

Activation of Methane Promoted by NeohexylPt(II) Complexes. Isolation of MethylPt(II) Complexes

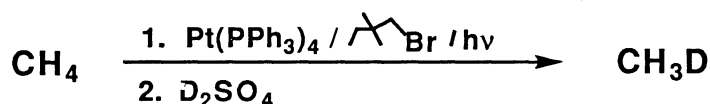
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trans-Pt(CH₂CMe₂Et)Br(PPh₃)₂ induced C-H bond activation of CH₄ under UV p irradiation leading to *trans*-PtMeBr(PPh₃)₂, while H-D exchange reaction of CH₄ with D₂ or D₂SO₄ took place in the photochemical reaction system containing Pt(PPh₃)₄ and neohexyl bromide. A possible reaction mechanism involving radical process is discussed on the basis of radical-trap experiment.

Activation of CH₄, the least reactive and most plentiful of the alkanes, is one of the most challenging studies in transition metal chemistry. Although a variety of metal complexes have been observed to react with the C-H unit of CH₄ by oxidative addition to metal center,¹⁻⁶ σ -bond metathesis of M-X units,⁷⁻⁹ and addition to M=X groups,¹⁰ only a few examples^{1, 3} are reported to be isolated as CH₃-M complexes. Recently, we have reported selective sp³ C-H bond activation of alkylaromatics promoted by Pt(0) complexes and proposed their tentative reaction mechanism.¹¹ For further extension of these studies, we would like to report here activation of CH₄ using Pt(0)L₄ and Pt(II)RBrL₂ and describe possible reaction mechanism involving radical process.

In the presence of 3 equiv. of neohexyl bromide, a mixture of CH₄ (6 atm) and Pt(0)(PPh₃)₄ in benzene was irradiated in a glass-pressure bottle by a high pressure Hg lamp equipped with a band path filter (U-350) in benzene for 5 h at room temperature. The resulting colorless solution was analyzed to contain neohexane (87% / Pt).



After removal of benzene, the resulting white solids were treated with excess of D₂SO₄. The resulting gaseous products were collected in a glass tube (20 ml) containing active carbon powder (3ml) under liquid N₂ temperature. GC-MS analysis of these products were found to be CH₃D (28% / Pt) and CH₃-CH₃ (4%).

In a stainless autoclave cell having a pair of quartz windows as illustrated in Fig. 1, the mixture of Pt(0)(PPh₃)₄ and neohexyl bromide was irradiated in the presence of CH₄ (10 atm) in benzene. The resulting colorless solution afforded neohexane (87% yield), and white crystalline solids after evaporation of the solvent.

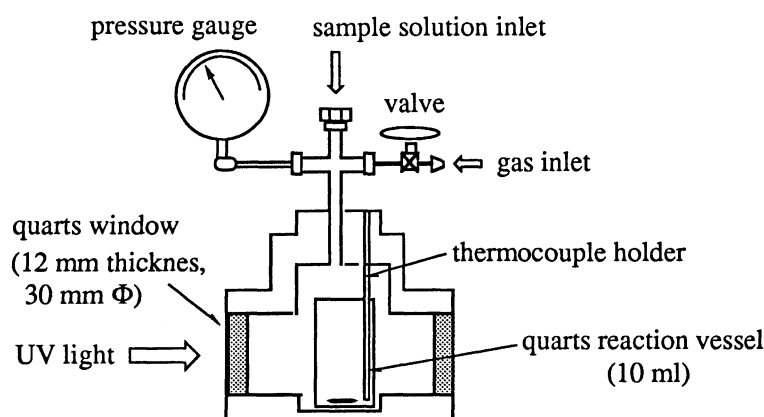
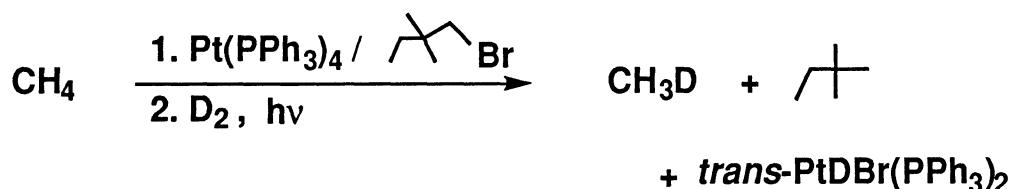


