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Ligand effects on the rates of protonolysis and isotopic exchange for platinum(II) alkyls

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Abstract

The protonolysis/deuterolysis of complexes L_2PtRX (L = phosphorus ligand, R = alkyl group, X = anionic ligand) has been investigated as a mechanistic probe of the reverse reaction, activation of alkanes by Pt(II). *Trans*-$(Et_3P)_2PtMeX$ (X^- = triflate (OTf^-), F^-, NO_3^-) solvolyze in acidic CD_3OD, forming $[trans\text{-}(Et_3P)_2PtMe(CD_3OD)]^+$ which reacts slowly with DOTf at room temperature liberating CH_3D. In dichloromethane, *trans*-$(Et_3P)_2PtMe(OTf)$ reacts with HOTf at low temperatures (−70 to −20°C) to give $(Et_3P)_2PtMe(H)(OTf)_2$ in rapid equilibrium with the reagents, while at higher temperatures rapid methane loss is preceded by extensive deuterium incorporation (with DOTf) into the Pt(II) methyl group. Upon treatment with acid in CD_3OD, *trans*-$(Et_3P)_2PtMeX$ (X = Cl, Br) also undergo H/D exchange before elimination of methane, while *trans*-$(Et_3P)_2PtMeI$, $(depe)Pt(CH_3)_2$ (depe = 1,2-bis(diethylphosphino)ethane) and *cis*-$[(MeO)_3P]PtMeCl$ do not. The α hydrogens of *trans*-$(Et_3P)_2PtRCl$ (R = Me, Et, Bz) exchange with deuterium in CD_3OD/DOTf with rates following the order Bz < Me < Et, while no exchange is observed in the protonolysis of *trans*-$(Et_3P)_2Pt(CH_2CMe_3)Cl$ which yields $(CH_3)_3CCH_2D$. These trends are interpreted in terms of effects on relative stabilities of key intermediates, Pt(IV) alkyl hydrides and Pt(II) alkane sigma complexes. © 1997 Elsevier Science S.A.

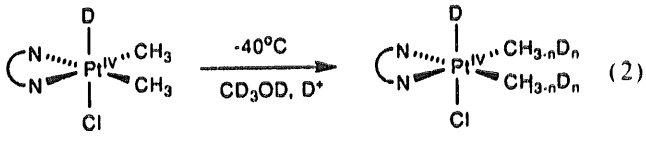
Keywords: Kinetics and mechanism; Protonolysis; Isotopic exchange; Platinum complexes; Alkyl complexes

1. Introduction

In the past fifteen years many examples of the activation of alkanes by metal complexes, often under remarkably mild conditions, have been reported [1]; however, relatively few have been demonstrated to lead to functionalization of alkanes. Among the latter, the oxidation of alkanes to alcohols by aqueous platinum salts [2], Eq. (1), has been studied extensively in recent years [3,4].

$$RH + [PtCl_6]^{2-} + H_2O \xrightarrow[120°C]{[PtCl_4]^{2-}} ROH + [PtCl_4]^{2-} + 2\,HCl \qquad (1)$$

The key initial step — the actual C–H activation — is difficult to probe directly, as neither meaningful kinetics nor observation of intermediates has been obtainable. We have been able to shed some light on several important mechanistic features of this step by studying its microscopic reverse, the protonolysis of Pt(II) alkyl complexes, and have proposed a general mechanism for the latter, depicted in Scheme 1. The Pt(IV) alkyl hydrides **1** were observed by NMR in several cases, while the postulated intermediates **2** (so-called alkane sigma complexes [5]) could not be observed but were inferred from the observation of isotopic H/D exchange between alkyl groups and solvent methanol, as shown in Eqs. (2) (where the N–N ligand is tetramethylethylenediamine (tmeda)) and (3) [6].



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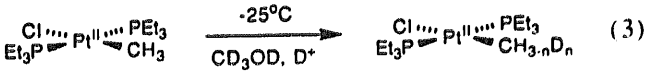

(3)

Although these studies involve Pt(II) complexes with stabilizing amine or phosphine ligands, we consider it highly probable that the corresponding intermediates play key roles in the ligand-free system of Eq. (1). This postulate is supported by the recent observation of intermolecular alkane activation by cationic (tmeda)Pt(II) complexes [7].

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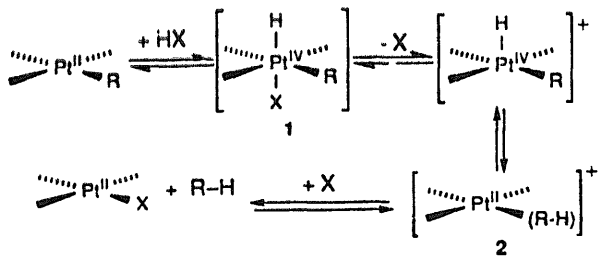


Scheme 1.

Accordingly, examination of the factors that govern the stabilities of these intermediates, and the rates of the processes that form and interconvert them, should provide valuable information towards our goal of understanding activity and selectivity of these C–H activations and designing improved catalysts for alkane functionalization. We report here on protonolysis reactions of complexes L_2PtRX, where we examine the effects of varying the phosphine ligand L, the alkyl group R and the 4th ligand X.

2. Experimental

2.1. General procedures

Phosphine ligands, $(COD)PtMe_2$ and $(COD)PtCl_2$ (COD = cyclooctadiene) were purchased from Strem and used as received. $(COD)PtEt_2$, $(COD)PtBz_2$, $(COD)PtMeCl$, $(COD)PtEtCl$ and $(COD)PtBzCl$ (Bz = benzyl) were prepared by the methods of Clark and Manzer [8]. $(COD)Pt(CH_2CMe_3)_2$ was prepared from $LiCH_2CMe_3$ and $(COD)PtCl_2$ following a procedure similar to that reported by Whitesides and co-workers [9], and converted to $(COD)Pt(CH_2CMe_3)Cl$ in the same manner as the Me analog [8] (excess acid, via acetyl chloride in methanol, was necessary). Standard workup procedures for the Pt(II) dialkyls and alkyl chlorides were carried out in air with solvents purchased from VWR and used as received; all other experiments were carried out using freshly distilled solvents under an inert atmosphere via standard Schlenk and glove box techniques.

