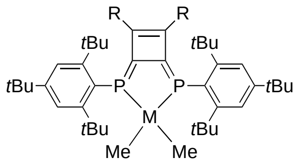
Synthesis and Reactions of Palladium and Platinum Complexes Bearing Diphosphinidenecyclobutene Ligands: A Thermally Stable Catalyst for Ethylene Polymerization**

Shintaro Ikeda, Fumie Ohhata, Masaki Miyoshi,
Rika Tanaka, Tatsuya Minami, Fumiyuki Ozawa,* and
Masaaki Yoshifuji*

Diphosphaalkenes are phosphorus analogues of diimines and form stable chelate rings with transition metal species.[1–3] The coordination structures resemble those of diimine complexes. However, owing to the unique electronic nature of P=C bonds, diphosphaalkene complexes are expected to possess rather intriguing chemical properties, significantly different from the diimine analogues. Thus, we have been interested in the reaction chemistry of diphosphaalkene complexes, particularly in catalytic systems; data for such systems is extremely limited.[2]

Herein we examine the synthesis, structures, and catalytic properties of some methylpalladium and platinum complexes (**1**–**4**) coordinated with 3,4-bis[(2,4,6-tri-*tert*-butylphenyl)-phosphinidene]cyclobutene derivatives.[4] A cationic monomethylpalladium complex derived from **1** exhibits good catalytic activity for ethylene polymerization.



1: M = Pd, R = Ph   **3**: M = Pd, R = H
2: M = Pd, R = SiMe$_3$ **4**: M = Pt, R = Ph

The diphosphaalkene ligands in **1**–**4** were chosen with reference to findings reported by Brookhart et al. on nickel- and palladium-based catalysts for ethylene polymerization.[5, 6] There the key to high catalytic activity was the use of α-diimine ligands having bulky aryl groups at the nitrogen atoms. The diphosphinidenecyclobutene ligands possess similar structural features.

Complexes **1** and **2** were prepared by ligand displacement of [PdMe$_2$(tmeda)] (tmeda = tetramethylethylenediamine) with phenyl- and trimethylsilyl-substituted ligands in Et$_2$O and isolated as orange crystals in 94% and 63% yields, respectively. Complex **3** was not obtained by this method but prepared in 60% yield by using [PdMe$_2$(cod)] (cod = cyclooctadiene) in place of [PdMe$_2$(tmeda)]. The platinum complex **4** was synthesized from [Pt$_2$Me$_4$(SMe$_2$)$_2$] in 89% yield. All complexes were characterized by NMR spectroscopy and elemental analysis (see Supporting information).

The X-ray structure of **4**,[7] which clearly shows chelate coordination of the diphosphinidenecyclobutene ligand (Figure 1). The two aryl rings on the phosphorus atoms are almost perpendicular to the square planar coordination plane, making a dihedral angle of 92.52(8)°. The distance between platinum and the methyl carbon (Pt–C(1) = 2.093(3) Å) is slightly longer than that of the diimine analogues (2.05–2.079 Å),[8] showing a *trans*-influence for the diphosphaalkene ligand that is slightly higher than that of the diimine ligands.

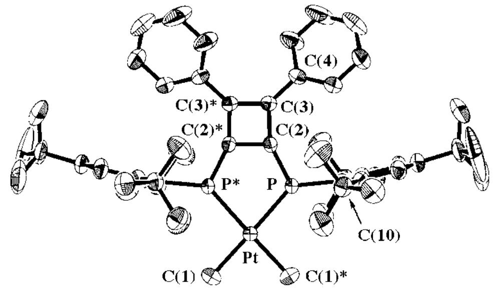


Figure 1. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt-C(1) 2.093(3), Pt-P 2.2909(8), P-C(2) 1.669(3), P-C(10) 1.829(3), C(2)-C(2)* 1.498(5), C(2)-C(3) 1.480(4), C(3)-C(3)* 1.410(6), C(3)-C(4) 1.449(4); P-Pt-P* 82.85(4), C(1)-Pt-C(1)* 85.1(2), P-Pt-C(1) 178.5(1), P-Pt-C(1)* 96.1(1), Pt-P-C(2) 111.2(1), Pt-P-C(10) 136.9(1), C(2)-P-C(10) 111.8(1), P-C(2)-C(2)* 117.3(1), P-C(2)-C(3) 154.4(2), C(2)*-C(2)-C(3) 88.3(2), C(2)-C(3)-C(3)* 91.7(2), C(2)-C(3)-C(4) 131.5(3), C(3)*-C(3)-C(4) 136.7(2).

Table 1 lists the results of the ethylene polymerization catalyzed by the palladium complexes. Similar to the diimine analogues, dimethylpalladium complexes **1**–**3** were inactive, while their monomethyl derivatives (**5**–**7**), generated in situ by the treatment of **1**–**3** with H(OEt$_2$)$_2$BAr$_4$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$),[9] catalyzed the polymerization.

Table 1. Ethylene polymerization catalyzed by diphosphinidenecyclobutene complexes of palladium.

