

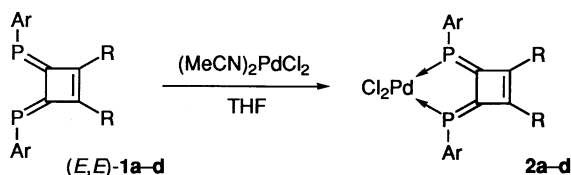
Preparation and Structure of Dichloropalladium(II) Complexes of Sterically Protected Diphosphinidene cyclobutenes and Their Synthetic Application as Homogeneous Catalyst

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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} phosphalkenes,^{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 we⁵ prepared some sterically protected diphosphinidene cyclobutenes **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



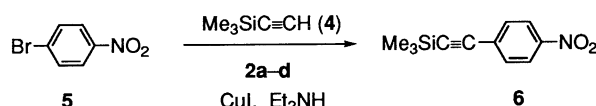
a: R = H; **b:** R = SiMe₃; **c:** R = Ph; **d:** R = *t*-Bu.
 Ar = 2,4,6-*t*-Bu₃C₆H₂

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 diphosphinidene cyclobutene 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)PdCl₂ (**3**) ($2.233(2)$ and $2.226(2)$ Å).¹⁰ The P–Pd–P angle ($84.4(1)^\circ$) is slightly narrower than that for **3** ($85.82(7)^\circ$). 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 ($94.5(1)^\circ$ for **2d** and $94.19(7)^\circ$ for **3**).

The catalytic aspects of phosphalkene-transition metal complexes were demonstrated by the following Pd-catalyzed coupling reaction¹¹ of trimethylsilylacetylene (**4**) with *p*-bromonitrobenzene (**5**) (Table 1). As typical reaction



conditions, 21.7 mg ($24 \mu\text{mol}$) of **2d** and 2.3 mg ($12 \mu\text{mol}$) 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 (Al₂O₃ / hexane-benzene) and recrystallization from hexane afforded 199.3 mg (74% yield) of *p*-nitro(trimethylsilyl)ethynylbenzene (**6**). When the reaction was performed at room temperature, the yield was low (Table 1, run 2), while Cl₂Pd(PPh₃)₂ gave **6** in good yield

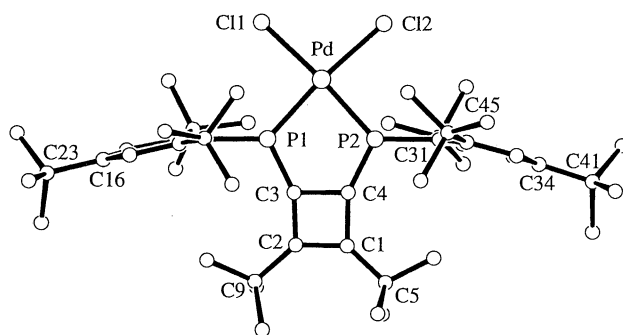


Figure 1. Molecular structure of **2d**. Hydrogen atoms and the solvent molecule are omitted for clarity. As for the disordered carbons, only those with the higher occupancy factor are shown. Some important bond lengths(Å) and angles($^\circ$): Pd–P(1), $2.235(4)$; Pd–P(2), $2.242(4)$; Pd–Cl(1), $2.331(4)$; 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 ₂ Pd(dppe) (3)	reflux	4	41 ^d
7	Cl ₂ Pd(PPh ₃) ₂	r.t.	4	91 ^e

^a Reaction conditions: palladium catalyst, 2 mol%; CuI, 1 mol%; in Et₂NH. ^b Yield based on **5**. ^c The complex **2a** was decomposed in Et₂NH 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 Cl₂Pd(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**.

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- 2a**: Yield 89%; orange needles, mp 220 °C (decomp); ¹H NMR (200 MHz, CDCl₃) δ = 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); ³¹P{¹H} NMR (81 MHz, CDCl₃) δ = 162.2; UV (CHCl₃) 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 (CDCl₃) δ = -0.21 (18H, s, SiMe₃), 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); ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 168.8 (P=C-C) and 173.6 (P=C-C); ³¹P{¹H} NMR (CDCl₃) δ = 163.1; UV (CHCl₃) 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 (CDCl₃) δ = 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); ¹³C{¹H} NMR (CDCl₃) δ = 150.2 (P=C-C) and 164.7 (P=C-C); ³¹P{¹H} NMR (CDCl₃) δ = 153.1; UV (CH₂Cl₂) 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 (CDCl₃) δ = 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); ¹³C{¹H} NMR (CDCl₃) δ = 164.4 (P=C-C) and 167.3 (P=C-C); ³¹P{¹H} NMR (CDCl₃) δ = 155.8; UV (CH₂Cl₂) 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).
- Crystal data of **2d**: Recrystallized from benzene. C₄₈H₇₆Cl₂P₂Pd•C₆H₆, *M_r* = 970.50. Monoclinic, space group *P*2₁/*n*, *a* = 10.907(10), *b* = 18.483(9), *c* = 27.264(7) Å, β = 91.43(4)°, *V* = 5494(5) Å³, *Z* = 4, ρ = 1.173 g cm⁻³, μ = 5.25 cm⁻¹; 5370 unique reflections with 2θ ≤ 40.0° were recorded on a four-circle diffractometer (MoKα radiation, graphite monochromator). Of these, 3714 with *I* > 3σ(*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).
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