^1H NMR spectra were recorded on a General Electric QE300 and a Bruker AM500 spectrometer. ^{31}P NMR spectra were recorded on a JEOL FNM400 spectrometer. (Multiplicities cited for NMR peaks do not include ^{195}Pt satellites; if the latter are present a coupling constant is given.) Low temperature kinetics were obtained as described in previous publications [5]. Mass spectra were obtained using a Hewlett-Packard 5990A GC/MS with a 70 eV ionizing voltage equipped with a 50 m PONA column (cross-linked methyl silicone gum). Elemental analyses were performed by Fenton Harvey of this department.

2.2. Synthesis of trans-$(Et_3P)_2PtRCl$ (R = Me, Et, Bz, CH_2CMe_3)

These complexes are all known, having been previously prepared from $(Et_3P)_2PtCl_2$ [10]. We obtained them by the addition of 2.1 equiv. of triethylphosphine to a dichloromethane solution of (COD)PtRCl. The solution was allowed to stir for several hours and the solvent was removed in vacuo, affording a white powder (or oil, in which case addition of diethyl ether and/or pentane followed by solvent removal converted it to a white solid). Complexes were characterized, and their purities determined, by ^1H NMR; if necessary recrystallization from concentrated, cooled dichloromethane solutions gave pure complexes.

2.3. Synthesis of trans-$(Et_3P)_2PtR(OTf)$ (R = Me, CH_2CMe_3; OTf = triflate)

Trans-$(Et_3P)_2Pt(CH_2CMe_3)(OTf)$ was synthesized using the published preparation for the Me_3P analog [11]. *Anal.* Calc. for $C_{18}H_{41}SO_3F_3P_2Pt$: C, 33.2; H, 6.3. Found: C, 33.4; H, 6.2%. ^1H NMR ($CDCl_3$): δ 1.0 (9H, s), 1.2 (18H, m), 1.45 (2H, t, J(P–H) = 8.4 Hz, J(Pt–H) = 89 Hz), 2.0 (12H, m).

Attempts to use the same procedure for *trans*-$(Et_3P)_2PtMe(OTf)$ generally gave products contaminated with Cl-containing impurities. Instead, *cis*-$(Et_3P)_2Pt(CH_3)_2$ was prepared quantitatively from 1.0 g of $(COD)Pt(CH_3)_2$ and 2 equiv. of triethylphosphine (0.9 ml) in 20 ml of dichloromethane. After solvent evaporation a white powder resulted, which was dissolved in methanol (30 ml) and 1 equiv. HOTf (1.8 ml of 1.67 M HOTf solution in methanol) was added dropwise. The solvent was removed after 20 min of stirring, and the resulting powder (yield: 1.65 g, 96%) was dried overnight under vacuum. *Anal.* Calc. for $C_{14}H_{33}O_3F_3SP_2Pt$: C, 28.23; H, 5.5. Found: C, 27.84; H, 5.23%. ^1H NMR (CD_2Cl_2): δ 0.52 (3H, t, J(P–H) = 6.6 Hz, J(Pt–H) = 100.2 Hz), 1.2 (18H, m), 1.8 (12H, m). ^{31}P NMR (CD_2Cl_2): δ 24.3 (J(Pt–P) = 2844 Hz).

2.4. Synthesis of trans-$(Et_3P)_2PtMeF$

Trans-$(Et_3P)_2PtMeF$ was prepared by metathesis of the corresponding chloride with AgF, as reported by Doherty and Critchlow [12], yielding a sticky yellow solid after drying in vacuum for several days. ^1H NMR (CD_2Cl_2): δ 0.2 (3H, t, J(P–H) = 5.7 Hz, J(Pt–H) = 85.2 Hz), 1.1 (18H, m), 1.8 (12H, m). ^1H NMR (CD_3OD): δ 0.42 (3H, t, J(P–H) = 6.6 Hz, J(Pt–H) = 86.7 Hz). After several weeks of storage under nitrogen, partial decomposition to a new species was indicated by ^1H NMR.

The analogous complexes *trans*-$(Et_3P)_2PtMeX$ (X = Br, NO_3) were prepared as reported previously [10a].

2.5. Generation of solutions of [trans-$(Et_3P)_2PtMe(CD_3OD)]^+$

Acidification of a solution of *trans*-$(Et_3P)_2PtMeF$ in CD_3OD results in significant changes in the ^1H and ^{31}P NMR spectra. ^1H NMR (0.2 M DOTf/CD_3OD): δ 0.52 (3H, t, J(P–H) = 6.6 Hz, J(Pt–H) = 100.0 Hz). ^{31}P NMR: δ 26.0

(J(Pt–P) = 2817 Hz). Under the same conditions, solutions of *trans*-$(Et_3P)_2PtMeX$ ($X^- = OTf^-, NO_3^-$) exhibit identical spectra. Therefore the cationic complex [*trans*-$(Et_3P)_2PtMe(CD_3OD)]^+$ must be the dominant species present in all these solutions.

2.6. Synthesis of trans-$(Me_3P)_2PtEtCl$

2.1 equiv. of trimethylphosphine, 180 μl, were added to a dichloromethane solution of (COD)PtEtCl (0.30 g). After 2 h stirring the solvent was removed under vacuum; addition and removal of 10 ml of diethyl ether (repeated three times) resulted in a white powder (yield: 0.30 g, 89%). ^{1}H NMR ($CDCl_3$): δ 1.1 (3H, t, J(P–H) = 6.3 Hz, J(Pt–H) = 78 Hz), 1.2 (2H, m), 1.5 (18H, t, J(Pt–H) = 30 Hz). *Anal.* Calc. for $C_8H_{23}P_2ClPt$: C, 23.33; H, 5.6. Found: C, 23.70; H, 5.87%. A small amount of contaminant, probably the *cis*-isomer, is indicated by a doublet at δ 1.63 in the ^{1}H NMR; it can be removed by recrystallization from diethyl ether.

