

Figure 2. Closeup view of the bis-complexed tetrameric repeating unit within the structure.

Table I. Selected Bond Lengths (Å) and Angles (deg)

|                   |           |                  |          |
|-------------------|-----------|------------------|----------|
| Li(1)-N(1)        | 2.131(8)  | Li(1)-C(4)       | 2.314(8) |
| Li(1)-C(2)        | 2.321(8)  | Li(1)-C(3)       | 2.326(8) |
| Li(2)-C(3)        | 2.166(11) | Li(2)-C(2)       | 2.210(7) |
| Li(3)-C(4)        | 2.145(11) | Li(3)-C(2)       | 2.164(7) |
| N(1)-Li(1)-C(4)   | 108.9(3)  | N(1)-Li(1)-C(2)  | 121.2(4) |
| C(4)-Li(1)-C(2)   | 101.7(3)  | N(1)-Li(1)-C(3)  | 109.8(3) |
| C(4)-Li(1)-C(3)   | 110.8(3)  | C(2)-Li(1)-C(3)  | 104.1(3) |
| C(3)-Li(2)-C(2)   | 113.7(3)  | C(2)-Li(2)-C(2') | 107.4(5) |
| C(4)-Li(3)-C(2)   | 113.0(3)  | C(2)-Li(3)-C(2') | 110.7(5) |
| Li(3)-C(2)-Li(2)  | 64.6(3)   | Li(3)-C(2)-Li(1) | 67.4(3)  |
| Li(2)-C(2)-Li(1)  | 66.4(3)   | Li(2)-C(3)-Li(1) | 67.0(3)  |
| Li(1)-C(3)-Li(1') | 67.6(4)   | Li(3)-C(4)-Li(1) | 67.8(3)  |
| Li(1)-C(4)-Li(1') | 68.0(4)   |                  |          |

chains protrude from the  $(\text{CLi})_4$  core in orientations which allow room for two of the four metal centers [Li(1) and its symmetry relation] to be ligated by TMEDA molecules. This additional N-Li bonding raises the coordination numbers of Li(1) and Li(1') to four (three C-Li bonds, one N-Li bond) while uncomplexed Li(2) and Li(3) remain only three-coordinate. The two TMEDA molecules each bridge two  $(\text{Bu}^n\text{Li})_4$  tetramers, thereby interacting with one  $\text{Li}^+$  center per tetramer in a monodentate manner, giving an overall  $\text{Bu}^n\text{Li}:\text{TMEDA}$  ratio of 4:1, not 4:2. Normally TMEDA adopts a didentate chelating mode toward  $\text{Li}^+$  cations, but occasionally, as here, a monodentate, bridging role is preferred.<sup>9</sup> Clear similarities exist between this crystal structure and that of  $[(\text{MeLi})_4 \cdot (\text{TMEDA})_2]_{\infty}$ <sup>10</sup> since both have  $(\text{CLi})_4$  pseudo-cubane units connected by Li-TMEDA-Li bridges. Significantly, however, the smaller steric demands of the methyl groups permit all four  $\text{Li}^+$  cations within the tetrameric clusters to be complexed by TMEDA molecules, resulting in an infinite, three-dimensional array rather than an infinite, zig-zag chain structure.

Table I lists important bond lengths and bond angles in the title structure. An examination reveals that the three-coordinate metal centers form noticeably shorter C-Li bonds [mean lengths: Li(2), 2.194 Å; Li(3), 2.158 Å] than the four-coordinate ones (mean length, 2.320 Å; cf. 2.262 Å in the methyl analogue<sup>10</sup>). Furthermore, the N-Li bonds between tetramers are only marginally shorter than corresponding ones in the methyl analogue [2.131(8) Å; cf. 2.214(5) Å<sup>10</sup>] even though the connectivity of the  $(\text{Bu}^n\text{Li})_4$  tetramers is half that of the  $(\text{MeLi})_4$  tetramers (2 vs 4). These

nitrogen-attached  $\text{Li}^+$  centers occupy distorted tetrahedral sites (mean angle at  $\text{Li}^+$ , 109.4°) with distortion most pronounced at N(1)Li(1)C(2) [121.2(4)°] to offset butyl-TMEDA repulsions. The mean bond angle at the three-coordinate, pyramidal  $\text{Li}^+$  centers is 111.9°. Atoms connected to the  $\text{Li}^+$  centers, the butyl  $\alpha$ -carbons and the TMEDA nitrogens, are six- and four-coordinate, respectively.

