylphosphine and its sulfonated counterpart, TPPTS, so that a nearly identical reaction in both an organic solvent (chloroform) and in water could quantify any beneficial or detrimental effects of the change in solvent system. To our knowledge, this type of direct comparison has never been reported for this type of system where the change in ligand should affect only the

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ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2011.624597

solubility of the complexes and any kinetic differences arising from the solvent system should present itself through the observed rate constant.

Even though solvent system effects on alkene exchange have not been studied, the lability of η^2-alkenes coordinated to Pt(II) has been investigated. Comparisons of ethylene lability on platinum and palladium complexes have shown a minimal effect of the solvent assisted pathway with THF or methanol on the overall rate of ethylene substitution [10]. Other studies have also investigated the mechanism of ethylene substitution in both chloro ethylene platinum(II) complexes and cyclometallated platinum(II) complexes [11, 12].

Here we report the solvent comparisons of the ligand exchange of propylene for ethylene in complexes of the form *cis*-$PtCl_2L(\eta^2\text{-}C_3H_6)$ [$L = PPh_3$ (triphenylphosphine), TPPTS (tris(*m*-sulfonatophenyl)phosphine)]. We also investigate the mechanistic preferences based on the solvent choice and reaction temperature.

2. Experimental

2.1. *Materials*

All materials were used as received unless otherwise noted. Hexachloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) was purchased from Strem Chemicals. Ethylene and propylene were purchased from Matheson and Praxair. Triphenylphosphine was purchased from Aldrich Chemicals and recrystallized from ethanol prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc.; methanol, toluene, and chloroform were purchased from EMD Chemicals, Inc., diethyl ether was purchased from J.T. Baker, and all other solvents were purchased from Fischer Chemicals.

2.2. *Methods*

^1H and ^{31}P NMR spectra were recorded on a Varian VXR Inova-400 MHz and Mercury-300 NMR spectrometers at room temperature unless otherwise stated. ^{31}P NMR spectra were proton decoupled and referenced to an external standard of 85% phosphoric acid in D_2O. ^1H NMR spectra were referenced to the known residual solvent peaks [13]. All chemical shifts (δ) are reported in parts per million and all coupling constants (J) are reported in Hz. All NMR tubes used in kinetics experiments were purchased from Wilmad LabGlass. The variable temperature NMR studies were set up and run using the Agilent VNMRJ software, using standard temperature calibrations. The temperatures in the probe were maintained using an FTS Airjet cooler attached to the spectrometer.

2.3. *Synthesis*

$PtCl_2$ [14], *cis*-$PtCl_2PPh_3(C_2H_4)$ [15] (**2a**), and *cis*-$PtCl_2PPh_3(C_3H_6)$ [15] (**1a**) were prepared *via* literature methods. TPPTS was prepared and used after analysis by ^{31}P NMR to assess purity.

2.3.1. *cis*-$PtCl_2TPPTS(C_2H_4)$ (2b). While the synthesis of this complex has been previously reported [9], the yield was improved from 48% to 85.7% (based on starting $PtCl_2$) and is described here. Into a lipless beaker was placed 0.20 g (0.351 mmol) of TPPTS, 0.094 g (0.353 mmol) $PtCl_2$, and 5 mL of DMF. The reactor was flushed twice with ethylene, pressurized with 500 psi of ethylene, and stirred under pressure. After 3 days, the reactor was depressurized, and the resulting brown suspension was filtered through a fine frit. The resulting yellow solution was treated with 250 mL of diethyl ether to induce precipitation. The white suspension was filtered through a medium frit. While filtering, the white solid was continually washed with diethyl ether to remove as much residual DMF as possible. Once the ether washes were clear, the sample was dried briefly under filtration and was then placed under vacuum overnight to dry while still on the frit. $^{31}P\{^1H\}$ NMR (D_2O): 12.96 ppm, ^1H NMR (D_2O) 4.0 (br).