2.7. Synthesis of trans-$(Ph_3P)_2PtMeCl$

This complex was previously prepared by oxidative addition of methyl iodide to $(Ph_3P)_2Pt(C_2H_4)$ followed by replacement of iodide with chloride [13]; we obtained it from the reaction of 0.27 g of (COD)PtMeCl with 0.4 g of triphenylphosphine in 20 ml of dichloromethane. The resulting slurry was stirred for 3 h, filtered and dried in vacuo. A white powder (yield: 0.45 g, 76%) was obtained. ^{1}H NMR ($CDCl_3$): δ −0.01 (3H t, J(P–H) = 6.5 Hz, J(Pt–H) = 77.4 Hz).

2.8. Synthesis of complexes of sulfonated triphenylphosphine

0.5 g of $(COD)PtMe_2$ was loaded into a 50 ml Schlenk tube with 2.0 g of $Na_3[(m\text{-}O_3SC_6H_4)_3P]$ (TPPTS). 10 ml of distilled water and 30 ml of tetrahydrofuran were added via syringe; the solution was degassed and heated to 40°C for 3 h. The solvent was removed in vacuo, and 30 ml of water was added. The solution was filtered through celite, and the resulting solution was placed for 2 days in a desiccator, with sodium hydroxide as drying agent, under a partial vacuum. $(TPPTS)_2PtMe_2$ was obtained as a yellow crystalline solid in nearly quantitative yields. *Anal.* Calc. for $C_{38}H_{30}S_6O_{18}P_2PtNa_6 \cdot (H_2O)_8$: C, 27.7; H, 2.8. Found: C, 28.0; H, 2.9%. ^{1}H NMR (D_2O): δ 0.41 (6H, t, J(Pt–H) = 68.7 Hz), 7.1–8.2 (24H, m). ^{31}P NMR (D_2O): δ 29.4, (J(Pt–P) = 1880 Hz).

1.0 g of $(TPPTS)_2PtMe_2$ was dissolved in 20 ml of H_2O and 2.05 ml of a 0.296 M HCl solution was added dropwise over 20 min. The solution was allowed to evaporate slowly over several days under a partial vacuum in a desiccator containing P_2O_5, during which isomerization from *cis*- to *trans*-complex occurred. *Trans*-$(TPPTS)_2PtMeCl$ (yield: 0.96 g, 96%) was obtained as an air-stable white solid. *Anal.* Calc. for $C_{37}H_{27}S_6O_{18}P_2PtClNa_6 \cdot (H_2O)_8$: C, 29.11; H, 2.84. Found: C, 27.75; H, 2.75%. ^{1}H NMR (D_2O): δ 0.05 (3H, t, J(Pt–H) = 68.7 Hz), 7.1–8.2 (24H, m). ^{31}P NMR (D_2O): δ 33.3 (J(Pt–P) = 3200 Hz). A small amount of *cis*-$(TPPTS)_2PtMeCl$ (^{1}H NMR (D_2O): δ 0.6 (q)) persists; there is also a weak shoulder at δ 0.0 attributed to an uncharacterized Pt–Me species.

2.9. Synthesis of cis-$[(MeO)_3P]_2PtMeCl$

(COD)PtMeCl, 0.211 g, was dissolved in 20 ml of dichloromethane. 142 μl of trimethylphosphite was added dropwise over several minutes via syringe. The resulting solution was stirred for several hours. Solvent removal under vacuum, followed by the addition and evaporation of diethyl ether, gave 0.28 g (93% yield) of a white solid. *Anal.* Calc. for $C_7H_{21}O_6P_2PtCl$: C, 17.03; H, 4.29. Found: C, 17.13; H, 4.38%. ^{1}H NMR ($CDCl_3$): δ 0.77 (3H, dd, J(P1–H) = 10.3 Hz, J(P2–H) = 2.4 Hz, J(Pt–H) = 68.7 Hz), 3.7 (9H, d), 3.8 (9H, d).

2.10. Synthesis of (depe)$PtMe_2$

This followed the preceding procedure, using 0.4 g of $(COD)PtMe_2$ with 280 μl of diethylphosphinoethane. *Anal.* Calc. for $C_{12}H_{30}P_2Pt$: C, 33.41; H, 7.01. Found: C, 32.83; H, 6.13%. ^{1}H NMR (CD_3OD): δ 0.36 (6H, t, J(P–H) = 6.9 Hz, J(Pt–H) = 67.2 Hz), 1.0 (12H, m), 1.6 (4H, m), 1.8 (8H, m).

2.11. Deuterolysis of L_2PtRX in CD_3OD

In a typical procedure 10 mg of *trans*-$(Et_3P)_2PtMeCl$, or the molar equivalent of another Pt(II) alkyl, was placed in a ^{1}H NMR tube and dissolved in 0.6 ml of CD_3OD. For low temperature kinetic runs, when [Cl] was varied, the ionic strength was kept constant at 0.725 M by addition of $LiClO_4$. 0.09 ml of a 1.80 M DOTf/CD_3OD solution was added via syringe while the samples were kept cold in a dry ice/acetone bath. H/D exchange was monitored (usually at −23°C) by following changes in the ^{1}H NMR peaks due to the α-alkyl protons. After exchange was complete the samples were allowed to warm to room temperature, and the alkane products characterized by GC/MS analysis of the gas in the head space and/or ^{1}H NMR (e.g., for $(CH_3)_3C(CH_2D)$: ^{1}H NMR: δ 0.88 (9H, s), 0.85 (2H, t); the MS fragmentation pattern included m/e 58 ($Me_2(CH_2D)C^+$) and m/e 57 (Me_3C^+) in a 3:1 ratio, as expected for the monodeuterated product [9,14]). In the case of R = Bz, formation of $C_6H_5CD_3$ was verified by vacuum-transferring the volatiles, after warming, and ^{1}H NMR analysis.

2.12. Protonation of trans-$(Et_3P)_2PtMe(OTf)$

1 equiv. of HOTf in dichloromethane was added via syringe to a solution of *trans*-$(Et_3P)_2PtMe(OTf)$ in CD_2Cl_2 which had been cooled in a dry ice acetone bath. ^{1}H NMR of

the sample at −70°C indicated complete conversion to $(Et_3P)_2PtMe(H)(OTf)_2$. ^1H NMR (CD_2Cl_2): δ −25.6 (1H, J(Pt–H) = 1500 Hz), 1.05 (18H, m), 1.37 (3H, J(Pt–H) = 65 Hz), 2.08 and 2.15 (12H, 2 multiplets). (The signals for both the hydride and methyl were too broad to resolve coupling to phosphorus.) On warming to −40°C, the NMR showed partial reversion to starting materials; these changes were fully reversible.

