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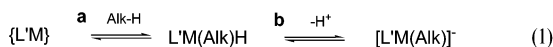
Synthesis and Reactivity of Dimethyl Platinum(IV) Hydrides in Water

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Alkane CH bond oxidative addition to transition-metal complexes {L'M} (eq 1a) is one of the important reactions utilized in hydrocarbon functionalization.¹

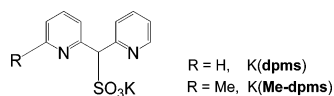


In the case where {L'M} is a platinum(II) precursor, alkyl hydrido platinum(IV) complexes L'M(Alk)H² may emerge as stable products of reaction 1^{3,4} or as plausible intermediates.⁵ The stability and reactivity of these species is primarily a function of their structure.^{2,4,6,7} Exposed to a highly reactive solvent such as water, L'Pt^{IV}(Me)H may undergo proton reductive elimination (eq 1b)^{8,9} or methane reductive elimination (reversal of eq 1a).

Studies of the mechanism of methane activation in aqueous solutions of platinum(II) salts⁹ and search for evidence of intermediacy of Pt^{IV}(Alk)H in these solutions were the subject of a number of publications.¹⁰ Recent results⁸ suggest that methane CH bond cleavage by aqueous platinum(II) compounds involves alkane oxidative addition to platinum(II) (eq 1a) with consecutive proton reductive elimination to form a platinum(II) alkyl (eq 1b). Despite a number of efforts, formation of L'PtMe₂H in purely aqueous solutions was never observed directly.^{11,12}

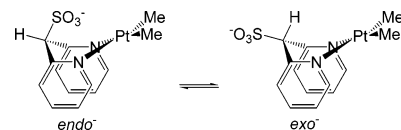
We report here the synthesis and the reactivity of a series of new methyl hydrido platinum(IV) complexes L'PtMe₂H featuring the ability to exchange their methyl groups with ¹³CH₄ and persistence in water, which is sufficient for observation of their reactivity and even for their isolation from aqueous solutions of corresponding anionic platinum(II) precursors. This wet hydrido platinum(IV) chemistry became possible by using the new hydrophilic anionic *fac*-chelating ligand L, di(2-pyridyl)methanesulfonate, (dpms)-, and its methyl analogue (Me-dpms)- (Chart 1). These

Chart 1



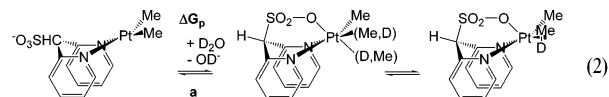
ligands were designed to allow the sulfonate group to play an *active solvent-dependent* role in coordination to the metal (compare with tris(pyrazolyl) methanesulfonates¹³). The donicity of the anionic SO₃⁻ tail toward the metal and therefore the ability of the ligands L to stabilize octahedral methane addition products L'PtMe₂H were expected to be a function of the solvent polarity. Strong interactions of the polar SO₃⁻ group with a polar solvent such as water could ultimately help break SO₃-Pt bonds, switch L to an η²-coordination mode, and form the unsaturated highly reactive transient (η²-L)-PtMe₂H. In weakly polar solvents such as dichloromethane not capable of interacting strongly with the SO₃⁻ group, more robust SO₃-Pt bonds are formed and the kinetically more inert (η³-L)-PtMe₂H could be expected.

Ligand exchange with Pt₂Me₄(SMe₂)₂¹⁴ in methanol gave the anionic platinum(II) complexes K(L)PtMe₂ that are stable in methanolic solutions as a mixture of *exo*- and *endo*-conformers,¹⁵ 7:1, respectively, for L = dpms (established by NOE experiments):



In contrast to the *exo*-conformer, the *endo*-conformer is preorganized¹⁶ for protonation. The sulfonate group in the latter is proximal to the metal atom and poised to form a bond with Pt when Pt changes the formal oxidation state from +2 to +4.

