CHEMISTRY LETTERS, pp. 2263-2266 1994.

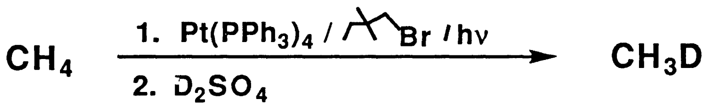
Activation of Methane Promoted by NeohexylPt(II) Complexes. Isolation of MethylPt(II) Complexes

Akira MIYASHITA* and Yoshiko SAIDA
Faculty of Engineering, Department of Applied Chemistry, Saitama University, Shimo-ohkubo 255, Urawa 338

trans-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ induced C-H bond activation of CH_4 under UV p irradiation leading to *trans*-$PtMeBr(PPh_3)_2$, while H-D exchange reaction of CH_4 with D_2 or D_2SO_4 took place in the photochemical reaction system containing $Pt(PPh_3)_4$ and neohexyl bromide. A possible reaction mechanism involving radical process is discussed on the basis of radical-trap experiment.

Activation of CH_4, 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 CH_4 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 examples1, 3) are reported to be isolated as CH_3-M complexes. Recently, we have reported selective sp^3 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 CH_4 using $Pt(0)L_4$ and $Pt(II)RBrL_2$ and describe possible reaction mechanism involving radical process.

In the presence of 3 eqiv. of neohexyl bromide, a mixture of CH_4 (6 atm) and $Pt(0)(PPh_3)_4$ 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 D_2SO_4. The resulting gaseous products were collected in a glass tube (20 ml) containing active carbon powder (3ml) under liquid N_2 temperature. GC-MS analysis of these products were found to be CH_3D (28% / Pt) and CH_3-CH_3 (4%).

In a stainless autoclave cell having a pair of quartz windows as illustrated in Fig. 1, the mixture of $Pt(0)(PPh_3)_4$ and neohexyl bromide was irradiated in the presence of CH_4 (10 atm) in benzene. The resulting colorless solution afforded neohexane (87% yield), and white crystalline solids after evaporation of the solvent.

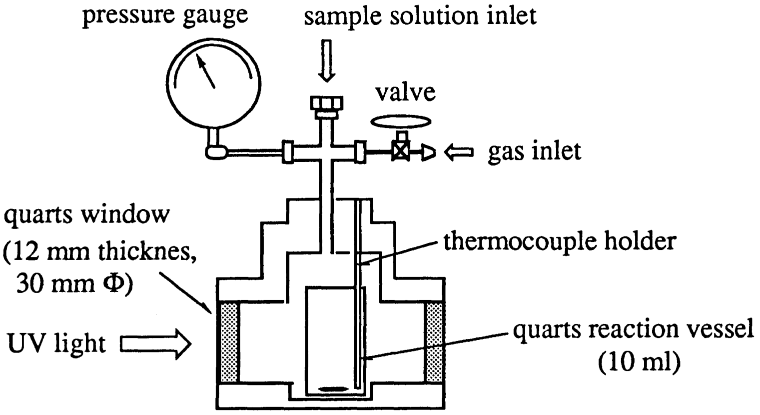
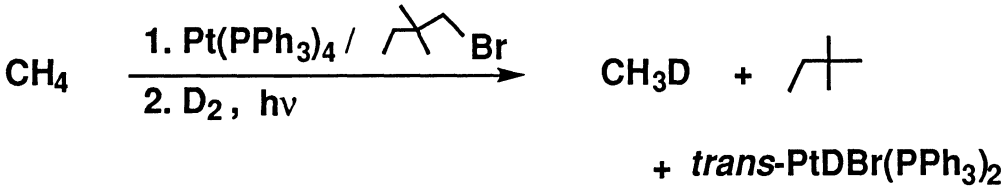


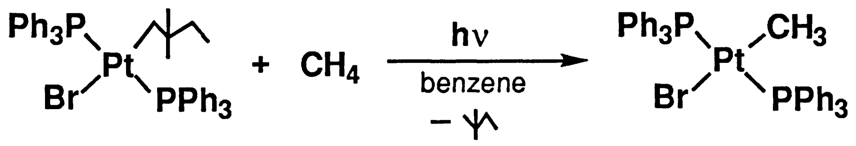
Fig. 1. Stenless steel autoclave cell.

The treatment of the resulting white solids with D_2 (5 atm) in benzene under irradiation at 50 °C afforded CH_3D (18% yield /Pt) together with trans-$PtDBr(PPh_3)_2$ (37%).12)

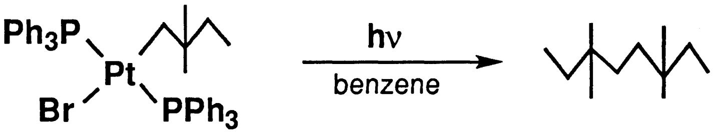


As reported previously, sp^3 C-H bond activation of alkylaromatics, performed by $Pt(PPh_3)_4$ / neohexyl bromide under UV irradiation, was induced by photochemical homolysis of *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ which was cleanly isolated as active intermediate.11) Therefore, we have attempted activation of CH_4 using *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ for understanding the factors governing the efficient CH_4-activation with transition metals. In a stainless autoclave cell, a benzene solution containing *trans*-$Pt(CH_2CMe_2Et)Br(PPh_3)_2$ and CH_4 (40 atm) was irradiated at 26 °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*-$PtMeBr(PPh_3)_2$ in 12% yield.13)