When the same reaction was carried out at room temperature, evolution of methane was immediately observed. Use of DOTf gave rise to a mixture of methane isotopomers. After completion, the solvent was removed under vacuum resulting in quantitative recovery of a white solid assigned as *cis*-$(Et_3P)_2Pt(OTf)_2$. ^1H NMR (CD_2Cl_2): δ 1.2 (18H, m), 1.9 (12H, m). ^{31}P NMR (CD_2Cl_2): δ 12.7 (J(Pt–P) = 3902 Hz). ^{31}P NMR (CD_3OD): δ 11.7 (J(Pt–P) = 3740 Hz).

2.13. Deuterolysis of trans-$(Ph_3P)_2PtMeCl$

15 mg of *trans*-$(Ph_3P)_2PtMeCl$ was dissolved in 0.7 ml of $CDCl_3$, 0.9 ml of 1.8 M DOTf/CD_3OD was added at room temperature, and acquisition of ^1H NMR spectra was immediately begun. Over a period of 1 h, the ^1H resonance for the methyl group showed incorporation of deuterons, while peaks assigned to CD_3H, CD_2H_2, CDH_3 and CH_4 simultaneously grew in.

2.14. Protonolysis of (depe)$PtMe_2$

The addition of triflic acid (either 1 equiv. or excess) to a solution of (depe)$PtMe_2$ in methanol results in the quantitative formation of (depe)PtMe(OTf) determined by ^1H NMR spectroscopy. ^1H NMR (CD_3OD): δ 0.35 (3H, d, J(P–H) = 7.2 Hz, J(Pt–H) = 43.5 Hz), 1.1 (12H, m), 1.7 (4H, m), 1.9 (8H, m).

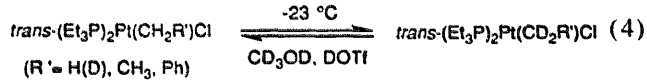
3. Results

3.1. Synthesis of complexes L_2PtRX

Complexes L_2PtR_2 and L_2PtRCl were readily obtained by displacement of COD from the corresponding (COD)PtR_2 and (COD)PtRCl. The majority of these complexes exhibit *trans* geometry, but $[(MeO)_3P]_2PtMeCl$ is obtained in *cis* form, as the methyl group signal exhibits unequal coupling to the two phosphorus nuclei in the ^1H NMR spectrum. (However the corresponding signal for (depe)$PtMe_2$, which obviously must be *cis* as well, is an apparent triplet, presumably because of 'virtual coupling'.) The remaining L_2PtRX complexes studied may be obtained by several routes: (i) metathesis of L_2PtRCl with AgX; (ii) careful stoichiometric protonolysis of L_2PtR_2 with HX; (iii) displacement of the weakly coordinatingly triflate anion from $L_2PtR(OTf)$ by X^-. Method (ii) generally is preferable for obtaining clean, easily isolable product; method (i) in particular is problematic for these studies, as small amounts of Cl-containing impurities can have a major effect on reactivity (see below).

3.2. Deuterolysis of trans-$(Et_3P)_2PtRCl$

We previously found that around −20°C *trans*-$(Et_3P)_2PtMeCl$ undergoes H/D exchange with D^+/CD_3OD, as shown in Eq. (3) above, with no Pt(IV) methyl hydride or methane detectable by ^1H NMR; elimination of alkane ensues on warming to room temperature [6]. Complexes *trans*-$(Et_3P)_2PtRCl$ (R = Et, Bz) exhibit the same behavior, represented by Eqs. (4) and (5). The high-temperature stage does not give a single clean Pt product, as some exchange of X groups competes with alkane liberation, generating inter alia *trans*-$(Et_3P)_2PtR(OTf)$ which undergoes protonolysis only slowly (see below).



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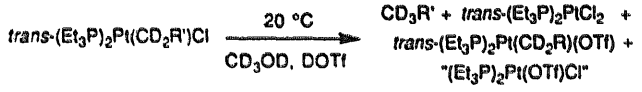
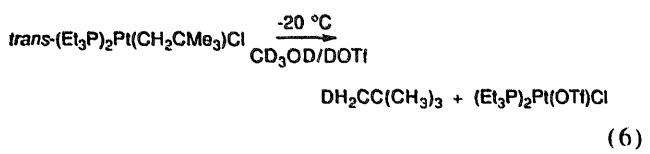


(5)

The kinetics of H/D exchange were monitored by ^1H NMR spectroscopy, following the rate of deuterium incorporation into the α-position of the alkyl group by the decrease in the corresponding ^1H signal. For R = Me and Bz, first order plots were obtained, from which rate constants (−23°C, [DOTf] = 0.2 M) $k_{obs} = 2.2 \times 10^{-4}$ s^{-1} and 7.8×10^{-5} s^{-1}, respectively, were derived. H/D exchange for R = Et appears to be the most rapid of the three complexes; while an accurate rate constant was not obtained because the key ^1H NMR resonsances are partially obscured by those from triethylphosphine, qualitatively it can be seen that approximately two hydrogens (by integration of the peaks in the region) exchange very quickly at −23°C. This was confirmed by examining exchange for *trans*-$(Me_3P)_2PtEtCl$ where there is no such interference. At −23°C deuteration of the methylene position was complete before the first ^1H NMR spectrum could be obtained, and over the course of 1 h at −23°C ^1H NMR revealed a significant amount of ethane evolution. The latter was shown to be primarily CD_3CH_3 by GC/MS analysis of the gas phase (*m/e* 33). There was no evidence by either NMR or MS for incorporation of deuterium into any other than the α-position.

In contrast, for *trans*-$(Et_3P)_2Pt(CH_2CMe_3)Cl$, deuterium incorporation into the Pt–neopentyl group was not observed. Instead, gradual formation of neopentane took place even at −23°C. ^1H NMR and MS established that the neopentane was monodeuterated $(CH_3)_3C(CH_2D)$, as shown in Eq. (6). In contrast to the reactions of Eq. (5), only a single Pt product was observed, probably because exchange of anionic ligands is slow at the lower temperature.