In conclusion, the failure of TMEDA to break down the tetrameric cluster and to assume its preferred chelating role in the butyllithium solid described herein adds further support to the recent claim that TMEDA is not a particularly effective ligand for the  $\text{Li}^+$  cation.<sup>11</sup>

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**Supplementary Material Available:** Details of the X-ray analysis and tables of atomic coordinates, bond lengths and angles, and thermal parameters (5 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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### Palladium(II)-Directed Assembly of Macrocyclic Dinuclear Complexes Composed of $(\text{en})\text{Pd}^{2+}$ and Bis(4-pyridyl)-Substituted Bidentate Ligands. Remarkable Ability for Molecular Recognition of Electron-Rich Aromatic Guests

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Self-assembly phenomena have been utilized recently for the construction of highly organized structures.<sup>1</sup> Application of these phenomena to macrocyclization<sup>2</sup> is quite attractive since cyclization

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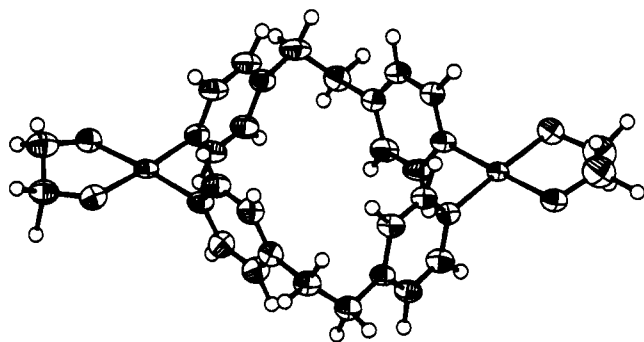
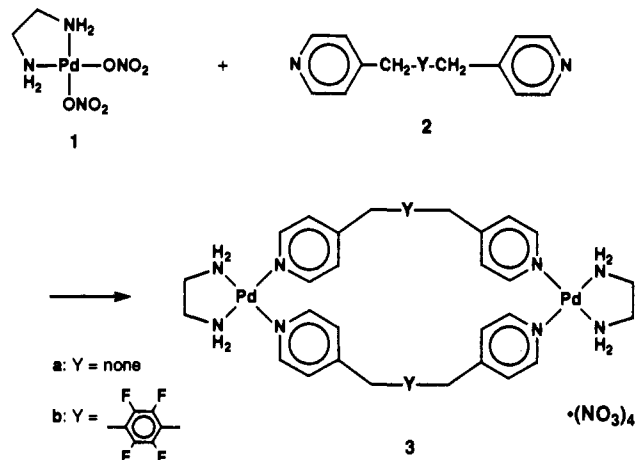


Figure 1. ORTEP diagram of **3a**. Nitrate ions and solvent molecules of crystallization are omitted for clarity.

of a large molecule by the usual synthetic methods is frequently a tedious and low-yield process. We recently reported the self-assembly of a macrocyclic tetranuclear Pd(II) complex, [(en)-Pd(4,4'-bpy)]<sub>4</sub>(NO<sub>3</sub>)<sub>8</sub> (en = ethylenediamine, bpy = bipyridine), in which adjacent Pd atoms are linked by 4,4'-bpy.<sup>2a</sup> Displacement of this rigid ligand by a flexible one might cause unfavorable oligomerization rather than cyclization. Against such anticipation we find that flexible bis(4-pyridyl)-substituted ligands **2** give macrocyclic dinuclear complexes **3** in high yields on treatment of the ligands with a *cis*-(en)Pd<sup>2+</sup> complex **1**.