2.3.2. *cis*-$PtCl_2TPPTS(C_3H_6)$ (1b). This previously unreported complex was prepared by two methods; one analogous to the synthesis of *cis*-$PtCl_2PPh_3(C_2H_4)$ and the other to that of *cis*-$PtCl_2PPh_3(C_3H_6)$ [9, 15]. In the first method, equimolar quantities of $PtCl_2$ and TPPTS were dissolved in DMF and placed in a lipless beaker. The beaker was then sealed in a Parr pressure reactor and pressurized with 100 psi of propylene. After stirring for 5 days, the reactor was depressurized and the resulting dark brown solution filtered through a fine frit. The now yellow filtrate was then treated with 400 mL of diethyl ether to remove any residual DMF. Without the extra wash, the product displayed a tendency to decompose. Finally, the solid was dried under vacuum overnight. This method led to a 75% yield, but was unreliable and often led to side product formation.

The second synthesis, which proved to be more reliable, was ligand exchange from *cis*-$PtCl_2TPPTS(C_2H_4)$. In a lipless beaker, ~0.11 g (0.127 mmol) of **2b** was dissolved in 10 mL of DMF, sealed in a Parr apparatus, and stirred under 100 psi of propylene for 40 h at room temperature. Upon depressurizing the reactor, the resulting yellow solution was treated with 200 mL of diethyl ether to induce precipitation. The resulting white solid was collected on a medium frit, washed repeatedly with 20 mL portions of diethyl ether, and immediately placed under vacuum to dry overnight. Some DMF was still present on the complex, even after repeated washing and extended drying. The DMF is likely coordinating, probably through TPPTS, or the sodium counter ions. This is supported by the fact that the ^1H NMR DMF peaks are slightly shifted downfield. This method afforded up to a 77% yield based on starting complex as determined *via* NMR. When dissolved in water, the complex undergoes alkene loss, with a disappearance of the alkene NMR signal within hours. Stability is increased when the solution is sealed in an NMR tube with an atmosphere of propylene. After being dried in the synthesis, the complex is stable for months at a time without special handling. $^{31}P\{^1H\}$ NMR (D_2O; δ (ppm): 12.96, ^1H NMR (D_2O; δ (ppm)): 4.35 (br), 3.57 (br), 1.80 (s).

2.4. *Kinetics experiments*

All kinetics experiments were carried out on an NMR scale. The NMR tube was charged with ~0.01–0.02 g of *cis*-$PtCl_2(C_3H_6)L$ dissolved in 0.2 mL of solvent. For **1a**, deuterated chloroform was used as the solvent, and for **1b**, a mixture of deuterated

methanol and deuterium oxide was used (50/50 by mass for experiments run at −30°C, 70/30 by mass CD_3OD/D_2O for −50°C). After dissolving the starting material, the resulting solution was frozen in liquid nitrogen and another 0.5 mL of ethylene saturated solvent was added and also frozen. The samples were kept frozen in liquid nitrogen until being placed in the NMR instrument. NMR scans were run sequentially for at least 10 min to reach completion.

To determine the k_{obs} value, the following method was used. The midpoint of each scan time was used for the time scale. The methyl protons on the coordinated propylene were used to track the concentration of starting material remaining. To account for any error in the integration between the scans and for the tendency of the reactions to go to equilibrium rather than 100% completion, this concentration was represented by the following equation:

$$\frac{(\text{Area of coordinated alkene})_n}{(\text{Internal standard})_n} - \frac{(\text{Area of coordinated alkene})_{eq}}{(\text{Internal standard})_{eq}} = A$$

where n indicates the time at the midpoint of the scan and eq represents the scan at which the sample reaches equilibrium. For reactions involving **1a**, the internal standard used was the aromatic region and for reactions involving **1b**, a peak from the residual DMF was used, since both of these values remain constant throughout the experiment. This method also allows for a zero point ($t = 0$) to be calculated since the ratio of the methyl protons on the coordinated propylene to the aromatic protons is 3/15 (0.2) in **1a**. In some cases, the first scan was distorted if the solvent was not completely melted.