(6)

3.3. Deuterolysis of trans-$(Et_3P)_2PtMeX$

The ^1H NMR spectra of acidic methanol solutions of *trans*-$(Et_3P)_2PtMeX$, where X = OTf, F or NO_3, are all identical, indicating that they undergo acid-promoted solvolysis, as shown in Eq. (7), to give the cationic complex [*trans*-$(Et_3P)_2PtMe(CD_3OD)]^+X^-$. In the absence of acid, the equilibrium for solvolysis of the fluoride complex does not lie so far to the right as for the triflate or nitrate complexes; reaction of CsF with *trans*-$(Et_3P)_2PtMeOTf$ in CD_3OD gives some *trans*-$(Et_3P)_2PtMeF$ as shown by ^1H NMR. However, a complicated mixture of products forms, and a large excess of CsF is required for nearly complete formation of the fluoride complex.

The course of deuterolysis of *trans*-$(Et_3P)_2PtMe(OTf)$ in DOTf/CD_3OD depends on the method of preparation. Samples prepared by metathesis from the chloride exhibited varying degrees of multiple H/D exchange and rates of methane formation. In contrast, samples prepared by protonolysis of the dimethyl complex gave consistently slow (about 1 week at room temperature for complete reaction) liberation of methane, which was exclusively monodeuterated; the same behavior was observed for methanol solutions of the fluoride and nitrate complexes. The Pt product in Eq. (8) is tentatively assigned a *cis* configuration because of the large $^1J(Pt-P) = 3740$ Hz [15].

(7)

(8)

Both H/D exchange and liberation of methane are catalyzed by added chloride. As $[Cl^-]$ is varied from 0 to 1 equiv. per Pt, while maintaining ionic strength, the H/D exchange rate (as detected by changes in the ^1H NMR signal for Pt–Me) increases from zero, as shown in Fig. 1. The ^1H NMR of solutions containing intermediate $[Cl^-]$ concentrations shows the presence of both [*trans*-$(Et_3P)_2PtMe(CD_3OD)]^+$ (δ 0.50) and *trans*-$(Et_3P)_2PtMeCl$ (δ 0.37); the methyl hydrogens in the two complexes exchange with solvent deuterium at the same rate. Under conditions of high [Pt] and low $[Cl^-]$ an additional Pt–Me signal is observed in the ^1H NMR (δ 0.43), tentatively attributed to a chloro-bridged dimeric complex as shown in Eq. (9).

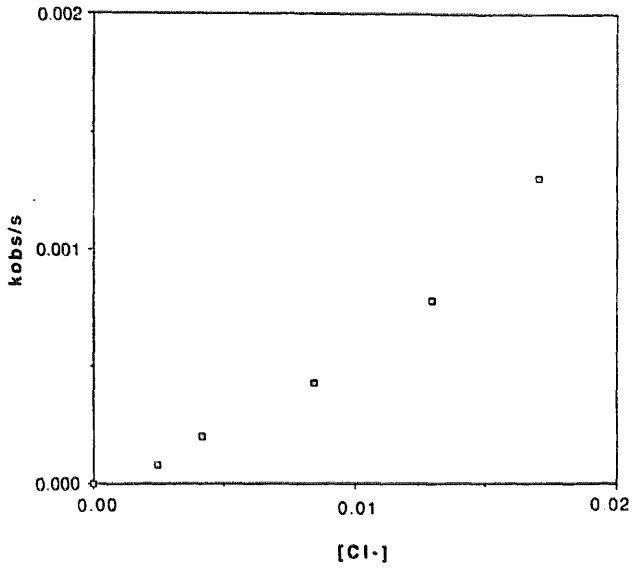
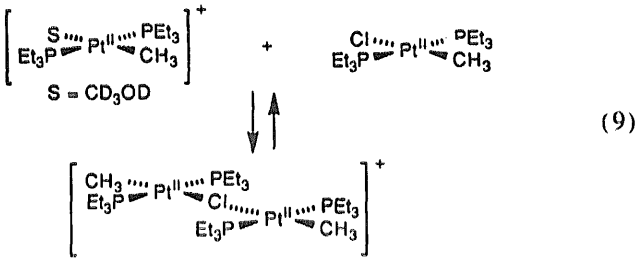
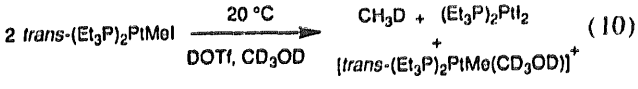


Fig. 1. Rate of exchange of deuterium into the Me position during deuterolysis of *trans*-$(Et_3P)_2PtMe(OTf)$ in CD_3OD, as a function of $[Cl^-]$. [Pt] = 0.0244 M; [DOTf] = 0.235 M; μ = 0.725 M; T = 13°C.



(9)

Addition of 1 equiv. of LiX (X = Br, I) to a methanol solution of *trans*-$(Et_3P)_2PtMeOTf$ results in the quantitative formation of *trans*-$(Et_3P)_2PtMeX$, as indicated by ^1H NMR. In deuterolysis of the resulting solutions with DOTf (−23°C, [DOTf] = 0.17 M) *trans*-$(Et_3P)_2PtMeBr$ incorporates deuterium into the methyl group with $k_{obs} = 1.0\times10^{-4}$ s^{-1}, similar to the $k_{obs} = 1.0\times10^{-4}$ s^{-1} found for *trans*-$(Et_3P)_2PtMeCl$. The reaction of DOTf with *trans*-$(Et_3P)_2PtMeI$ could not be followed at low temperatures because of limited solubility. The reaction of *trans*-$(Et_3P)_2PtMeBr$ with DOTf in CD_3OD at 20°C gives rapid H/D exchange competing with deuterolysis, leading to immediate formation of CD_4, CH_3D, CH_2D_2 and CHD_3. In contrast, similar treatment of *trans*-$(Et_3P)_2PtMeI$ resulted only in formation of monodeuterated methane, while the platinum product consisted of $(Et_3P)_2PtI_2$ (a yellow precipitate), and [*trans*-$(Et_3P)_2PtMe(S)]^+$ (Eq. (10)).