Preparation of **3** is quite simple. Typically, a methanol solution (1 mL) of 1,2-bis(4-pyridyl)ethane (0.5 mmol) was added to a methanol-water (1:1, 4 mL) solution of (en)Pd(NO<sub>3</sub>)<sub>2</sub><sup>3</sup> (**1**, 0.5 mmol) at ambient temperature. After most of the solvent was evaporated, addition of ethanol precipitated **3a** (92%) as light yellow powder. Elemental analysis and the NMR spectrum supported assignment of the product as **3a**,<sup>4</sup> and the FAB mass spectrum showed fragment peaks at *m/z* = 885 (*M* - HNO<sub>3</sub>), 822 (*M* - (HNO<sub>3</sub>)<sub>2</sub>), and 759 (*M* - (HNO<sub>3</sub>)<sub>3</sub>) (based on <sup>106</sup>Pd) with the peaks of reasonably distributed isotopic fragments.

The macrocyclic dinuclear structure of **3a** was confirmed by crystallographic analysis (Figure 1).<sup>5</sup> The X-ray crystal structure

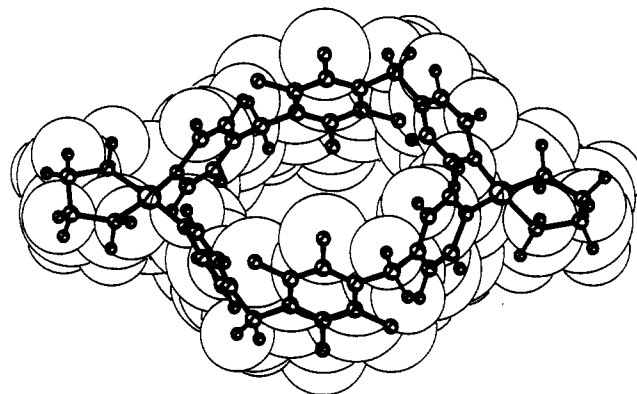


Figure 2. Computer-generated model of **3b**. Circles show approximate van der Waals radii of each atom.

Table I. Association Constants (L mol<sup>-1</sup>)<sup>a</sup> between Various Guest Compounds and **3b** or **4** (25 °C, D<sub>2</sub>O)

| guest                               | host      |                       |
|-------------------------------------|-----------|-----------------------|
|                                     | <b>3b</b> | <b>4</b> <sup>b</sup> |
| 1,3,5-trimethoxybenzene             | 2500      | 750                   |
| <i>p</i> -dimethoxybenzene          | 2680      | 330                   |
| <i>m</i> -dimethoxybenzene          | 1560      | 580                   |
| <i>o</i> -dimethoxybenzene          | 1300      | 30                    |
| <i>p</i> -bis(methoxymethyl)benzene | 560       | 10                    |
| <i>p</i> -dicyanobenzene            | 80        | nd <sup>c</sup>       |
| <i>p</i> -dinitrobenzene            | 30        | nc <sup>d</sup>       |
| 1,4-dimethoxycyclohexane            | nc        | nc                    |
| <i>N</i> -(2-naphthyl)acetamide     | 15        | 1800                  |

<sup>a</sup> Estimation of the association constants: see supplementary material. <sup>b</sup> Reference 10. <sup>c</sup> Not determined. <sup>d</sup> No complexation.

showed a nearly perpendicular array of the pyridine rings, which form a cube-shaped inner cavity (ca. 4 × 4 × 6 Å). Neither solvent molecules nor nitrate ions were clathrated in the cavity.

The self-assembly of the dinuclear macrocycle was also successful when a tetrafluorophenylene unit was incorporated in the skeleton of **2a**: treatment of 1,4-bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene<sup>6</sup> (**2b**) with **1** gave macrocycle **3b** in quantitative yield. The formation of **3b** was confirmed by NMR, elemental analysis, and FAB mass spectrometry.<sup>7</sup> Computer-assisted modeling of **3b**<sup>8</sup> (Figure 2) clearly showed the more expanded inner cavity, in which all aromatic nuclei are arrayed nearly perpendicularly.