Owing to the possibility for dinuclear side products in **1b**, the aromatic region was not used in the calculation of the zero point. Instead, the area of one of the residual DMF peaks served as the internal reference peak. This was referenced to the sum of the area of the free and the coordinated methyl protons from propylene in the first clean scan of the sample. This ratio of the area of methyl protons : DMF protons trended to 0.4 as the starting point, or ~2.5 DMF molecules per propylene ligand.

Once these ratios were established and applied to all the scans for a sample, the data were treated as pseudo first order and the plot of ln(A) *vs.* time (s) yields a plot that is linear over the initial rate of the reaction. The slope over this interval yielded k_{obs} for the sample, which was then averaged for each temperature and solvent system examined.

2.5. *Equilibrium studies*

In order to determine the equilibrium constants for the reactions of interest, NMR tubes were charged with ~6.5 mg of starting complex and the appropriate solvent (per the kinetics experiments) that had been saturated with a 50/50 mix (by pressure) of ethylene and propylene, and was allowed to react *via* the following reaction:

$$PtCl_2L(C_3H_6) + C_2H_4 \leftrightarrow PtCl_2L(C_2H_4) + C_3H_6. \quad (1)$$

The samples were then analyzed by NMR at −50°C, −30°C, and 20°C and the equilibrium constants were calculated based on the relative integrations.

3. Results and discussion

To our knowledge, there have been no studies of the effects of solvent on the exchange of η^2-alkenes of platinum(II) complexes. In order to accomplish this, we have developed a method that utilizes triphenylphosphine and its sulfonated form, TPPTS, to change the solubility of the complexes employed herein, while minimizing any effects from change in phosphine.

3.1. *NMR studies*

Since there is considerable overlap of the hydrogens of the η^2-bound carbons in both the coordinated ethylene and propylene, the chemical shift of the propylene methyl group was used to track the alkene exchange reaction, since there is a difference of 0.2–0.3 ppm in the chemical shifts of the coordinated and uncoordinated alkenes. Previous work has shown the preference of shorter chain alkenes in square planar platinum(II) compounds, while the substitution to a longer chain alkene involves higher pressures or concentrations of the incoming alkene than are useable in NMR conditions, which led to the decision to exchange from propylene to ethylene [16–18]. The proposed reaction mechanism which is equivalent to the standard square planar exchange mechanism is shown in figure 1, where scheme 1 represents the solvent assisted pathway and scheme 2 represents the associative pathway. In these reactions, the rate-determining steps are shown as k_1 and k_2 for scheme 1 and scheme 2, respectively. Both pathways can occur simultaneously and, when the reaction is performed under pseudo-first order conditions with an excess of ethylene, the rate law is expressed as

$$\text{Rate} = k_{\text{obs}}[\text{PtCl}_2\text{L}(\text{C}_3\text{H}_6)], \tag{2}$$

where

$$k_{\text{obs}} = k_1 + k_2[\text{C}_2\text{H}_4]. \tag{3}$$

Reactions involving **1a** were carried out at -10°C, -30°C, and -50°C. At -10°C, the dissolution of ethylene into chloroform appears to be a limiting factor to the reaction rate. Normally under these conditions, the NMR signal for the free ethylene could be seen to almost completely disappear, while the reaction continued to proceed, presumably at the same rate at which the ethylene dissolved into solution. This led to the decision to run the reaction at -30°C, which produced more reliable results.

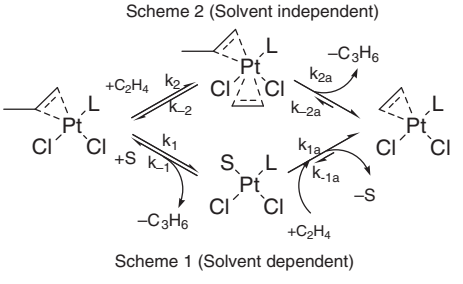

Figure 1. Reaction schemes for alkene exchange.