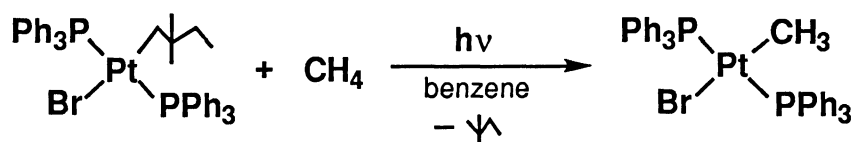
Fig. 1. Stainless steel autoclave cell.

The treatment of the resulting white solids with D_2 (5 atm) in benzene under irradiation at $50\text{ }^\circ\text{C}$ afforded CH_3D (18% yield /Pt) together with $trans\text{-PtDBr(PPh}_3)_2$ (37%).¹²⁾

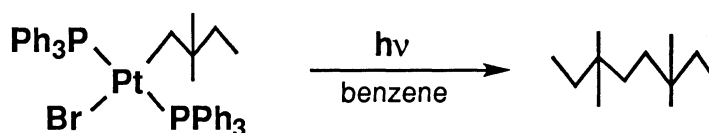


As reported previously, sp^3 C-H bond activation of alkylaromatics, performed by $Pt(PPh_3)_4$ / neohexyl bromide under UV irradiation, was induced by photochemical homolysis of $trans\text{-Pt(CH}_2\text{CMe}_2\text{Et)Br(PPh}_3)_2$ which was cleanly isolated as active intermediate.¹¹⁾ Therefore, we have attempted activation of CH_4 using $trans\text{-Pt(CH}_2\text{CMe}_2\text{Et)Br(PPh}_3)_2$ for understanding the factors governing the efficient CH_4 -activation with transition metals. In a stainless autoclave cell, a benzene solution containing $trans\text{-Pt(CH}_2\text{CMe}_2\text{Et)Br(PPh}_3)_2$ and CH_4 (40 atm) was irradiated at $26\text{ }^\circ\text{C}$. After 6h reaction, the resulting solution was analyzed to contain neohexane in 93% based on the starting Pt complex. Addition of dry ether to the light yellow solution resulted in the precipitation of light yellow solid which was identified as $trans\text{-PtMeBr(PPh}_3)_2$ in 12% yield.¹³⁾

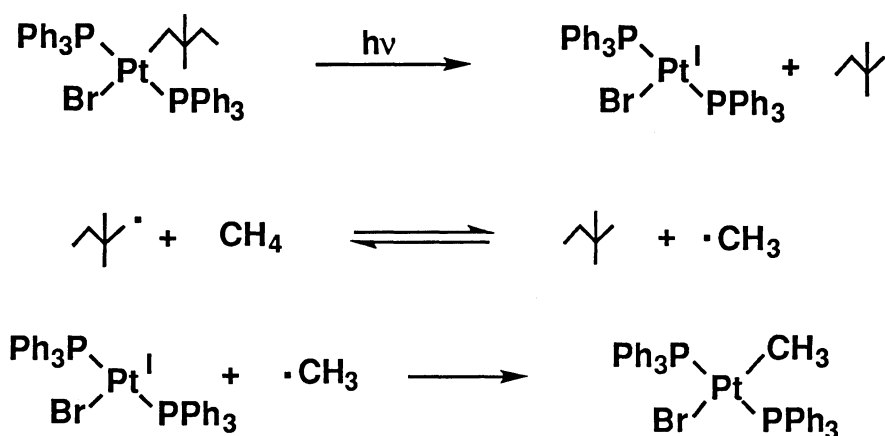
$trans\text{-PtCH}_2\text{PhBr(PPh}_3)_2$ also reacted with CH_4 (10 atm) in benzene to give $trans\text{-PtMeBr(PPh}_3)_2$ in 7% yield, whereas $trans\text{-PtCD}_3\text{Br(PPh}_3)_2$ and $trans\text{-PtPhBr(PPh}_3)_2$ were inactive for activation of CH_4 under the reaction conditions employed above.¹⁴⁾