The striking aspect of macrocycle **3b** is its high ability for molecular recognition of electron-rich aromatic compounds with high shape specificity.<sup>9</sup> As shown in Table I, polymethoxybenzenes were specifically bound with **3b** while other substrates were poorly or hardly recognized. This behavior sharply contrasts with those of the usual cyclophanes that prefer electron-deficient guests.<sup>9</sup> Although the previously reported macrocyclic complex [(en)Pd(4,4'-bpy)]<sub>4</sub>(NO<sub>3</sub>)<sub>8</sub> (**4**) also recognized electron-rich benzene derivatives,<sup>10</sup> the association constants were smaller by

(5) Crystal data of **3a**: C<sub>28</sub>H<sub>40</sub>N<sub>12</sub>O<sub>12</sub>Pd<sub>2</sub>·CH<sub>3</sub>OH·H<sub>2</sub>O; FW = 999.61; monoclinic; space group, *P2<sub>1</sub>/n*; *a* = 26.753(10) Å, *b* = 12.942(4) Å, *c* = 13.221(3) Å, α = 90.00(0)°, β = 119.32(2)°, γ = 90.00(0)°; *V* = 3991.74(232) Å<sup>3</sup>; *d*<sub>calcd</sub> = 1.661 g cm<sup>-3</sup>; *z* = 4. The final refined *R* value was 0.0668. More details: see supplementary material.

(6) Preparation of **2b**: see supplementary material.

(7) Preparation of **3b**: a methanol (1.5 mL) solution of **2b** (0.2 mmol) was added to an aqueous solution (1.0 mL) of **1** (0.2 mmol), and the mixture was stirred for 0.5 h at room temperature. Concentration of the resulting solution afforded **3b** as an amorphous solid. Although purification was unsuccessful in this form, addition of NaClO<sub>4</sub> or NaBF<sub>4</sub> to an aqueous solution of **3b** gave its perchlorate salt (57%) or tetrafluoroborate salt (59%), respectively, as a pure material. Physical data of **3b**: see supplementary material.

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(4) Physical data of **3a**: see supplementary material.

almost 1 order (Table I). Since macrocycle **3a** showed no sign of complexation with any guest molecules, the complexation between **3b** and the aromatic guests must occur in the cavity. Naphthalene derivatives such as *N*-(2-naphthyl)acetamide, a good guest for **4**, were hardly bound with **3b**, possibly due to their steric demand.<sup>11</sup> In addition to the good fit of the cavity size, the specific recognition of electron-rich benzene derivatives is apparently ascribable to the electronic environment in the cavity surrounded by tetrafluorophenylene and coordinated pyridyl groups, both of which are extremely electron-deficient.

**Supplementary Material Available:** A procedure for the preparation of **2b**, physical data of **2b** and **3a,b**, FAB mass spectrum of **3a,b**, X-ray crystallographic data for **3a**, details on the computer modeling of **3b**, and details on the NMR determination of the host-guest association constants (15 pages). Ordering information is given on any current masthead page.

(11) *N*-(1-Naphthyl)acetamide and 1,4- and 1,5-dimethoxynaphthalenes were not complexed with **3b**.

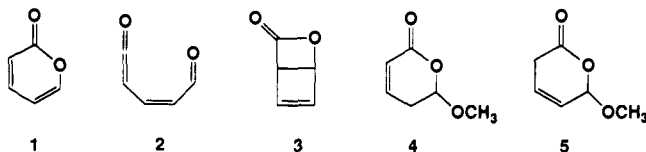
### Solution Photochemistry of 2*H*-Pyran-2-one: Laser Flash Photolysis with Infrared Detection of Transients<sup>1</sup>

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The photochemistry of 2*H*-pyran-2-one (**1**) and its derivatives has been a source of continued interest for more than 30 years. Its complexity is perfectly suited for demonstrating the usefulness of laser flash photolysis with infrared detection (LFP-TRIR) to obtain mechanistic information and kinetic details in a situation where other techniques are difficult or impossible to apply.