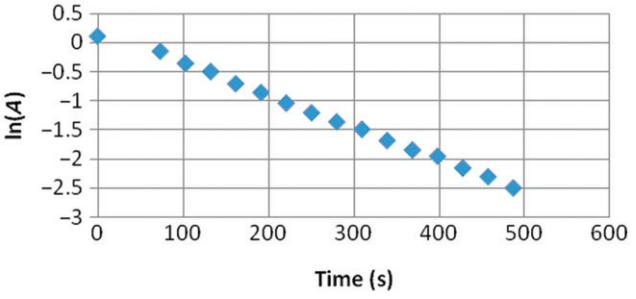

Figure 2. Plot of ln(*A*) *vs.* time for the reaction of **1a** with ethylene at −50°C.

Table 1. Average k_{obs} (s^{-1}) values for comparison kinetics.

Temperature	$CDCl_3$	CD_3OD/D_2O
−30°C	$(2.6 \pm 0.3)*10^{-2}$	$(1.9 \pm 0.2)*10^{-2}$
−50°C	$(1.5 \pm 0.2)*10^{-2}$	$(5.4 \pm 0.3)*10^{-3}$

The reactions performed at −50°C also provided reliable results, an example of which is shown in figure 2.

The calculated k_{obs} values for these experiments at −30°C and −50°C are given in table 1. The initial rate $= k_{obs}$ [$PtCl_2(C_3H_6)$(TPPTS)] values are shown in table 2. These data show that, under the same temperature conditions, the overall rate of reaction is doubled in chloroform over CD_3OD/D_2O at −30°C and by ~3*x* at −50°C. With the k_{obs} value determined, that information can be used to determine the k_1 and k_2 as long as the concentration of ethylene can be determined, as shown by equation (3). By plotting k_{obs} *versus* $[C_2H_4]_i$, k_1 is represented as the *y*-intercept and k_2 is represented by the slope of the resulting line, as shown in figures 3 and 4. The results of these plots are shown in table 3 for the chloroform system at −30°C and for both systems at −50°C. Data for the CD_3OD/D_2O system at −30°C was uncertain due to overlap between the chemical shifts of the free ethylene and the solvent peak for water. From these *k* values, it is shown that in the reaction run in chloroform, the solvent assisted pathway (k_1) becomes less significant as the temperature decreases (essentially zero at −50°C within error limits) compared to the k_2 value, which also sees a decrease in magnitude between −30°C and −50°C, but becomes even more predominant in determining k_{obs}. This is likely due to the increased solubility of ethylene at the lower temperatures, which should also account for the increase in the relative rate of reaction. For the D_2O/CD_3OD system at −50°C, the k_{obs} is dominated by the solvent independent pathway, but the solvent assisted pathway plays a significant role.

In comparing the reactions for L = PPh_3 in $CDCl_3$ and L = TPPTS in CD_3OD/D_2O, there are two factors that affect the reactions in the same direction: (1) For the solvent assisted (k_1) path CD_3OD/D_2O are much more effective at coordinating to Pt(II) than is $CDCl_3$ such that the k_1 path should be much more important in CD_3OD/D_2O, as observed in table 3. (2) Ethylene is considerably more soluble in $CDCl_3$ than in CD_3OD/D_2O (approximately twice the solubility). This added concentration of C_2H_4

Table 2. Average initial rates (mol L^{-1} s^{-1}) of reaction (1), obtained by rate = k_{obs} [$PtCl_2(C_3H_6)$(TPPTS)].