Importantly, these reactions are completely inhibited by the addition of a radical scavenger such as 1,4-benzoquinone (4 equiv. to Pt complex).¹⁵⁾ In addition, *trans*-Pt(CH₂CMe₂Et)Br(PPh₃)₂ in benzene-d₆ underwent photochemical degradation to give a dimer of neohexyl radical, 3,3,6,6-tetramethyloctane in 43% yield based on the starting Pt complex in the absence of CH₄.



These experimental results may be consistent with a reaction pathway involving a radical process¹⁶⁾ by homolytic Pt-CH₂CMe₂Et bond cleavage which generates neohexyl radicals as depicted in the following scheme.



Further extensive studies on kinetic study and catalytic activation of CH₄ by other transition metal complexes are now in progress. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 04241203).

References

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- 12) ^1H -NMR(CDCl_3); δ 7.1-7.7 (m, Ph), ^{31}P -NMR(CDCl_3); 29.9 (s, $J_{\text{Pt-P}} = 2990$ Hz), IR(KBr); 1572 cm^{-1} ($\nu_{\text{Pt-D}}$). Hydrogenolysis of these white solids with H_2 (5 atm) under UV-irradiation at 50 $^\circ\text{C}$ yielded *trans*- $\text{PtHBr}(\text{PPh}_3)_2$ in 28%: ^1H -NMR(CDCl_3); δ -14.9 (t, Pt-H, 1H, $J_{\text{P-H}} = 13.1$ Hz, $J_{\text{Pt-H}} = 241$ Hz), ^{31}P -NMR(CDCl_3); 29.9 (s, $J_{\text{Pt-P}} = 2990$ Hz), IR(KBr); 2213 cm^{-1} ($\nu_{\text{Pt-H}}$).
- 13) ^1H -NMR(C_6D_6); δ 0.43 (t, Pt- CH_3 , 3H, $J_{\text{Pt-H}} = 68$ Hz, $J_{\text{P-H}} = 6.5$ Hz), 7.1-7.6 (m, Ph, 30H), ^{31}P -NMR(C_6D_6); 14.4 (s, $J_{\text{Pt-P}} = 3697$ Hz).
- 14) Tertiary phosphine ligands on the Pt complexes affected considerably on activation of CH_4 . *trans*- $\text{Pt}(\text{CH}_2\text{CMe}_2\text{Et})\text{Br}(\text{PR}_3)_2$ (R= Me, Et) were inactive for CH_4 activation, although photo-induced homolytic cleavage of Pt-neohexyl bond took place by generating a dimer of neohexyl radical, 3,3,6,6-tetramethyloctane (35% per Pt). This puzzling question why Pt complexes having σ -donative phosphines were insufficient for this particular reaction, should remain to be properly answered.
- 15) GC-MS analysis of the reaction residue suggested the formation of neohexyl adduct of 1,4-benzoquinone.
- 16) Photochemical homolysis of transition metal-alkyl bonds are precedent: see, G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979; G. N. Schrauzer and J. H. Grate, *J. Am. Chem. Soc.*, **103**, 541(1981); E. G. Samsel and J. K. Kochi, *ibid.*, **108**, 4790(1986); S. Fukuzumi, K. Ishikawa, and T. Tanaka, *Organometallics*, **6**, 358(1987). And references are cited therein.

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