Entry[a]	Precursor complex	Temperature [°C]	Pressure [kgf cm^{-2}]	Activity [kg h^{-1} (mol cat)$^{-1}$]	M_w (M_w/M_n)[b] [kg mol^{-1}]
1	**1**	60	10	86.3	13.9 (10.5)
2	**1**	70	5	54.3	21.2 (9.2)
3	**1**	70	10	128	18.7 (14.8)
4	**1**	70	30	121	4.2 (6.6)
5	**1**	80	10	123	28.9 (13.9)
6	**1**	100	10	90.7	28.6 (12.4)
7	**2**	70	10	4.1	33.1 (5.2)
8	**3**	70	10	2.6	11.8 (6.8)

[a] Reactions were performed in chlorobenzene (20 mL) for 1 h using 10 μmol of catalysts generated from the precursor complexes and H(OEt$_2$)$_2$BAr$_4$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$). [b] Determined by GPC based on polyethylene standards.

---

[*] Prof. Dr. F. Ozawa, S. Ikeda, F. Ohhata, M. Miyoshi, R. Tanaka,
Dr. T. Minami
Department of Applied Chemistry, Faculty of Engineering
Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81) 6-6605-2978
E-mail: ozawa@a-chem.eng.osaka-cu.ac.jp

Prof. Dr. M. Yoshifuji
Department of Chemistry, Graduate School of Science
Tohoku University
Aoba, Sendai 980-8578 (Japan)
Fax: (+81) 22-217-6562
E-mail: yoshifj@mail.cc.tohoku.ac.jp

[**] This work was supported by a Grant-in-Aid for Scientific Research on Priority Area “The Chemistry of Inter-element Linkage” from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

A typical procedure for polymerization (entry 3) is as follows. An orange solution of **5**, which was prepared by the reaction of **1** (9.30 mg, 10 µmol) with $H(OEt_2)_2BAr_4$ (10.7 mg, 10 µmol) in chlorobenzene (5 mL) at room temperature, was transferred by cannula into a 150 mL pressure bottle and diluted with chlorobenzene (15 mL). Ethylene gas was charged, and the mixture was mechanically stirred at 70 °C for 1 h under a constant pressure (10 $\mathrm{kgf\,cm^{-2}}$; 1 kgf = 9.81 N). At this stage, the reaction system was a clear orange solution containing a small quantity of white precipitates. The mixture was poured into MeOH (80 mL), and the resulting precipitates were collected by filtration and dried under vacuum to give a white solid of polyethylene (1.34 g). The reaction could be carried out in 1,2-dichloroethane in place of chlorobenzene at almost the same catalytic activity (124 $\mathrm{kg\,h^{-1}\,(mol\,cat)^{-1}}$). In this case, however, precipitation of polymer from the reaction solution was considerable and the molecular weight was lowered ($M_w = 12.9\ \mathrm{kg\,mol^{-1}}$, $M_w/M_n = 7.1$).

As seen from entries 3, 7, and 8 in Table 1, the catalytic activity was highly sensitive to the R groups of the diphosphinidenecyclobutene ligands; the phenyl-substituted catalyst **5** derived from **1** exhibited much higher activity than the others. The activity thus observed is similar to the level of the diimine-based palladium catalysts.[6] Higher pressure tends to improve the catalytic activity but causes a drop in the molecular weight (entries 2–4). The activity reached the maximum at around 70 °C (entry 3).

Noteworthy is that the present catalysts bearing diphosphinidenecyclobutene ligands possess extremely high thermal stability in the reaction solutions; no sign of decomposition was observed even at 100 °C (entry 6). This property is remarkable when compared with the diimine analogues[10] and may be attributed to good coordination ability of the phosphorus-based ligands with a soft palladium center.

Received: August 4, 2000 [Z15585]

---

[1] a) A. Jouaiti, M. Geoffroy, G. Terron, G. Bernardinelli, *J. Chem. Soc. Chem. Commun.* **1992**, 155; b) A. Jouaiti, M. Geoffroy, G. Terron, G. Bernardinelli, *J. Am. Chem. Soc.* **1995**, *117*, 2251; c) A. Jouaiti, M. Geoffroy, G. Bernardinelli, *Chem. Commun.* **1996**, 437; d) H. Kawanami, K. Toyota, M. Yoshifuji, *Chem. Lett.* **1996**, 533; e) M. van der Sluis, V. Beverwijk, A. Termaten, E. Gavrilova, F. Bickelhaupt, H. Kooijman, N. Veldman, A. L. Spek, *Organometallics* **1997**, *16*, 1144; f) M. Yoshifuji, Y. Ichikawa, N. Yamada, K. Toyota, *Chem. Commun.* **1998**, 27; g) M. van der Sluis, V. Beverwijk, A. Termaten, F. Bickelhaupt, H. Kooijman, A. L. Spek, *Organometallics* **1999**, *18*, 1402.

[2] K. Toyota, K. Masaki, T. Abe, M. Yoshifuji, *Chem. Lett.* **1995**, 221.

