

Self-Assembly of a Macrocyclic Dinuclear Pd(II)–Phosphine Complex

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(Received December 9, 1992)

Synopsis. Reaction of a diphosphine ligand, bis[4-[2-(diphenylphosphino)ethyl]phenyl] ether (**1**) with Na_2PdCl_4 gave a macrocyclic dinuclear complex $[\text{PdCl}_2(\mu\text{-1})]_2$ (**2**) in a 58% isolated yield. The formation of **2** appears to result from a spontaneous self-assembly process under thermodynamic control, and thus, no special technique such as a high-dilution method was needed.

The spontaneous self-assembly of macrocyclic structures has received increasing attention in relation to molecular recognition as well as supramolecular chemistry.^{1,2)} Recently, it was found that coordination of pyridine-based bridged ligands to Pd^{2+} brought about the self-assembly of macrocyclic polynuclear Pd(II)–diamine complexes,^{1a,1c)} which specifically recognized electron-rich molecules in an aqueous media.^{1c,3)} Use of diphosphines instead of diamines for the metal-directed assembly of macrocycles is attractive since the products will have both binding ability and catalytic activity,⁴⁾ and may mimic enzyme functions. Although there are several examples of macrocyclic dinuclear transition metal–diphosphine complexes,⁵⁾ the organic framework linking the two phosphorous atoms reported therein consists of only a polymethylene group. To bind an organic substrate in the cavity, the presence of aromatic rings is quite effective, as is often found in cyclophane chemistry.⁶⁾ This paper reports an efficient approach to a macrocyclic Pd(II)–diphosphine complex having aromatic rings in the cyclic framework via a spontaneous self-assembly process (Chart 1).

Of many possible diphosphines, bis[4-[2-(diphenylphosphino)ethyl]phenyl] ether (**1**) was designed as the bidentate diphosphine ligand for the following reasons: (i) the two coordination sites are separated enough by the diphenyl ether unit to prevent undesired mononuclear (1:1) complexation, (ii) the two benzene rings of the diphenyl ether moiety prefer the “face” orientation⁷⁾

making a cavity suitable for molecular recognition, and (iii) no significant ring strain remains in the skeleton of **2** since lone electron pairs on the two phosphorous atoms are almost parallel in the stable conformation of **1**. This compound was easily prepared by treating bis[4-(bromomethyl)phenyl] ether with (diphenylphosphinyl)methylolithium (2 mol equiv) followed by deoxygenation with $\text{HSiCl}_3\text{-NEt}_3$.⁸⁾

The reaction of **1** with Na_2PdCl_4 was carried out in dichloromethane–ethanol at room temperature. After 2 d, GPC analysis of the crude product showed predominant formation of a single component (M_w ca. 1500 with polystyrene standard) contaminated by a small amount of polymeric components. Purification by preparative GPC afforded the major component in a pure form, which was the desired macrocyclic complex **2** (58% yield). FAB MS of **2** showed M, M–HCl, M–2HCl fragments at $m/z = 1540, 1504, \text{ and } 1468$, respectively (based on ^{106}Pd , Fig. 1). No contamination with higher molecular weight compounds was detected both in FAB MS or GPC analysis. ^1H NMR, IR, and elemental analyses were fully consistent with the structure of **2**. Although the stereochemistry on Pd remains uncertain, formation of a single isomer after enough reaction time suggests the configuration of **2** to be the thermodynamically-favored trans.

The formation of **2** appears to result from a spontaneous self-assembly process under thermodynamic control. The advantage of this process is further clarified by comparing the reaction of **1** and Pd^{2+} with that of **1** and Pt^{2+} . Since ligand dissociation on platinum is very much slower than that on palladium,⁹⁾ **1** probably reacts with Pt^{2+} under kinetic control¹⁰⁾ and thus self-assembly is not expected. Indeed a similar treatment of **1** with K_2PtCl_4 gave an intractable mixture of oligomeric materials.¹¹⁾

Presence of the $-\text{CH}_2\text{CH}_2-$ units of **1** is important for the self-assembly of **2** since an attempted reaction of bis[4-(diphenylphosphino)phenyl] ether with Na_2PdCl_4 afforded an insoluble polymeric material. Apparently, the $-\text{CH}_2\text{CH}_2-$ units reduce the steric repulsion among the aromatic rings after cyclization, which otherwise prevents the assembling of the macrocycle.

Selective reactions promoted by metal-containing macrocycles are currently under investigation.