(10)

In contrast to the behavior in methanol, *trans*-$(Et_3P)_2PtMe(OTf)$ reacts immediately with DOTf in dichloromethane at room temperature, forming *cis*-$(Et_3P)_2Pt(OTf)_2$ (assigned a *cis* configuration based on $^1J(Pt-P)$

Table 1
Temperature dependence of K_{eq} for Eq. (11)

T (K)	K_{eq} (M^{-1})
220	13.2
230	5.47
240	2.37
250	1.27

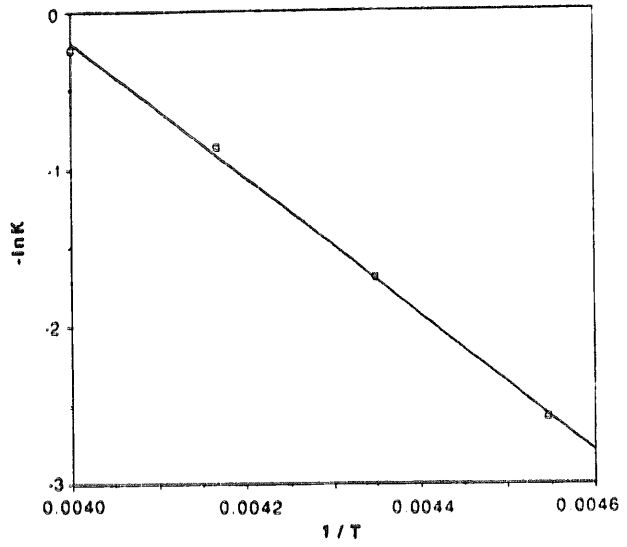
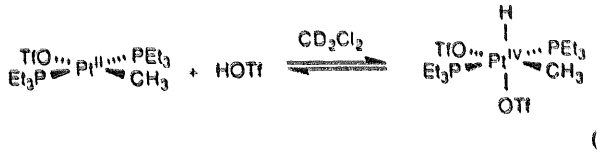


Fig. 2. van't Hoff plot for the equilibrium of Eq. (11) (data from Table 1).

= 3902 Hz) as well as a mixture of methane isotopomers. At −70°C 1 equiv. of HOTf in dichloromethane reacts cleanly with *trans*-$(Et_3P)_2PtMe(OTf)$ forming the Pt(IV) alkyl hydride. The ^1H NMR spectrum reveals a downfield shift of the methyl resonance from $\delta = 0.50$ ($J(Pt-H) = 100$ Hz) to $\delta = 1.4$ ($J(Pt-H) = 65$ Hz) and the appearance of a hydride resonance at $\delta = -25.6$ ($J(Pt-H) = 1500$ Hz). On warming to −40°C, the signal at δ 0.50 reappears; the change with temperature is fully reversible, indicating a rapid equilibrium as shown in Eq. (11). The equilibrium constant was calculated at various temperatures by integration of respective methyl resonances; results are displayed in Table 1 and the resulting van't Hoff plot is shown in Fig. 2. The thermochemical parameters calculated from the latter plot are $\Delta H^\circ = -8.6 \pm 1$ kcal mol^{-1} and $\Delta S^\circ = -34.0 \pm 5$ cal K^{-1} mol^{-1}. Evolution of methane with concomitant formation of *cis*-$(Et_3P)_2Pt(OTf)_2$ begins at temperatures above −20°C. The reaction of *trans*-$(Et_3P)_2PtMe(OTf)$ with DOTf in CH_2Cl_2 at room temperature causes immediate production of a mixture of methane isotopomers.



(11)

3.4. Deuterolysis of $L_2PtMeCl$

Trans-$(Ph_3P)_2PtMeCl$ could not be studied in methanol because it is not sufficiently soluble. When treated at 20°C in chloroform with excess DOTf (as a 1.8 M solution in CD_3OD), during a 1 h period substantial H/D exchange of the Pt–Me group is observed along with formation of methane isotopomers. The analogous complexes of tris-metasulphonated triphenylphosphine (TPPTS) were prepared in order to examine protonolysis in water, the solvent of the original alkane activation system. $(TPPTS)_2PtMe_2$ was synthesized in high yield by heating (40°C) 2 equiv. of $[Na_3(H_2O)_8][(m\text{-}O_3SC_6H_4)_3P]$ with $(COD)Pt(CH_3)_2$ in a mixture of tetrahydrofuran and water. In D_2O $(TPPTS)_2Pt(CH_3)_2$ reacts with 1 equiv. of either HOTf or HCl to liberate 1 equiv. of methane, and give a monomethyl Pt(II) product. Since the ^1H NMR spectrum is the same for the products obtained by reaction with the two acids, the dominant species in solution is probably the aquo cation $[(TPPTS)_2PtMe(D_2O)]^-$. Initially the methyl resonance appears as an approximate quartet which changes over several days to a regular triplet, indicating that the first product is the *cis* complex, which gradually isomerizes to *trans*. Addition of excess acid to an aqueous solution of $[(TPPTS)_2PtMe(D_2O)]^-$ cleaves the second Pt–Me group; only monodeuterated methane is observed.

Treatment of $(depe)PtMe_2$ in CD_3OD with DOTf at −70°C results in the immediate formation of CH_3D and a new monomethyl-Pt(II) complex, presumably $[(depe)PtMe(CD_3OD)]OTf$. On warming the solution to room temperature, the latter resonance disappears accompanied by further liberation of CH_3D. In contrast, under similar conditions *cis*-$((MeO)_3P)_2PtMeCl$ is stable towards methane loss over the course of 1 h at −23°C; decomposition along with CH_3D formation takes place around 0°C.

4. Discussion

Our previous work strongly supports the mechanism shown in Scheme 1 (clockwise) for the protonolysis of Pt(II) alkyl complexes [6,7]. The rationale of the present study is that the reverse process should describe alkane activation by Pt(II) (although it must of course be recognized that because of differences in ligands, solvent and reaction conditions the principle of microscopic reversibility is not rigorously applicable). Hence systematic examination of how the protonolysis process is affected by changes in the Pt(II) ligand environment offers the potential for valuable information on key issues such as: what determines the unusual selectivity patterns in C–H activation by Pt(II) [3,4]? Can we improve reactivity by varying the nature of the Pt(II) complex, the solvent or other reaction parameters? Is it possible to design a Pt(II) complex that activates alkanes but is stabilized by ligands against Pt(0) formation, thus overcoming a major limitation to catalytic alkane functionalization [16]?

