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Synthesis of Novel Neutral Five-coordinated Pt(II) Complexes Comprised of π-Acceptor Ligands Alone and Their Application to Electrophilic Activation of C-H Bond of Saturated Hydrocarbons

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Neutral five-coordinated platinum(II) complexes ($[Pt(SnCl_3)_2(P(OR)_3)_3]$; R = Me, Et) with high solubility to hydrocarbon solvents have been newly synthesized. The characteristic ligand composition (all π-acceptor ligands) gives the Pt(II) center both enhanced electrophilicity and stability against reduction, due to which thermal (non-photolytic) catalytic dehydrogenation of cyclooctane in homogeneous solutions was achieved under mild reaction conditions, including electrophilic C-H bond activation.

It has been known that solutions of $[PtCl_4]^{2-}$ ion activate the C-H bond of hydrocarbons to cause H-D exchange with solvent under mild conditions, and this reaction is considered to proceed via Pt(II) alkyl intermediates formed by the electrophilic attack of Pt(II) center to the C-H bond.1) If a strong π-acceptor (weak σ-donor) ligand is introduced here, it should decrease the electron density of the central metal ion, and hence cationic character of the metal ion would be enhanced. So that, higher reactivity for the C-H bond activation is expected.

The ionic form of this type of complex (*e.g.*, $[Pt(SnCl_3)_5]^{3-}$) is, however, scarcely soluble in hydrocarbons; an attempt of C-H bond activation in 1,1,2,2-tetrachloroethane solution resulted in the considerable formation of reaction products with solvent.2) In order to surmount this unfavorable point, we have synthesized here novel neutral five-coordinated Pt(II) complexes with π-acceptor ligands alone ($[Pt(SnCl_3)_2(P(OR)_3)_3]$), and tried thermal (non-photolytic) catalytic dehydrogenation of cyclooctane as a test reaction.

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All the complexes were synthesized under Ar atmosphere. $(PPh_4)_3[Pt(SnCl_3)_5]$ (1.0 g, 0.43 mmol) was dissolved in acetonitrile (30 ml). Addition of $P(OR)_3$ (R = Me or Et, [P]/[Pt] = 3) and stirring at 25°C for 48 h afforded a yellow solution. The solution was concentrated and cooled at -20 °C for 12 h. The resulting white precipitate ($(PPh_4)SnCl_3$, confirmed by ^{31}P NMR) was removed by filtration. This separation procedure was repeated until the peak of the PPh_4^+ ion disappeared completely in the ^{31}P NMR spectrum. Finally, the solvent was reduced further and yellow precipitates were obtained (yield 22% for R = Me and 64% for R = Et). The ^{31}P and ^{119}Sn NMR characteristics of the complexes were tabulated in Table 1, together with those of $[Pt(SnCl_3)_3(P(OR)_3)_2]^-$ (R = Me and Et) and *trans*-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$.[3)] Both of the chemical-shift values are in the range of five-coordinated complex, and the elemental analysis data were satisfactory for this structure.[4)]

Dehydrogenation of cyclooctane was carried out under N_2 atmosphere (1 atm) at 151 °C (refluxing). The reaction solution was prepared by dissolving the Pt(II) complex (0.010 mmol, approximately saturated) in cyclooctane (200 ml). The reactor was equipped with a reflux condenser to which a gas buret was attached. The products in the liquid and gas phases were analyzed by gas chromatography (OV-101 and active carbon columns, respectively).