[3] a) F. Mathey, P. Le Floch, *Chem. Ber.* **1996**, *129*, 263; b) P. Le Floch, S. Mansuy, L. Ricard, F. Mathey, *Organometallics* **1996**, *15*, 3267; c) B. Breit, *Chem. Commun.* **1996**, 437; d) C. E. Garrett, G. C. Fu, *J. Org. Chem.* **1997**, *62*, 4534; e) S. Qiao, G. C. Fu, *J. Org. Chem.* **1998**, *63*, 4168; f) B. Breit, *J. Mol. Catal. A* **1999**, *143*, 143.

[4] a) R. Appel, V. Winkhaus, F. Knoch, *Chem. Ber.* **1987**, *120*, 243; b) M. Yoshifuji, K. Toyota, M. Murayama, H. Yoshimura, A. Okamoto, K. Hirotsu, S. Nagase, *Chem. Lett.* **1990**, 2195; c) K. Toyota, K. Tashiro, M. Yoshifuji, S. Nagase, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2297.

[5] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414; b) C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664; c) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005; d) S. A. Svejda, M. Brookhart, *Organometallics* **1999**, *18*, 65; e) S. A. Svejda, L. K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **1999**, *121*, 10634.

[6] For review, see: a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169; b) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448; *Angew. Chem. Int. Ed.* **1999**, *38*, 428.

[7] Crystallographic data for **4**: $C_{54}H_{74}P_2Pt$, $M_r = 980.22$, orthorhombic, space group *Pbcn* (No. 60), $a = 17.9602(2)$, $b = 18.3428(2)$, $c = 15.2851(2)$ Å, $V = 5035.5(1)$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.293\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 28.71\ \mathrm{cm^{-1}}$, $T = 296$ K, $R(F^2)$ ($R_w(F^2)$) = 0.031 (0.042) for 3202 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147540. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] K. Yang, R. J. Lachicotte, R. Eisenberg, *Organometallics* **1998**, *17*, 5102.

[9] The formation of **5** in solution was supported by NMR spectroscopy. The monomethyl structure of **5** was further confirmed by using its acetonitrile adduct which was isolated. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.39$ (dd, $J_{P,H} = 9.3$, 3.3 Hz, 3H; PdMe), 1.44, 1.45, 1.59, 1.60, 1.60, 1.61 (each s, each 9H; *t*Bu), 2.30 (s, 3H; MeCN), 6.78 (d, $J_{H,H} = 7.8$ Hz, 2H; *o*-Ph), 6.84 (d, $J_{H,H} = 8.1$ Hz, 2H; *o*-Ph), 6.97 (t, $J_{H,H} = 8.1$ Hz, 2H; *m*-Ph), 6.98 (t, $J_{H,H} = 7.8$ Hz, 2H; *m*-Ph), 7.24 (t, $J_{H,H} = 7.8$ Hz, 2H; *p*-Ph), 7.57 (s, 4H; BAr), 7.61 (d, $J_{P,H} = 2.7$ Hz, 2H; PAr), 7.71 (d, $J_{P,H} = 4.2$ Hz, 2H; PAr), 7.73 (s, 8H; BAr); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): $\delta = 3.4$ (s, *Me*CN), 14.5 (dd, $J_{C,P} = 94$, 3 Hz, PdMe), 31.3, 31.5, 33.8, 33.8, 34.1, 34.1 (each s, C*Me*$_3$), 35.8, 36.0, 38.7, 38.7, 39.8, 39.9 (each s, *C*Me$_3$), 122.7 (s, N*C*Me); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): $\delta = 133.6$, 159.9 (each d, $J_{P,P} = 30$ Hz); elementary analysis calcd (%) for $C_{87}H_{86}BF_{24}NP_2Pd$: C 58.68, H 4.87, N 0.79, found: C 58.25, H 4.75, N 0.73.

[10] It was found that the diimine complex $[\mathrm{PdMe\{Ar'N{=}C(Me)\text{-}C(Me){=}NAr'\}}]^+[\mathrm{BAr_4}]^-$ ($\mathrm{Ar'} = 2,6\text{-}(i\mathrm{Pr})_2\mathrm{C_6H_3}$)[5a] under the reaction conditions of entry 3 in Table 1 immediately starts to decompose giving metallic palladium and loses all catalytic activity within 15 min, 1.10 g of a sludgy, dark polymer was obtained using 10 µmol of the catalyst.

Highly Selective Ring-Opening/Cross-Metathesis Reactions of Norbornene Derivatives Using Selenocarbene Complexes as Catalysts**

Hiroyuki Katayama, Hideto Urushima,
Tsuneo Nishioka, Chikaya Wada, Masato Nagao, and
Fumiyuki Ozawa*

With the advent of well-defined alkylidene catalysts of molybdenum[1] and ruthenium,[2] olefin-metathesis has been invested with a great deal of utility in synthetic organic

---

[*] Prof. Dr. F. Ozawa, Dr. H. Katayama, H. Urushima, T. Nishioka,
C. Wada, M. Nagao
Department of Applied Chemistry, Faculty of Engineering
Osaka City University
Sumiyoshi-ku, Osaka 558-8585 (Japan)
Fax: (+81)6-6605-2978
E-mail: ozawa@a-chem.eng.osaka-cu.ac.jp

[**] This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.