Temperature	$CDCl_3$	CD_3OD/D_2O
−30°C	$8.3*10^{-4}$	$4.3*10^{-4}$
−50°C	$2.7*10^{-4}$	$9.4*10^{-5}$

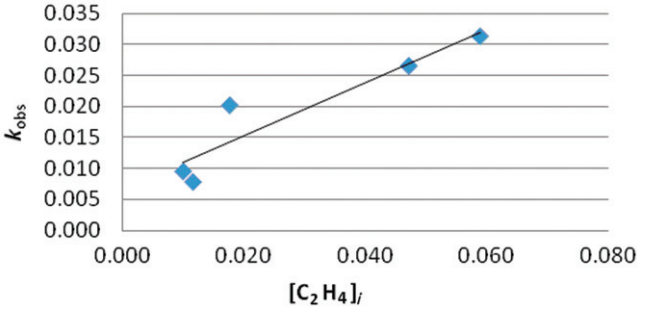

Figure 3. k_{obs} *vs.* $[C_2H_4]_i$ for L = PPh_3, $T = -30°C$.

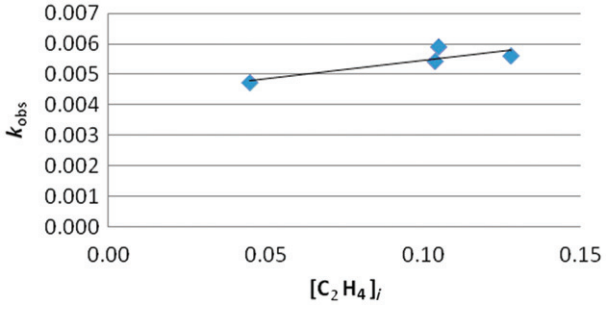

Figure 4. k_{obs} *vs.* $[C_2H_4]_i$ for L = TPPTS, $T = -50°C$.

Table 3. Calculated k_1 and k_2 values.

Solvent	Temperature	k_1 (s^{-1})	k_2 ((mol L^{-1})$^{-1}$$s^{-1}$)	$[C_2H_4]_i$ (mol L^{-1})
$CDCl_3$	−30°C	$(7 \pm 3)*10^{-3}$	$(4.3 \pm 0.9)*10^{-1}$	$2.90*10^{-2}$
$CDCl_3$	−50°C	$(6.0 \pm 10)*10^{-4}$	$(7.7 \pm 0.5)*10^{-2}$	$1.84*10^{-1}$
D_2O/CD_3OD	−50°C	$(4.3 \pm 0.5)*10^{-3}$	$(1.2 \pm 0.5)*10^{-2}$	$9.54*10^{-2}$

makes the k_2 pathway enhanced in $CDCl_3$ over CD_3OD/D_2O as also observed in table 3.

These two factors essentially represent a change in mechanism between the two solvent systems. In $CDCl_3$ the k_2 term dominates, with k_2 $[C_2H_4]$ almost twice the value of k_1 at −30°C; at −50°C in $CDCl_3$ the k_1 is essentially zero such that the k_2 $[C_2H_4]$ is at least contributing 90%. In CD_3OD/D_2O, the k_1 term contributes about 80% to the

total rate. Thus direct comparison of a reaction rate between the two solvent systems depends significantly on the ethylene concentration. At high pressures the reaction rate would be larger in $CDCl_3$ while at low pressures of C_2H_4 the reaction rate in CD_3OD/D_2O would be larger. At the pressure we are using ($\sim$0.6 atm) at -50°C, the rate is somewhat faster in $CDCl_3$, while at -30°C (lower $[C_2H_4]$ in solution) the rates are about the same in the two solvent systems.