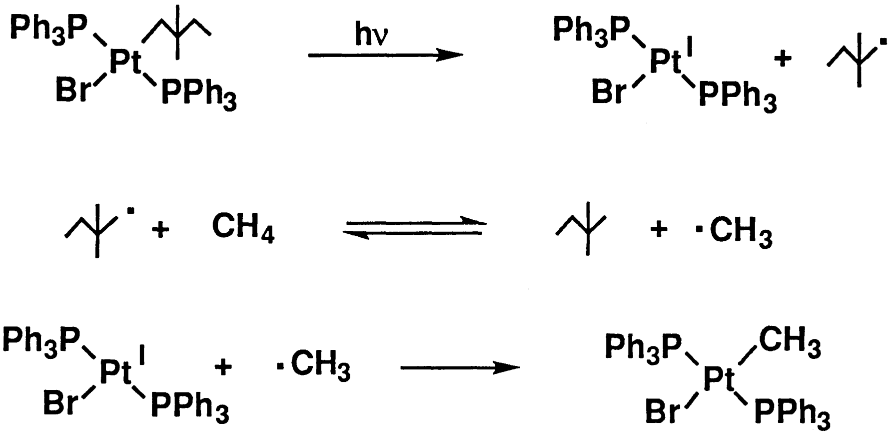
trans-$PtCH_2PhBr(PPh_3)_2$ also reacted with CH_4 (10 atm) in benzene to give *trans*-$PtMeBr(PPh_3)_2$ in 7% yield, whereas *trans*-$PtCD_3Br(PPh_3)_2$ and *trans*-$PtPhBr(PPh_3)_2$ were inactive for activation of CH_4 under the reaction conditions employed above.14)



Importantly, these reactions are completely inhibited by the addition of a radical scavenger such as 1,4-benzoquinone (4 eqiv. to Pt complex).[15] In addition, *trans*-Pt(CH_2CMe_2Et)Br(PPh_3)$_2$ in benzene-d_6 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 CH_4.



These experimental results may be consistent with a reaction pathway involving a radical process[16] by homolytic Pt-CH_2CMe_2Et bond cleavage which generates neohexyl radicals as depicted in the following scheme.



Further extensive studies on kinetic study and catalytic activation of CH_4 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

1) J. K. Hayano, A. D. McMaster, and W. A. G. Graham, J. Am. Chem. Soc., **105**, 7190(1983).
2) A. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, **105**, 3929(1983).
3) R. G. Bergman, P. F. Seidler, and T.T. Wenzel, *J. Am. Chem. Soc.*, **108**, 4856(1986).
4) M. Hackett and G. M. Whitesides, *J. Am. Chem. Soc.*, **110**, 1449(1988).
5) T. G. Harper, R. S. Shinomoto, M. A. Deming, and T. C. Flood, *J. Am. Chem. Soc.*, **110**, 7915(1988).
6) B. B. Wayland, S. Ba, and A. E. Sherry. *J. Am. Chem. Soc.*, **113**, 5305(1991).
7) P. Watoson, *J. Am. Chem. Soc.*, **105**, 6491(1983).
8) C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, **108**, 625(1986).
9) M. E. Thompson, S. M. Baxter, B. J. Burger,W. P. Schaefer, and J. E. Bercaw, *J. Am. Chem. Soc.*, **109**, 8109(1987).
10) C. C. Cummins, S. M. Baxter, and P. T. Wolczanski, *J. Am. Chem. Soc.*, **110**, 8731(1988).
11) A. Miyashita, M. Hotta, and Y. Saida, *J. Organometal. Chem.*, **473**, 353(1994).
12) ^{1}H-NMR(CDCl$_3$); δ 7.1-7.7 (m, Ph), ^{31}P-NMR(CDCl$_3$); 29.9 (s, J_{Pt-P} =2990 Hz), IR(KBr); 1572 cm^{-1} (ν_{Pt-D}). Hydrogenolysis of these white solids with H$_2$ (5 atm) under UV-irradiation at 50 °C yielded *trans*-PtHBr(PPh$_3$)$_2$ in 28%: ^{1}H-NMR(CDCl$_3$); δ -14.9 (t, Pt-H, 1H, J_{P-H} =13.1 Hz, J_{Pt-H} =241 Hz), ^{31}P-NMR(CDCl$_3$); 29.9 (s, J_{Pt-P} =2990 Hz), IR(KBr); 2213 cm^{-1} (ν_{Pt-H}).
13) ^{1}H-NMR(C$_6$D$_6$); δ 0.43 (t, Pt-CH$_3$, 3H, J_{Pt-H} =68 Hz, J_{P-H} =6.5 Hz), 7.1-7.6 (m, Ph, 30H), ^{31}P-NMR(C$_6$D$_6$); 14.4 (s, J_{Pt-P} = 3697 Hz).
14) Tertiary phosphine ligands on the Pt complexes affected considerably on activation of CH$_4$. *trans*-Pt(CH$_2$CMe$_2$Et)Br(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.

(Received August 26, 1994)