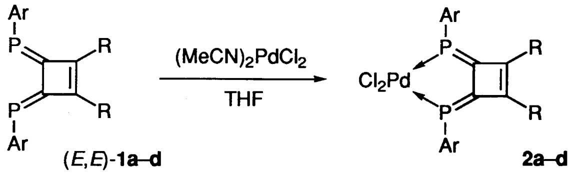
Preparation and Structure of Dichloropalladium(II) Complexes of Sterically Protected Diphosphinidenecyclobutenes and Their Synthetic Application as Homogeneous Catalyst

Kozo Toyota, Kazuto Masaki, Tetsuya Abe, and Masaaki Yoshifuji*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980-77

(Received December 1, 1994)

Sterically protected 3,4-bis[(2,4,6-tri-*t*-butylphenyl)-phosphinidene]cyclobutenes reacted with bis(acetonitrile)-dichloropalladium(II) to give the corresponding dichloropalladium complexes and the structure of one of the complexes was confirmed by X-ray crystallography. The complexes were utilized as a homogeneous catalyst in the coupling reaction of trimethylsilylacetylene and 1-bromo-4-nitrobenzene.

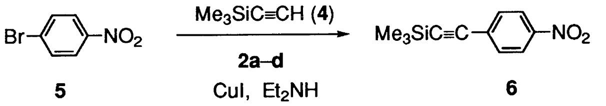
Low-coordinated phosphorus compounds and their transition metal complexes have become of a considerable interest in recent years.[1] Steric protection using an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter, abbreviated to the Ar group) has provided us with several unusual compounds such as diphosphenes,[2a] phosphaalkenes,[2b] and phosphacumulenes[2c,d] as stable species. However, little has been known about the catalytic aspects of transition metal complexes whose ligand contains low-coordinated phosphorus atom(s). Recently, Appel et al.,[3] Märkl et al.,[4] and we[5] prepared some sterically protected diphosphinidenecyclobutenes **1**. Furthermore, we have reported the preparation and structure of group-6 metal(0) carbonyl complexes of (*E*,*E*)-**1b**.[6] We report here the preparation, structure, and catalytic aspects of dichloropalladium complexes of **1a**–**d**.[7]



a: R = H; **b**: R = SiMe$_3$; **c**: R = Ph; **d**: R = *t*-Bu.
Ar = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

The cyclobutenes **1a**,[5b] **1b**,[5a] **1c**,[3] and **1d**[5c] were prepared according to the methods described in the literature. Then, the diphosphinidene cyclobutenes (*E*,*E*)-**1a**–**d** were allowed to react with ca. 1 equiv of bis(acetonitrile)dichloropalladium(II) in THF at room temperature to give the corresponding dichloropalladium complexes **2a**–**d**.[8] The structure of **2d** was unambiguously determined by X-ray crystallography.[9]

Figure 1 depicts the molecular structure of **2d**, which clearly shows the σ-coordination of the phosphorus atoms to the metal center. The atoms P(1), P(2), and C(1)–C(4) are on the same plane within ±0.03 Å and the atoms Pd, Cl(1), Cl(2), C(5), and C(9) deviates from the plane by 0.132, 0.376, 0.284, –0.061, and 0.222 Å, respectively. The two aromatic rings (C(13)–C(18) and C(31)–C(36)) are almost perpendicular to the diphosphinidenecyclobutene plane [P(1), P(2), C(1)–C(4)] making interplanar angles of 88° and 93°, respectively. The P=C bond lengths (1.66(1) Å for both P(1)–C(3) and P(2)–C(4)) are close to those for uncoordinated (*E*,*E*)-**1b** (1.678(6) and 1.676(5) Å).[6b] The Pd–P bond distances for **2d** (2.235(4) and 2.242(4) Å) are close to those for (dppe)PdCl$_2$ (**3**) (2.233(2) and 2.226(2) Å).[10] The P–Pd–P angle (84.4(1)°) is slightly narrower than that for **3** (85.82(7)°). The Pd–Cl bond lengths (2.333(4) and 2.331(4) Å) are shorter than those for **3** (2.361(2) and 2.357(2) Å), although the Cl–Pd–Cl angles are similar (94.5(1)° for **2d** and 94.19(7)° for **3**).