Methanol-*d*₄ and its mixtures with D₂O caused fast reversible H/D exchange in the Pt-Me fragments of [L'PtMe₂]⁻ as opposed to slow H/D exchange accompanied by irreversible methanolysis reported earlier for a number of dimethylplatinum(II) complexes.^{11,17} The observed pseudo-first-order rate constants (e.g., 2.10(4) × 10⁻³ s⁻¹ at 62.3 mol % D₂O at 296 K) increased linearly with a molar concentration of water in solution leading to a second-order rate constant *k* = 8.5(3) × 10⁻⁵ M⁻¹ s⁻¹ and effective Gibbs activation energy of the H/D exchange Δ*G*_{ex}[‡] ≈ 22.8 kcal/mol. These results imply both facile protonation of [L'PtMe₂]⁻ by D₂O to produce two isomeric L'PtMe₂D (see below) and very fast D-C reductive coupling to form an intermediate methane complex without elimination of methane (eq 2; Δ*G*_{rc}[‡] < Δ*G*_{re}[‡], Figure 1) in contrast to earlier observations.^{11,18}



Indeed, an 11.6 mM aqueous (H₂O) solution of K(dpms)PtMe₂ is alkaline (pH = 10.1, 1.1% of (dpms)PtMe₂H at equilibrium); fast evaporation of this solution at 0 °C allows recovery of K(dpms)-PtMe₂ quantitatively. More convincing, L'PtMe₂H (5% yield, L = dpms; 50% yield, L = Me-dpms) was isolated from solutions of K(L)PtMe₂ in H₂O by extracting them with dichloromethane, which shifts the equilibrium (eq 2a) to neutral and more lipophilic L'PtMe₂H. These observations suggest that platinum(IV) alkyl hydrides can form in the Shilov-type systems as well as they can undergo a reversible proton loss in water (eqs 1b, 2a) to give platinum(II) alkyls. On the basis of pD measured (eq 2a) we estimated Δ*G*_p ≈ 10.5 kcal/mol and therefore the effective activation barrier for the reductive coupling, Δ*G*_{rc}[‡] ≈ 12.3 kcal/mol.

In contrast to methanol-*d*₄, D₂O solutions of K(dpms)PtMe₂ (2.3:1 *endo*-/*exo*-, respectively) slowly liberate methane (7.3(2) × 10⁻⁷ M⁻¹ s⁻¹, τ_{1/2} = 290 min, 296 K) to form cleanly the K(dpms)-PtMe(OD) complex and imply an effective barrier for methane reductive elimination of (dpms)PtMe₂D, Δ*G*_{re}[‡] ≈ 15.1 kcal/mol. In the presence of air, clean oxidation of K(L)PtMe₂, but not hydrolysis, occurred to produce (dpms)PtMe₂(OH) (Figure 2a).

Thus, the ligand-enhanced basicity of [L'PtMe₂]⁻ allows for the formation of L'PtMe₂H at low concentrations in water and estimation of the rate constants of very fast CH reductive coupling and reductive elimination of these species at room temperature.¹⁹

The complexes L'PtMe₂H were also obtained in 35–55% yield as white precipitates by protonation of aqueous solutions of K(L)-

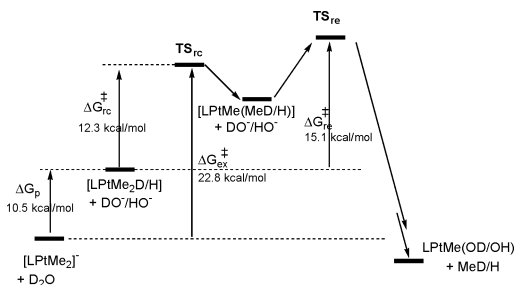


Figure 1. Energy of protonation of $[LPtMe_2]^-$, ΔG_p^\ddagger , the observed effective activation energy of H/D exchange in PtMe groups, ΔG_{ex}^\ddagger , reductive coupling, ΔG_{rc}^\ddagger , and reductive elimination, ΔG_{re}^\ddagger , of $LPtMe_2D$ in D_2O solution ($L = dpms$), molarity scale.