Figure 1 shows the time course for cyclooctene formation from cyclooctane with $[Pt(SnCl_3)_2(P(OR)_3)_3]$ complexes. In both cases, cyclooctene is formed without any induction period and other products (*e.g.*, cyclooctadiene) were not observed at all (confirmed by OV-1 capillary column and GC-MS (DB-1 capillary column)). The lack of induction period suggests that metallic Pt species which may be gradually formed by the catalyst deactivation are not catalytically active. The turnover numbers exceeded unity (9.8 and 4.4 at 50 h for $[Pt(SnCl_3)_2(P(OR)_3)_3]$ (R =

Table 1. ^{31}P and ^{119}Sn NMR characteristics of Pt(II) complexes with π-acceptor ligands

Complexes	$\delta(^{31}P)$/ppm	$\delta(^{119}Sn)$/ppm	$^1J(PPt)$/Hz	
$[Pt(SnCl_3)_2(P(OMe)_3)_3]$	80.3	-128.9	3965	this work[a)]
$[Pt(SnCl_3)_2(P(OEt)_3)_3]$	73.5	-112.8	3931	this work[a)]
$[Pt(SnCl_3)_3(P(OMe)_3)_2]^-$	83.3	-121	2939	ref. (3)[b)]
$[Pt(SnCl_3)_3(P(OEt)_3)_2]^-$	77.0	-117	2883	ref. (3)[c)]
trans-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$	104.4	-22	3610	ref. (3)[d)]

a) NMR spectra were measured in CH_3CN using a Jeol FX-60Q spectrometer (24.21 MHz for ^{31}P and 22.30 MHz for ^{119}Sn) at 25 °C.

b) In $(CD_3)_2CO$ at -90 °C. c) In $(CD_3)_2CO$ at -40 °C. d) In $CH_2Cl_2/CDCl_3$ (1/1) at -50 °C.

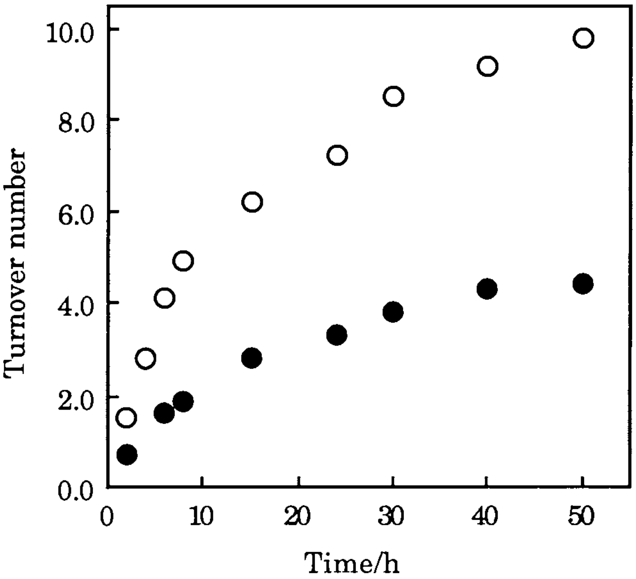

Fig. 1. Time course of cyclooctene formation from cyclooctane with $[Pt(SnCl_3)_2(P(OMe)_3)_3]$ (○) and $[Pt(SnCl_3)_2(P(OEt)_3)_3]$ (●) catalysts; catalyst 0.010 mmol, cyclooctane 200 ml, reaction temperature 151 °C (refluxing).

Me and Et), respectively), which ensures the reaction is catalytic; this is believed to be the second example of homogeneous catalytic dehydrogenation of saturated hydrocarbon under non-photolytic conditions.[5)] Evolution of dihydrogen was observed in every case.[6)] It is noteworthy that *cis*-$[PtCl_2(P(OMe)_3)_2]$ complex,[7)] which has no tin(II) ligand, showed low activity (turnover number of 3.0 at 50 h), and furthermore black metallic species were observed from the early stage of reaction. This feature obviously indicates that the $SnCl_3^-$ ligand prevented the reduction of Pt(II) to Pt(0) by virtue of its strong π-accepting property ($SnCl_3^- > P(OR)_3$).[8)]

There have been many examples of non-catalytic or catalytic C-H bond activation of alkanes which involve the oxidative addition of C-H bond to a coordinatively-unsaturated species generated photochemically[9)] (or thermally[5)]) from low-valent transition-metal complexes; it is pointed out that a high energy of HOMO is important in the oxidative addition process.[10)] In the present case, however, since the π-acceptor ligands ($SnCl_3^-$ and $P(OR)_3$) should lower the energy level of both HOMO and LUMO and also enhance the cationic character of central Pt(II) ion, an electrophilic attack of the electron-poor metal center to the C-H bond[11)] will be important.[12)] As Sen et al. demonstrated recently,[13)] this kind of C-H bond activation would become a new type of functionalization process of saturated alkanes, being a promising clue to the effective utilization of natural gas (methane) by means of transition-metal complex catalysts.

