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 $[PdCl_2(\mu\text{-}\mathbf{1})]_2$ (**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" orientation[7] 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 phosphorus atoms are almost parallel in the stable conformation of **1**. This compound was easily prepared by treating bis[4-(bromomethyl)phenyl] ether with (diphenylphosphinyl)methyllithium (2 mol equiv) followed by deoxygenation with $HSiCl_3$–NEt_3.[8]

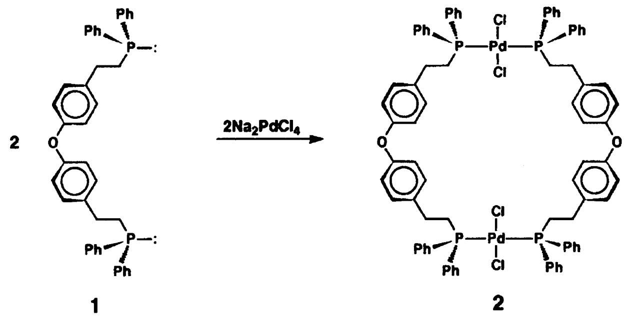

Chart 1.

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, 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. ^{1}H 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 control[10] 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 $-CH_2CH_2-$ 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 $-CH_2CH_2-$ 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. ^{1}H and ^{13}C NMR spectra were obtained at 270 and 126 MHz, respectively; chemical shifts

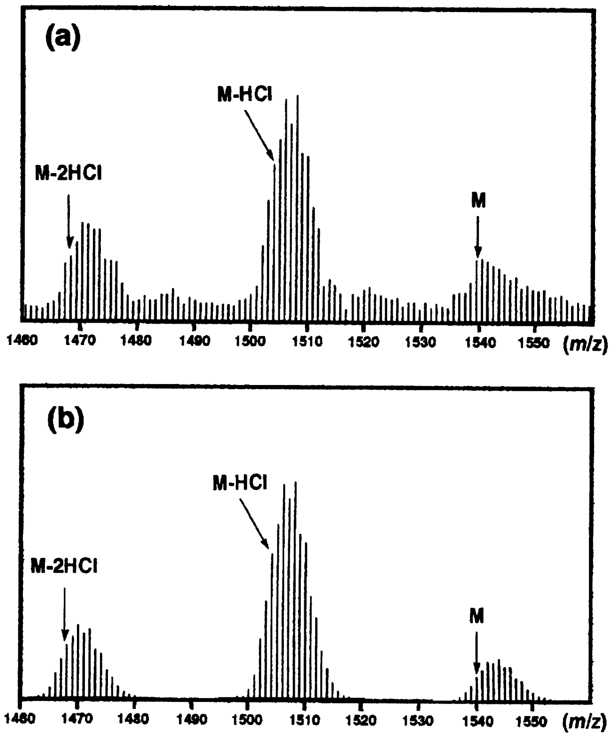

Fig. 1. FAB MS of **2**: (a) found; (b) theoretical distributions for M, M–HCl, and M–2HCl fragments.

are respective to TMS. Microanalytical data were provided by the Chemical Analysis Center of Chiba University. Methyldiphenylphosphine oxide,[12)] bis[4-(bromomethyl)phenyl] ether,[13)] and bis[4-(diphenylphosphino)phenyl] ether[14)] 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 methyldiphenylphosphine 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 $MgSO_4$ 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; ^{1}H NMR ($CDCl_3$) δ=7.8—7.7 (m, 8 H, P-ArH_α), 7.6—7.4 (m, 12 H, P-Ar$H_{\beta,\gamma}$), 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, ArCH_2, 4 H), and 2.65—2.5 (m, PCH_2, 4 H); IR (KBr) 1493, 1430, 1230, 1169, and 1113 cm^{-1}. Found: C, 75.48; H, 5.80%. Calcd for $C_{40}H_{38}O_3P_2 \cdot 0.5H_2O$: 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 $MgSO_4$ 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: ^{1}H NMR ($CDCl_3$) δ=7.5—7.4 (m, 8 H, P-ArH_α), 7.4—7.3 (m, 12 H, P-Ar$H_{\beta,\gamma}$), 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, ArCH_2, 4 H), and 2.4—2.3 (m, PCH_2, 4 H); ^{13}C NMR ($CDCl_3$) 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, CH$_2$), and 30.33 (d, J=12.9 Hz, CH$_2$); IR (neat) 1493, 1428, and 1230 cm^{-1}. Found: m/z 595.2326 (FAB, *m*-nitrobenzyl alcohol). Calcd for $C_{40}H_{39}OP_2$: MH$^+$, 595.2320.

Reaction of 1 with Na_2PdCl_4. An ethanol solution (5 mL) of Na_2PdCl_4 (50.5 mg, 0.17 mmol) was added to a CH_2Cl_2 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 CH_2Cl_2 (20 mL×3). The organic layer was washed with sat aq NaCl, dried over $MgSO_4$, and concentrated. The residue was subjected to preparative gel permeation chromatography (eluent: $CHCl_3$) 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 $[PdCl_2(\mu\text{-}\mathbf{1})]_2$ (**2**) (108 mg, 58%) as a yellow powder: Mp 270 °C decomp; ^{1}H NMR ($CDCl_3$) 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, –CH_2CH_2–); IR (KBr) 1495, 1233, 726, 687, and 485 cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol, based on ^{106}Pd and ^{35}Cl) m/z 1540 (M$^+$), 1504 (M–HCl), and 1468 (M–2HCl). Found: C, 61.99; H, 4.75%. Calcd for $C_{80}H_{72}Cl_4O_2P_4Pd_2$: 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 Na_2PdCl_4. A CH_2Cl_2 solution (1.0 mL) of **3** (31 mg, 0.058 mmol) was added to an ethanol solution (1.0 mL) of Na_2PdCl_4 (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 CH_2Cl_2 (5 mL×3), and dried under reduced pressure to give a fine yellow powder (31 mg) whose elemental analysis was consistent with **3**–$PdCl_2$ 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 $C_{36}H_{28}Cl_2OP_2Pd \cdot 0.5H_2O$: C, 59.65; H, 4.03%.

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