The formation of methyl ester products during the photolysis of an alkylated derivative of **1** in methanol led de Mayo to postulate the existence of a ketene intermediate.<sup>3,4</sup> While ketene **2** was later characterized in a glass at low temperature by infrared spectroscopy,<sup>5-8</sup> its intermediacy in the ester formation was put in serious doubt.<sup>9</sup>

It has been shown that **2** is formed reversibly from **1** upon irradiation and that a photostationary state between the ketene and pyrone is rapidly reached. Continued irradiation leads to the slow buildup of bicyclic lactone **3**.<sup>6,7,10</sup> The possibility that the

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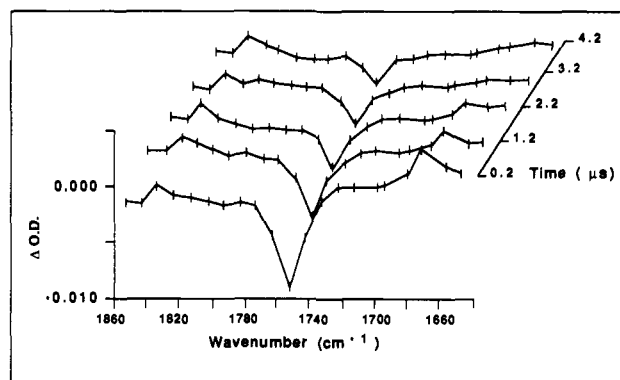


Figure 1. 3D representation of LFP-TRIR spectra showing the bleaching and partial recovery of **1** and the formation of the photoproducts **2** and **3** (see text).

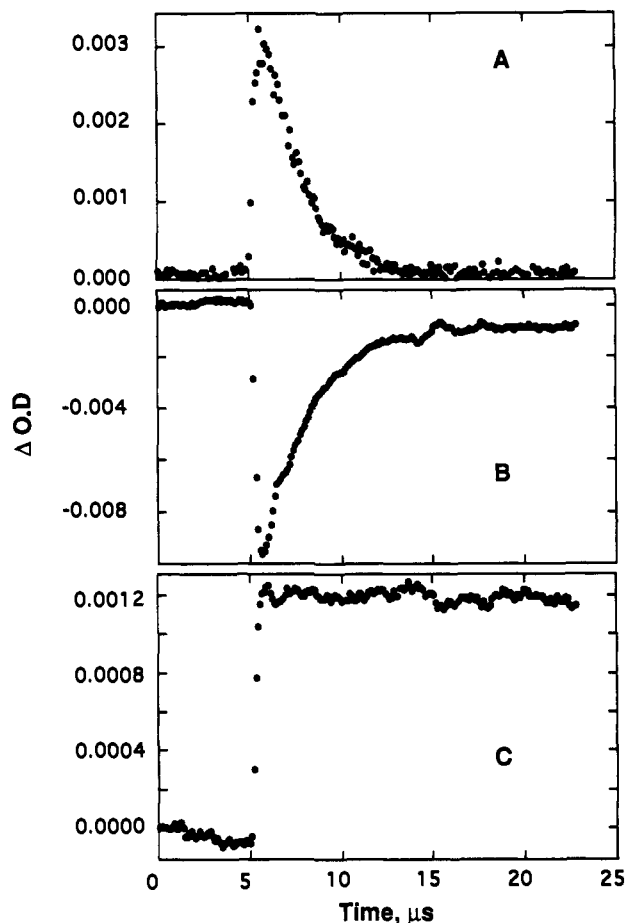


Figure 2. Kinetic traces of the transient absorptions observed after irradiation of **1**: (A) decay at 1690 cm<sup>-1</sup> (aldehyde stretch of the ketene, **2**); (B) bleaching and partial recovery of **1** at 1750 cm<sup>-1</sup> (carbonyl stretch); (C) absorption at 1850 cm<sup>-1</sup> (carbonyl stretch of lactone, **3**).

lactone is not a direct photoproduct from **1** but is instead produced from the ketene either thermally or photochemically cannot be addressed by matrix experiments.

While extensive studies of **1** and its derivatives have been carried out under matrix isolation conditions, the intermediates, including the excited states of the pyrone, have never been characterized in solution. Further, the mechanism of their interconversion is unknown and information concerning their reactivity is scarce. The present study was undertaken to address these questions.

Our preliminary studies indicating that **1** and **2** absorb in similar regions of the ultraviolet ( $\lambda_{\max} \approx 300$  and 295 nm, respectively) combined with the fact that **3** shows only end absorption ( $\lambda_{\max} < 250$  nm)<sup>10</sup> convinced us that unraveling the mechanistic and kinetic information by means of laser flash photolysis with UV-