References

1) A. E. Shilov, "Activation of Saturated Hydrocarbons by Transition Metal Complexes," ed by R. Ugo and B. R. James, D. Reidel, Dordrecht (1984).

2) T. Yamakawa, T. Fujita, and S. Shinoda, *J. Mol. Catal.*, **52**, L41 (1989); **66**, 321 (1991).

3) A. Albinati, P. S. Pregosin, and H. Rüegger, *Inorg. Chem.*, **23**, 3223 (1984). In this report, however, *trans*-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$ complex was only characterized in the form as generated in solution, and has not been isolated yet.

4) $[Pt(SnCl_3)_2(P(OMe)_3)_3]$ Found: C, 11.26; H, 2.96%. Calcd for $C_9H_{27}O_9P_3Cl_6Sn_2Pt$: C, 10.62; H, 2.67%. Mp 128 - 130 °C.
$[Pt(SnCl_3)_2(P(OEt)_3)_3]$ Found: C, 19.57; H, 4.19%. Calcd for $C_{18}H_{45}O_9P_3Cl_6Sn_2Pt$: C, 18.90; H, 3.97%. Mp 106 - 108 °C.

5) T. Fujii and Y. Saito, *J. Chem. Soc., Chem. Commun.*, **1990**, 757.

6) Very small amount of dihydrogen due to the reaction size prevented accurate quantitative analysis.

7) M. J. Church and M. J. Mays, *J. Inorg. Nucl. Chem.*, **33**, 253 (1971).

8) M. S. Holt, W. L. Wilson, and J. H. Nelson, *Chem. Rev.*, **89**, 11 (1989).

9) M. J. Burk, R. H. Crabtree, and D. V. McGrath, *J. Chem. Soc., Chem. Commun.*, **1985**, 1829; K. Nomura and Y. Saito, *J. Mol. Catal.*, **54**, 57 (1989); T. Sakakura, T. Sodeyama, and M. Tanaka, *New J. Chem.*, **13**, 737 (1989); J. A. Maguire, W. T. Boese, and A. S. Goldman, *J. Am. Chem. Soc.*, **111**, 7088 (1989); T. Hanaoka, H. Arakawa, K. Takeuchi, T. Matsuzaki, and Y. Sugi, Jpn. Kokai Tokkyo Koho, JP 2-212438; T. Sakakura, F. Abe, and M. Tanaka, *Chem. Lett.*, **1991**, 297.

10) T. Ziegler, V. Tschinke, L. Fan, and A. D. Becke, *J. Am. Chem. Soc.*, **111**, 9177 (1989).

11) J. D. Koola and D. M. Roddick, *J. Am. Chem. Soc.*, **113**, 1450 (1991).

12) From the simple concept of coordinative saturation, d^8 ML_5 (18-electron) species as in the present case may lack substantial electrophilicity. On the other hand, Rossi and Hoffmann concluded the presence of an empty d-based orbital as LUMO even in this case (*Inorg. Chem.*, **14**, 365 (1975)). It seems, however, possible that the C-H bond is activated here by the coordinatively-unsaturated d^8 ML_4 (16-electron) species formed by the ligand dissociation.

13) E. Gretz, T. F. Oliver, and A. S. Sen, *J. Am. Chem. Soc.*, **109**, 8109 (1987); L.-C. Kao, A. C. Hutson, and A. Sen, *ibid.*, **113**, 700 (1991).

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