Experimental

General. ^1H and ^{13}C NMR spectra were obtained at 270 and 126 MHz, respectively; chemical shifts

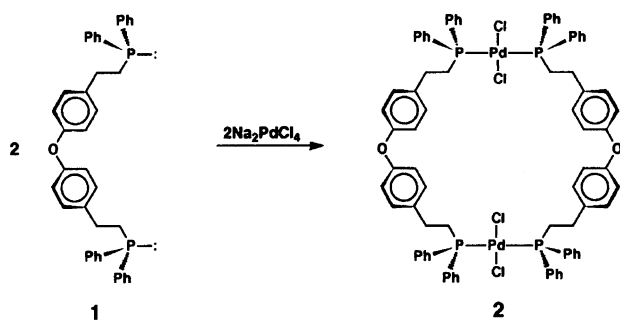


Chart 1.

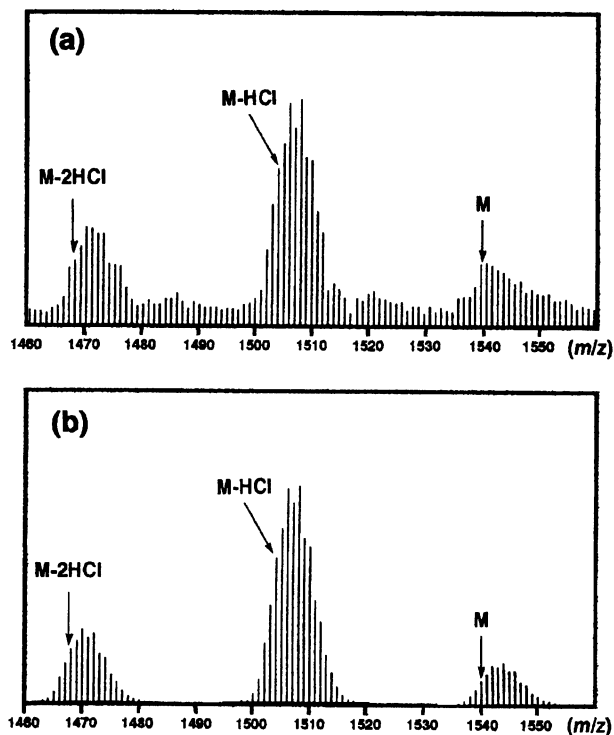


Fig. 1. FAB MS of **2**: (a) found; (b) theoretical distributions for M, M-HCl, and M-2HCl fragments.

are respective to TMS. Microanalytical data were provided by the Chemical Analysis Center of Chiba University. Methylidiphenylphosphine oxide,¹² bis[4-(bromomethyl)phenyl] ether,¹³ and bis[4-(diphenylphosphino)phenyl] ether¹⁴ were prepared by the literature methods.

Bis[4-[2-(diphenylphosphinyl)ethyl]phenyl] Ether. A pentane solution of *t*-butyllithium (1.7 M, 0.29 mL, 0.50 mmol, 1 M=1 mol dm⁻³) was added to a THF solution (2 mL) of methylidiphenylphosphine oxide (108 mg, 0.50 mmol) at -78 °C and the solution was stirred for 20 min at -78 °C and for 40 min at 0 °C. After the mixture was again cooled to -78 °C, a THF solution (2 mL) of bis[4-(bromomethyl)phenyl] ether (71 mg, 0.2 mmol) was added and the mixture was stirred for 0.5 h at -78 °C and 0.5 h at room temperature. Water (1 mL) was added and the mixture was extracted with dichloromethane (2 mL×3). The combined organic layers were dried over MgSO₄ and evaporated. The residue was subjected to column chromatography (silica gel, ethyl acetate-methanol 20:0—19:1) to give the titled compound (109 mg, 87%) as colorless crystals: Mp 173—174 °C; ¹H NMR (CDCl₃) δ =7.8—7.7 (m, 8 H, P-ArH _{α}), 7.6—7.4 (m, 12 H, P-ArH _{β,γ}), 7.10 (d-like, J =8.4 Hz, O-ArH _{α} , 4H), 6.85 (d-like, J =8.4 Hz, O-ArH _{β} , 4 H), 3.0—2.85 (m, ArCH₂, 4 H), and 2.65—2.5 (m, PCH₂, 4 H); IR (KBr) 1493, 1430, 1230, 1169, and 1113 cm⁻¹. Found: C, 75.48; H, 5.80%. Calcd for C₄₀H₃₈O₃P₂·0.5H₂O: C, 75.58; H, 5.87%.