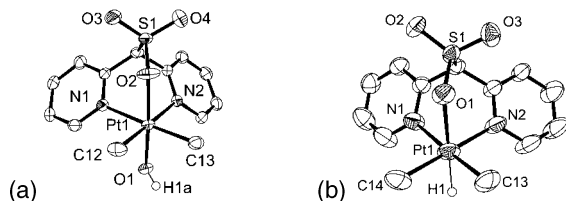


Figure 2. ORTEP drawings (50% probability ellipsoids) of (a) $(dpms)PtMe_2(OH)$ and (b) $(dpms)PtMe_2H \cdot CH_2Cl_2$ (CH_2Cl_2 is not shown). H atoms are omitted for clarity except for the PtH and Pt(OH) fragments.

$PtMe_2$ with triflic acid at $0^\circ C$. Thus, a transition to a solid or liquid weakly polar phase stabilizes $LPtMe_2H$ complexes by helping stronger coordination of SO_3^- group and Pt^{IV} as opposed to the ability of water to cause dissociation of the SO_3^- tail due to strong solvation. Such coordination disfavors formation of low-coordinate platinum species prone to facile methane elimination.²⁰

The $LPtMe_2H$ complexes synthesized are not thermodynamically stable in water. When isolated $LPtMe_2H$ was stirred with H_2O at $25^\circ C$ in the absence of organic solvent, it dissolved slowly to form methane and the *endo*- $LPtMe(OH_2)$. The methane reductive elimination was preceded by very fast and reversible CH reductive coupling. Thus, in H_2O - D_2O mixtures isotopomeric $LPt(CH_3, D_{3-n})(OH_2)$ ($n = 0, 1, 2, 3$) was observed, but no methyl group exchange was detected when this solution was exposed to 2 atm of $^{13}CH_4$ at room temperature for one week.

Similarly, the protonation of $K(L)PtMe_2$ with triflic acid in CH_2Cl_2 at $-80^\circ C$ yielded $LPtMe_2H$ (40–55%). $LPtMe_2H$ is stable in the solid state but decomposes in dichloromethane in the course of several days at room temperature, producing an unidentified white precipitate. According to 1H NMR data, $(dpms)PtMe_2H$ exists in CH_2Cl_2 as a mixture of two isomers that slowly eliminate methane at 296 K. The Pt–H resonance for the predominant species of C_s symmetry is at -26.15 ppm (s, $^1J_{Pt-H} = 1813$ Hz) with a hydrido ligand trans to the sulfonate group. This geometry was also established by XRD (Figure 2b). The position of the Pt–H resonance at -20.30 ppm ($^1J_{Pt-H} = 1428$ Hz) for the other isomer having C_1 symmetry is consistent with a structure with the hydride trans to one of the pyridine fragments.

In contrast to aqueous solutions, $(dpms)PtMe_2H$ is kinetically more stable in weakly polar and weakly coordinating CH_2Cl_2 , whereas the corresponding solvent–complex $LPtMe(solvent)^{21}$ is much more reactive. The mixture of isomeric complexes reacts with Et_3SiH in the course of few days at room temperature, producing cleanly a single isomer of $(dpms)PtMe(SiEt_3)H$ with the Pt–H resonance at -18.76 ppm (s, $^1J_{Pt-H} = 1360$ Hz). The reaction of $(dpms)PtMe_2H$ with benzene (30 % vol) dissolved in dichloromethane is slower than its rate of decomposition. The methyl analogue $(Me-dpms)PtMe_2H$, however, reacts faster²² and produces methane and a single isomer of $LPtMe(Ph)H$ with the Pt–H resonance at -24.80 ppm (s, $^1J_{Pt-H} = 1816$ Hz). Moreover, $(Me-dpms)PtMe_2H$ exposed

to 2 atm of $^{13}CH_4$ in CH_2Cl_2 solution reacted to produce ^{13}C -isotopomer (10% enrichment after 30 h). This is the first, to our knowledge, published report of a reaction between methane and a platinum complex leading to platinum(IV) methyl hydride.

In summary, we have shown that anionic hydrophilic ligands of the di(2-pyridyl)methanesulfonate family open new opportunities to control reactivity of $LPtMe_2H$ in aqueous and organic media.

Acknowledgment. We thank the University of Maryland for financial support of this work.

Supporting Information Available: Experimental details, characterization data, and CIF files for $(dpms)PtMe_2H$ and $(dpms)PtMe_2(OH)$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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