The catalytic aspects of phosphaalkene-transition metal complexes were demonstrated by the following Pd-catalyzed coupling reaction[11] of trimethylsilylacetylene (**4**) with *p*-bromonitrobenzene (**5**) (Table 1). As typical reaction conditions, 21.7 mg (24 μmol) of **2d** and 2.3 mg (12 μmol) of CuI were added to a mixture of **4** (0.21 mL, 1.5 mmol) and **5** (246.1 mg, 1.2 mmol) in diethylamine (5 mL), and the resulting mixture was refluxed for 7 h. Removal of the solvent in vacuo followed by chromatographic separation (Al$_2$O$_3$ / hexane-benzene) and recrystallization from hexane afforded 199.3 mg (74% yield) of *p*-nitro(trimethylsilylethynyl)benzene (**6**). When the reaction was performed at room temperature, the yield was low (Table 1, run 2), while Cl$_2$Pd(PPh$_3$)$_2$ gave **6** in good yield

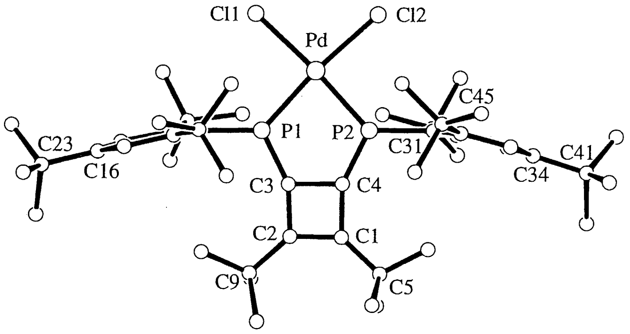


Figure 1. Molecular structure of **2d**. Hydrogen atoms and the solvent molecule are omitted for clarity. As for the disordered carbons, only those with the higher occupancy factor are shown. Some important bond lengths(Å) and angles(°): Pd–P(1), 2.235(4); Pd–P(2), 2.242(4); Pd–Cl(1), 2.331(4); Pd–Cl(2), 2.333(4); P(1)–C(3), 1.66(1), P(2)–C(4), 1.66(1); C(1)–C(2), 1.44(2), C(2)–C(3), 1.46(2); C(3)–C(4), 1.51(1); C(1)–C(4), 1.49(2); P(1)–Pd–P(2), 84.4(1); P(1)–Pd–Cl(1), 91.3(1); P(2)–Pd–Cl(2), 89.9(1); Cl(1)–Pd–Cl(2), 94.5(1); Pd–P(1)–C(3), 111.0(4); Pd–P(2)–C(4), 111.0(4); P(1)–C(3)–C(4), 116.8(8); P(2)–C(4)–C(3), 116.6(9); C(1)–C(2)–C(3), 93.1(10); C(2)–C(3)–C(4), 88.1(9); C(1)–C(4)–C(3), 89.2(9); C(2)–C(1)–C(4), 89.7(10); C(3)–P(1)–C(13), 116.2(6); C(4)–P(2)–C(31), 116.0(6).

Table 1. Preparation of **6** Using **2a**–**d** as Catalyst[a]

Run	Catalyst	Temp	Time / h	Yield/%[b]
1	**2a**	r.t.	4	trace[c]
2	**2b**	r.t.	4	10
3	**2b**	reflux	4	69
4	**2c**	reflux	2	77
5	**2d**	reflux	7	74
6	$Cl_2Pd(dppe)$ (**3**)	reflux	4	41[d]
7	$Cl_2Pd(PPh_3)_2$	r.t.	4	91[e]

[a] Reaction conditions: palladium catalyst, 2 mol%; CuI, 1 mol%; in Et_2NH. [b] Yield based on **5**. [c] The complex **2a** was decomposed in Et_2NH and **5** was recovered in 94% recovery. [d] Recovery of **5**: 30%. [e] The reported yield in Ref. 11 is 92%.

(run 7). However, the complexes **2b**,**c** were more effective in catalytic activity than **3** (run 6). This may be due to the weaker metal-phosphorus bond in **2** than that in **3**. Reaction of (*E*,*E*)-**1c** (1 equiv), dppe (1 equiv), and $Cl_2Pd(MeCN)_2$ (1 equiv) in THF-d_8 or THF-DMSO-d_6 (1:1) afforded **3** almost exclusively, which may indicate that the ligand affinity to Pd is stronger in dppe than in **2**.

This work was supported in part by the Grants-in-Aid for Scientific Research Nos. 05740380, 05236204, and 06227209 from the Ministry of Education, Science and Culture, Japanese Government.

References and Notes

1 "Multiple Bonds and Low Coordination in Phosphorus Chemistry," ed by M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart (1990).

2 a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); *J. Am. Chem. Soc.*, **104**, 6167 (1982); b) M. Yoshifuji, K. Toyota, and N. Inamoto, *Tetrahedron Lett.*, **26**, 1727 (1985); c) M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, *Tetrahedron Lett.*, **25**, 1809 (1984); d) M. Yoshifuji, K. Toyota, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 689.

3 R. Appel, V. Winkhaus, and F. Knoch, *Chem. Ber.*, **120**, 243 (1987).

4 G. Märkl, P. Kreitmeier, H. Nöth, and K. Polborn, *Angew. Chem., Int. Ed. Engl.*, **29**, 927 (1990).

5 a) M. Yoshifuji, K. Toyota, M. Murayama, H. Yoshimura, A. Okamoto, K. Hirotsu, and S. Nagase, *Chem. Lett.*, **1990**, 2195; b) K. Toyota, K. Tashiro, M. Yoshifuji, and S. Nagase, *Bull. Chem. Soc. Jpn.*, **65**, 2297 (1992); c) K. Toyota, K. Tashiro, T. Abe, and M. Yoshifuji, *Heteroatom Chem.*, in press.