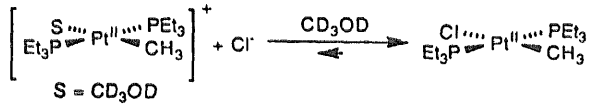
Our initial experiments were carried out on *trans*-$(Et_3P)_2PtMe(OTf)$, and considering our previous work several results were surprising. First, protonolysis was very slow

in methanol, in contrast to complexes (tmeda)PtMeCl and (tmeda)$PtMe_2$ where loss of methane on protonation appears much more facile in methanol than in a non-polar solvent such as CD_2Cl_2. Second, facile H/D exchange of the Pt–Me group was not observed, unlike the chloro analog, although slow exchange was sometimes observed, at a rate that varied between samples.

The key observation that allowed us to interpret these apparent anomalies was that the ^1H NMR spectra of *trans*-$(Et_3P)_2PtMeX$ solutions in acidic CD_3OD are identical for $X^- = OTf^-$, F^- and NO_3^-. Clearly, then, all these relatively weak ligands are easily solvolyzed, and the actual species present in solution is the cationic methanol complex, [*trans*-$(Et_3P)_2PtMe(CD_3OD)]^+$. It is reasonable that protonation to generate a Pt(IV) hydride, the first step in the sequence that leads to H/D exchange and/or protonolysis (Scheme 1), should be much more difficult for a cationic than for a neutral complex. Thus an energy diagram such as that shown in Fig. 3 must describe this system, with the initial protonation being the rate-determining step. This contrasts with the case of protonolysis of *trans*-$(Et_3P)_2PtMeCl$, where the last step, loss of alkane from the sigma complex, is apparently rate-determining [6b].

When the protonolysis of *trans*-$(Et_3P)_2PtMe(OTf)$ is carried out in dichloromethane the result is dramatically different: liberation of methane is immediate at room temperature, in contrast to the reaction in methanol which takes several days. Furthermore, H/D exchange takes place when DOTf is used. Presumably, the covalent bond between triflate and the Pt(II) center is retained in this non-polar solvent, and therefore protonation occurs much more readily at a neutral Pt(II) center. As with some of the tmeda complexes [6], the Pt(IV) alkyl hydride intermediate may be observed at low temperatures, in equilibrium with the alkyl Pt(II) and the proton source.

The non-reproducibility of H/D exchange was readily traced to contamination by small amounts of Cl in samples prepared by metathesis of *trans*-$(Et_3P)_2PtMeCl$ with AgOTf; when an alternate preparation (protonolysis of *trans*-$(Et_3P)_2PtMe_2$ by HOTf) was substituted, the reaction with D^+ proceeded very slowly to yield CH_3D. This suggests that the equilibrium of Eq. (12) lies far to the right, and that small amounts of Cl^- can catalyze both H/D exchange and protonolysis, as the small amounts of *trans*-$(Et_3P)_2PtMeCl$ thus formed will undergo both rapidly at room temperature, giving (isotopomers of) methane and $[(Et_3P)_2PtCl(CD_3OD)]^+$. The latter apparently undergoes facile anion exchange to regenerate free Cl^- (see below) and continue the process. In support of this model, the rate of H/D exchange (and formation of methane) increases with added $[Cl^-]$, as shown in Fig. 1. The non-linearity of that plot probably is a consequence of the presence of additional species in solution, shown by NMR (see Eq. (9) above).



(12)

Both *trans*-$(Et_3P)_2PMeX$ (X = Br, I) exist primarily as the neutral halo complexes in CD_3OD as well. For X = Br, H/D exchange at low temperature takes place at a rate only slightly slower than that for X = Cl. For X = I the complex is too insoluble at low temperatures to follow H/D exchange; but the two complexes behave quite differently at room temperature. In each case treatment with DOTf gives prompt formation of methane, but the methane consists of a mixture of isotopomers when X = Br, and only CH_3D for X = I. Also the latter reaction is incomplete: significant amounts of Pt(II)-CH_3 remains in the form of $[(Et_3P)_2PtMe$-

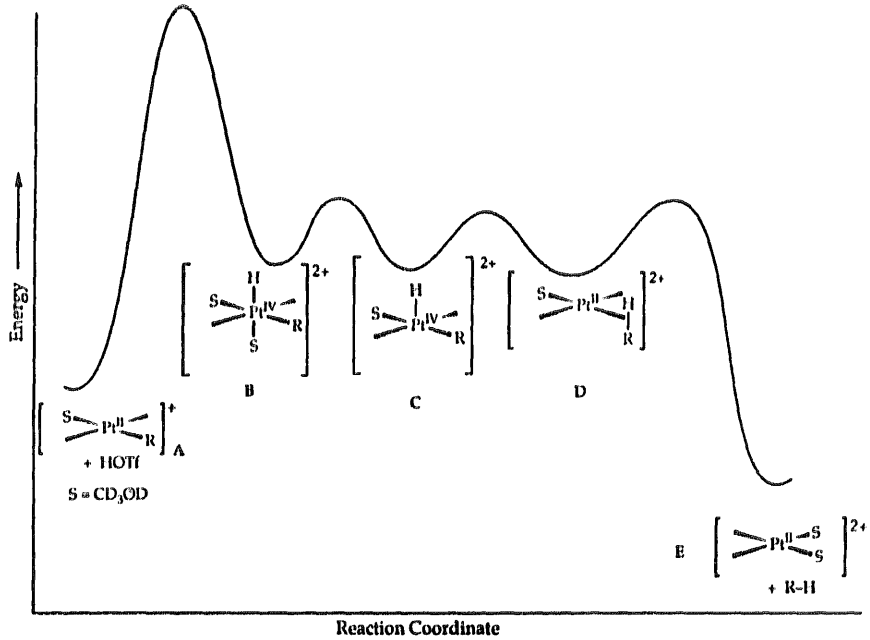


Fig. 3. Qualitative reaction coordinate diagram for the protonolysis of [*trans*-$(Et_3P)_2Pt(CH_3)(CD_3OD)]^+$ in methanol.