Bis[4-[2-(diphenylphosphino)ethyl]phenyl] Ether (1). Triethylamine (0.1 mL) and trichlorosilane (0.1 mL) were added to a benzene solution (1 mL) of the phosphine oxide prepared above (46 mg, 0.073 mmol) at 0 °C and the mixture was refluxed for 4 h. NaOH (10 wt% aqueous solution, 5 mL) was then added, and the mixture was extracted with dichloromethane (5 mL×3). The combined

organic layers were dried over MgSO₄ and evaporated. The crude product was subjected to preparative TLC (silica gel, hexane-dichloromethane 1:1) to give **1** (31 mg, 72%) as a colorless oil: ¹H NMR (CDCl₃) δ =7.5—7.4 (m, 8 H, P-ArH _{α}), 7.4—7.3 (m, 12 H, P-ArH _{β,γ}), 7.15 (d-like, J =8.7 Hz, O-ArH _{α} , 4H), 6.87 (d-like, J =8.7 Hz, O-ArH _{β} , 4 H), 2.75—2.65 (m, ArCH₂, 4 H), and 2.4—2.3 (m, PCH₂, 4 H); ¹³C NMR (CDCl₃) δ =155.64 (C_q), 138.41 (d, J =12.9 Hz, C_q), 137.31 (d, J =12.9 Hz, C_q), 132.75 (d, J =19.4 Hz, CH), 129.33 (CH), 128.66 (CH), 128.48 (d, J =6.4 Hz, CH), 118.75 (CH), 31.47 (d, J =17.2 Hz, CH₂), and 30.33 (d, J =12.9 Hz, CH₂); IR (neat) 1493, 1428, and 1230 cm⁻¹. Found: m/z 595.2326 (FAB, *m*-nitrobenzyl alcohol). Calcd for C₄₀H₃₉OP₂: MH⁺, 595.2320.

Reaction of **1 with Na₂PdCl₄.** An ethanol solution (5 mL) of Na₂PdCl₄ (50.5 mg, 0.17 mmol) was added to a CH₂Cl₂ solution (5 mL) of **1** (84.3 mg, 0.14 mmol) at room temperature and the solution was stirred for 2 d at room temperature. Water (10 mL) was added and the mixture was extracted with CH₂Cl₂ (20 mL×3). The organic layer was washed with sat aq NaCl, dried over MgSO₄, and concentrated. The residue was subjected to preparative gel permeation chromatography (eluent: CHCl₃) performed with an LC-908 (Japan Analytical Industry, Co., Ltd.) equipped with JAIGEL-1H and -2H (i.d. 20×600 mm). A component appearing around M_w =1500 (with polystyrene standard) was collected after five cycles and concentrated to give [PdCl₂(μ -1)]₂ (**2**) (108 mg, 58%) as a yellow powder: Mp 270 °C decomp; ¹H NMR (CDCl₃) δ =7.81—7.68 (m, 16 H, ArH), 7.58—7.35 (m, 24 H, ArH), 7.16 (d, J =8.64 Hz, 8 H, ArH), 6.87 (d, J =8.64 Hz, 8 H, ArH), and 2.76 (broad s, 16 H, -CH₂CH₂-); IR (KBr) 1495, 1233, 726, 687, and 485 cm⁻¹; MS (FAB, *m*-nitrobenzyl alcohol, based on ¹⁰⁶Pd and ³⁵Cl) m/z 1540 (M⁺), 1504 (M-HCl), and 1468 (M-2HCl). Found: C, 61.99; H, 4.75%. Calcd for C₈₀H₇₂Cl₄O₂P₄Pd₂: C, 62.23; H, 4.70%. This material was stored in a chloroform solution since it gradually polymerized in the solid state.

Reaction of Bis[4-(diphenylphosphino)phenyl] Ether (3**) with Na₂PdCl₄.** A CH₂Cl₂ solution (1.0 mL) of **3** (31 mg, 0.058 mmol) was added to an ethanol solution (1.0 mL) of Na₂PdCl₄ (18 mg, 0.061 mmol) at room temperature. The mixture was stirred for 13 h at room temperature and the precipitates were filtered, washed with water (5 mL) and CH₂Cl₂ (5 mL×3), and dried under reduced pressure to give a fine yellow powder (31 mg) whose elemental analysis was consistent with **3**-PdCl₂ 1:1 complex: Mp 270—280 °C decomp; IR (KBr) 2920, 1573, 1480, 1429, 1229, 1168, 1091, and 688 cm⁻¹. Found: C, 59.36; H, 3.94%. Calcd for C₃₆H₂₈Cl₂OP₂Pd·0.5H₂O: C, 59.65; H, 4.03%.

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