6 a) K. Toyota, K. Tashiro, and M. Yoshifuji, *Chem. Lett.*, **1991**, 2079; b) K. Toyota, K. Tashiro, M. Yoshifuji, I. Miyahara, A. Hayashi, and K. Hirotsu, *J. Organomet. Chem.*, **431**, C35 (1992).

7 A part of this work was presented at the 7th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis, Kobe, Sept. 19–23, 1993, Abstr. No. 74B.

8 **2a**: Yield 89%; orange needles, mp 220 °C (decomp); ^1H NMR (200 MHz, $CDCl_3$) $\delta = 1.35$ (18H, s, *p*-*t*-Bu), 1.73 (36H, s, *o*-*t*-Bu), 4.75 (2H, d, $^3J_{PH} = 4.4$ Hz, PCCH), and 7.56 (4H, pseudo t, $J_{PH} = 2.1$ Hz, *m*-Ar); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) $\delta = 162.2$; UV ($CHCl_3$) 290 (log ε 3.48), 335 (3.15), and 404 nm (2.37); FAB-MS *m/z* 743 (M^+–Cl). **2b**: Yield 78%; fine orange needles, mp 260 °C (decomp); ^1H NMR ($CDCl_3$) $\delta = -0.21$ (18H, s, $SiMe_3$), 1.32 (18H, s, *p*-*t*-Bu), 1.74 (36H, s, *o*-*t*-Bu), and 7.56 (4H, pseudo t, $J_{PH} = 2.0$ Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 168.8$ (P=$\underline{C}$-C) and 173.6 (P=C-$\underline{C}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 163.1$; UV ($CHCl_3$) 300 (log ε 4.69), 342 (sh, 4.28), and 462 nm (sh, 2.93); FAB-MS *m/z* 887 (M^+–Cl). **2c**: Yield 63%; deep orange plates, mp 233–236 °C (decomp); ^1H NMR ($CDCl_3$) $\delta = 1.41$ (18H, s, *p*-*t*-Bu), 1.69 (36H, s, *o*-*t*-Bu), 6.86 (4H, d, *o*-Ph), 6.95 (4H, dd, *m*-Ph), 7.22 (2H, t, *p*-Ph), and 7.61 (4H, pseudo t, $J_{PH} = 2.0$ Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 150.2$ (P=C-$\underline{C}$) and 164.7 (P=$\underline{C}$-C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 153.1$; UV (CH_2Cl_2) 243 (log ε 4.61), 297 (sh, 4.43), 328 (sh, 4.56), 360 (4.67), and 431 nm (sh, 3.95); FAB-MS *m/z* 896 (M^+–Cl) and 860 (M^+–2Cl). **2d**: Yield 81%; orange prisms, mp 260–263 °C (decomp); ^1H NMR ($CDCl_3$) $\delta = 0.85$ (18H, s, *t*-Bu), 1.31 (18H, s, *p*-*t*-Bu), 1.75 (36H, s, *o*-*t*-Bu), and 7.52 (4H, pseudo t, $J_{PH} = 2.0$ Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta = 164.4$ (P=C-$\underline{C}$) and 167.3 (P=$\underline{C}$-C); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 155.8$; UV (CH_2Cl_2) 243 (log ε 4.65), 294 (4.68), 334 (sh, 4.28), and 456 nm (sh, 2.90); FAB-MS *m/z* 855 (M^+–Cl) and 819 (M^+–2Cl).

9 Crystal data of **2d**: Recrystallized from benzene. $C_{48}H_{76}Cl_2P_2Pd{\bullet}C_6H_6$, $M_r = 970.50$. Monoclinic, space group $P2_1/n$, $a = 10.907(10)$, $b = 18.483(9)$, $c = 27.264(7)$ Å, $\beta = 91.43(4)°$, $V = 5494(5)$ Å^3, $Z = 4$, $\rho = 1.173$ g cm^{-3}, $\mu = 5.25$ cm^{-1}; 5370 unique reflections with $2\theta \leq 40.0°$ were recorded on a four-circle diffractometer (MoKα radiation, graphite monochrometer). Of these, 3714 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86. The methyl carbons on C(23), C(41), and C(45) are disordered (occupancy factors for the dominant: 0.64, 0.60, and 0.57, respectively). H-atoms and the disordered C-atoms were refined isotropically. $R = 0.068$, $R_w = 0.086$. Further details of the crystal structure investigation are available from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

10 W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **15**, 2432 (1976).

11 S. Takahashi, Y. Kuroyama, K. Sonogashira, and N. Hagihara, *Synthesis*, **1980**, 627.