It has been previously observed that both k_1 and k_2 are affected by solvent. Since k_1 depends on nucleophilic attack on platinum by the solvent, that dependence is obvious. A previous study on chloride exchange showed a 10^7 dependence of k_2 between CCl_4 and DMF as solvents [19]. This large dependence was attributed to unsolvated Cl^- being a better nucleophile [19]. In our case the change from $CDCl_3$ to D_2O/CD_3OD is much smaller, only a factor of seven less. Solvation of C_2H_4 would not be expected to be significant, but the platinum complex, with two chlorides and three sulfonates would be expected to be significantly solvated through hydrogen-bonding in D_2O/CD_3OD accounting for the somewhat smaller k_2 term in D_2O/CD_3OD.

A study of ethylene exchange by line broadening on platinum(II) reinforces some of the features we observe for reaction (1) [12]: (1) The reactions of alkenes with Pt(II) are very rapid at room temperature. We worked at -30°C to -50°C and Plutino *et al.* report $k_2 = 10^4$–$10^5\,s^{-1}\,(mol\,L^{-1})^{-1}$ at room temperature for ethylene exchange on cyclometallated platinum complexes [12]. (2) The rates depend on the [alkene] and in $CDCl_3$ the k_1 term is negligible.

3.2. *Equilibrium studies and thermodynamic properties*

Equilibrium values were also quantified for reaction (1) in order to determine the extent of ethylene preference in the reactions that were studied at varying temperatures. The results of these experiments are shown in table 4. Based on this information, there is a higher dependence of K_{eq} on temperature in chloroform than in CD_3OD/D_2O. In both systems, ethylene coordination is shown to be preferred over propylene. From this information it is also seen that the propylene complex is relatively more stable for the triphenylphosphine when compared to the TPPTS containing complexes. This may explain why **1a** tends to be more stable in solution than **1b**.

Using these data, it was possible to determine the Gibbs free energy, enthalpy, and entropy for the alkene exchange reaction. To calculate these values, the free energy values were assumed to be temperature dependent while the enthalpy and entropy values were assumed to remain relatively constant over the course of the temperature range studied [20]. The results are shown in table 5. The thermodynamic parameters presented in table 5 provide quantification of the spontaneity of the reaction taking place and also show that the alkene exchange (reaction (1)) is entropically driven, as expected from the larger entropy of free propylene over free ethylene.

4. Summary

We have used PPh_3 and TPPTS to compare the effects that solvent has on alkene exchange. When the reaction is performed in chloroform, lower temperatures lead to

Table 4. K_{eq} values for ligand exchange.

Temperature	$CDCl_3$	CD_3OD/D_2O
20°C	75 ± 9	120 ± 6
−30°C	59 ± 5	116 ± 3
−50°C	48 ± 1	110 ± 5

Table 5. Thermodynamic parameters for the reaction of $PtCl_2(C_3H_6)L$ with C_2H_4.

Value	$L = PPh_3$	L = TPPTS
ΔG^o, $T = -50$°C (kJ∗mol^{-1})	−7.17 ± 0.07	−8.71 ± 0.09
ΔG^o, $T = -30$°C (kJ∗mol^{-1})	−8.3 ± 0.2	−9.61 ± 0.06
ΔG^o, $T = 20$°C (kJ∗mol^{-1})	−10.6 ± 0.3	−11.7 ± 0.1
ΔH^o (kJ∗mol^{-1})	3.5 ± 0.5	0.7 ± 0.2
ΔS^o (J∗mol^{-1}∗K^{-1})	48 ± 2	42.1 ± 0.9

the dominance of the $[C_2H_4]$-dependent pathway, which is aided by the increased solubility of ethylene in solution at lower temperatures. When the exchange is performed in methanol/water, the solvent assisted pathway is dominant. In reaction (1), the relative rates between $CDCl_3$ and CD_3OD/D_2O depend on the $[C_2H_4]$ such that at −50°C the reaction in $CDCl_3$ is faster and at room temperature, reaction in CD_3OD/D_2O would be faster. We have also demonstrated reliable syntheses of **2a** and **2b** that improve on previous methods.

Acknowledgments

The authors greatly appreciate the careful reading and advice of Professor Jerome B. Keister.

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