$$L_2PtMeI + DOTf \xrightarrow[(S)]{CD_3OD} [L_2PtI(S)]^+OTf^- + MeD$$

$$L_2PtMeI + [L_2PtI(S)]^+ \underset{}{\overset{fast}{\rightleftharpoons}} L_2PtI_2\downarrow + [L_2PtMe(S)]^+$$

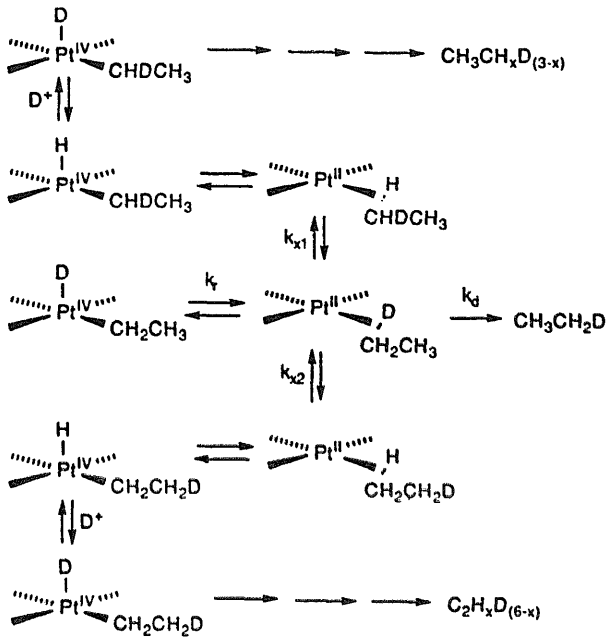
Scheme 2.

$(CD_3OD)]^+$, with the rest of the Pt precipitating as $(Et_3P)_2PtI_2$. The latter difference may be ascribed to a combination of the rapid anionic ligand exchange these systems exhibit at room temperature (but not at low temperature; see below), the very low solubility of the diiodide complex, and the slow reactivity towards protonolysis of the cationic methanol solvate, as shown in Scheme 2.

As for the apparent difference in H/D exchange, we ascribe this to the effect of the *trans* ligand on the rate of alkane dissociation from the sigma complex. It can be seen from Scheme 1 that the formation of multiply deuterated methane will depend on the relative rates of the exchange process (not shown in the Scheme; see below) and the loss of alkane; the latter in turn is expect to show a considerable *trans* effect, following typical patterns of square-planar Pt(II) substitution chemistry. Thus we find that the phosphine complexes with *cis* geometry, (depe)$PtMe_2$ and $((MeO)_3P)_2PtMeCl$, give only monodeuterated methane on deuterolysis, as does *trans*-$(Et_3P)_2P(CH_3)I$; whereas *trans*-$(Et_3P)_2P(CH_3)X$ (X = Cl, Br) and (tmeda)$PtMe_2$ [6] show multiple exchange, in keeping with the standard *trans* effect series: phosphine > I^- > Br^- > Cl^- > amine [17].

The above interpretation is not definitive, of course, since we have not as yet been able to observe directly any alkane sigma complex, and hence cannot be sure whether some other step(s) in the complex mechanism are responsible for these trends. In attempting to sort out the effects of changing the phosphine ligand without changing the geometry, we examined *trans*-$(Ph_3P)_2PMeCl$, which indeed shows multiple exchange, consistent with the weak *trans* effect of Cl^-, but in a different solvent (chloroform); the low solubility in methanol precludes a quantitative comparison of exchange rates. The sulfonated triphenylphosphine complex [*trans*-$(TPPTS)_2PtMeCl]^{6-}$ is deuterolyzed in D_2O to monodeuterated methane only; however, NMR spectra indicate that it actually exists as the aquo complex [*trans*-$(TPPTS)_2PtMe(H_2O)]^{5-}$ instead, so that protonation may well be rate-limiting here as in the case of $[(Et_3P)_2PtCl(CD_3OD)]^+$. In studies on some related dihydrogen complexes, where the sigma complex (of H_2) is observable, we can correlate the rate of loss of H_2 with the *trans* effect [18].

We have also examined H/D exchange for different alkyl groups R. For R = Me, Et or Bz, reaction of *trans*-$(Et_3P)_2PtRCl$ with DOTf in CD_3OD at −23°C gives H/D exchange without loss of alkane, with the rates following the order $R = CH_2Ph < Me < Et$. It should be noted that the observed rate constants for alkane loss from *trans*-$(Et_3P)_2PtRCl$ in an acidic methanol/water solution follow the same order [19]. For $R = CH_2CMe_3$, H/D exchange is



Scheme 3.

not observed, rather alkane loss proceeds even at −23°C to give monodeuterated neopentane. The latter reaction, carried out at low temperature, gives a single clean Pt(II) product, whereas the room temperature protonolyses of the other alkyls lead to the mixture of complexes shown in Eq. (5). This is another manifestation of the anion exchange process, fast at room temperature but considerably slower at −20°C, that accounts for the ability of small amounts of chloride to catalyze reactions of [*trans*-$(Et_3P)_2PtMe(CD_3OD)]^+$ as well as for the persistence of the latter, along with precipitation of *trans*-$(Et_3P)_2PtI_2$, in the protonolysis of *trans*-$(Et_3P)_2PtMeI$.

As before, in the absence of direct observation of the sigma complexes any interpretation of these trends must be tentative. The various processes involved in determining the extent of multiple deuteration are shown (illustrated for R = Et) in Scheme 3. Clearly the lower part of this Scheme (k_{x2}) does not compete at all here: no evidence for exchange of D into any position other than α is observed. This contrasts with the behavior of $Cp^*(Me_3P)RhD(Et)$, where deuterium incorporation is seen in the methylene moiety of the ethyl group at −80°C and in the methyl position at −30°C, prior to reductive elimination of ethane at higher temperatures [20]. If we try to tease out the effects of R on the relative rates of the formation of the sigma complex (k_r), the exchange process (k_{x1}) and the dissociation of alkane (k_d), the most economical way to account for the parallel trends in exchange and alkane loss is to have the sequence $R = CH_2Ph < Me < Et$ operate for both k_{x1} and k_d, with the latter rate-limiting. Also k_d would have to be considerably faster for $R = CH_2CMe_3$. But an explanation on a detailed molecular level, based on steric and/or electronic properties of the various R groups, does not appear at all straightforward at this time.

Acknowledgements

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