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Palladium(II) Cage Compounds Based on Diphenylglycoluril

Frank G. M. Niele and Roeland J. M. Nolte

Contribution from the Department of Organic Chemistry, University of Utrecht, 3584 CH Utrecht, The Netherlands. Received May 19, 1987

Abstract: A four-armed tetra-l-imidazolyl ligand (Lig) equipped with the concave framework of diphenylglycoluril (tetrahydro-3a,6a-diphenylimidazol[4,5-d]imidazol-2,5(1H,3H)-dione) has been designed to construct a host that contains a potentially catalytically active metal center in or close to a cavity. Reaction of Lig (arm = CH₂(OCH₂CH₂)₂Im) with Pd(CH₃CN)₂Cl₂ results in the formation of a complex with the general formula [Pd(Lig)]Cl₂. This complex has a cavity structure that is unstable and collapses. The collapsed structure has either a left or a right twisted conformation. These conformations interconvert rapidly, the activation free energy of the process being 30 ± 2 kJ-mol⁻¹. Ligands without oxygen atoms or only one oxygen atom per arm react with Pd(CH₃CN)₂Cl₂ to afford cage complexes with the molecular formula [Pd(Lig)]Cl. The cages of these complexes do not collapse. The imidazolyl groups and the chloride ions are involved in a scrambling process in such a way that at any moment the Pd(II) ion is surrounded by three imidazolyl groups and one chloride ion. Data are presented suggesting that intramolecular H bonding is a driving force for cage collapse.

Scheme I

Route A:

\[
\begin{align*}
\text{Ph}_2\text{GU-H}_4 & \quad \xrightarrow{X-A-X} \quad \text{Ph}_2\text{GU-(A-X)}_4 \\
1c & \quad 5c, 6a \\
X & = \text{Cl, Br}
\end{align*}
\]

Route B:

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \xrightarrow{\text{OH}^-} \quad \text{Ph}_2\text{GU-(CH}_2\text{OH})_4 \\
1c & \quad 2 \\
H^+ & \quad \rightarrow
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{GU-(CH}_2\text{OCH}_2)_2 & \quad \xrightarrow{p-\text{TSOH}} \quad \text{Ph}_2\text{GU-(A-X)}_4 \\
3b & \quad 4a, 5c, 5a \\
X & = \text{Cl, Br}
\end{align*}
\]

Scheme II

\[
\begin{align*}
\text{Ph}_2\text{GU-(A-X)}_4 & \quad \xrightarrow{\text{ImH}} \quad \text{Ph}_2\text{GU-(A-Im)}_4 \\
X & = \text{Cl, Br}
\end{align*}
\]

Natl

Synthesis of Tetrapodands. The general synthesis of the tetrapodands begins with the coupling to diphenylglycoluril of four spacer units, each of which is suitably terminated with a halogenide.


(3) Part of this work has been described in a preliminary communication: Nolie, F. G. M.; Zwikker, J. W.; Nolie, R. J. M. Tetrahedron Lett. 1986, 27, 243-246. In this paper it was erroneously concluded that the two twisted forms of [Pd(4H)]⁺ do not interconvert rapidly.

(4) Cram, D. J. Science (Washington, D.C.) 1983, 219, 1177-1183. (2) We propose the general name dipteranes for compounds derived from the two-winged diphenylglycoluril unit (from the Greek διπτέρας = twi-winged).


(6) Present address: Department of Organic Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands.
Palladium(II) Cage Compounds

Figure 1. MSB concept.

Figure 2. Strategy for preparing a metallocage from diphenylglycoluril.

Figure 3. Crystal structure of compound 4a.

Figure 4. Results of gel permeation chromatography.

Table I. Molar Conductivities of Palladium Complexes

<table>
<thead>
<tr>
<th>compd</th>
<th>$\Lambda_m \cdot \Omega^{-1}$ cm$^2$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(4d)Cl]$_2$</td>
<td>170</td>
</tr>
<tr>
<td>[Pd(5b)Cl]Cl</td>
<td>106</td>
</tr>
<tr>
<td>[Pd(5d)Cl]Cl</td>
<td>110</td>
</tr>
<tr>
<td>[Pd(6b)Cl]Cl</td>
<td>94</td>
</tr>
<tr>
<td>TEBA$^b$</td>
<td>101</td>
</tr>
</tbody>
</table>

$^a$In methanol at 25 °C. $^b$TEBA = triethylbenzylammonium chloride.

as a leaving group for the following synthetic step. Two routes have been used for the spacer coupling (see Scheme I). Route A is the straight-on alkylation of the ureylene nitrogen atoms with a $\omega$-dihalogenide to produce the tetrachlorides 5c and 6a. Route B is a three-step synthesis that starts from 4c with the formation of the unstable tetrabromide 2. In the second step 2 is treated with acid to generate the more stable tetracyclic ether 3. In the final step the strong acid-induced transetherification of 3 with n-hexyl spacers; see Scheme II.

During these investigations X-ray structural characterization of a tetracyclic ether (3a) and of a tetrapodand 4a has been carried out. The crystal structure of 3a shows a compound with two cis-tied imidazolidon rings and two six-membered ether rings. The latter rings are in the chair conformation. The structure determination of the short-armed tetrabromide 4a not only confirms the primary structure of the compound but also shows the steric shielding by the two phenyl groups on the convex side of the glycoluril unit (see Figure 3).

Palladium Complexes. Reaction of tetrapodand 4d (containing the ethylene glycol spacers) with Pd(CH$_3$CN)$_2$Cl$_2$ in methanol as a solvent yields a product which, according to elemental analysis, has the molecular formula Pd(4d)Cl$_2$. In the FAB mass spectrum the ion [Pd(4d)]$^+$ was detected with an isotope pattern that perfectly matches the one simulated for C$_{48}$H$_{62}$N$_2$O$_5$Pd.

To check that no oligomeric or polymeric networks had been formed, we determined the molecular weight of this new product. The ebulliometric value (in methanol MW 1125 ± 75; calcd 1143) as a leaving group for the following synthetic step.

is in agreement with a monomeric palladium-tetrapodand system. In addition, gel permeation chromatography was applied to obtain information on relative molecular sizes. The results (Figure 4) show clearly that Pd(4d)Cl₂ has a molecular size of the same order of magnitude as that of the free tetrapodand 4d. This supports the molecular weight determination, and it is therefore concluded that the complex Pd(4d)Cl₂ is monomeric in solution.

The following step was to identify the ligands comprising the coordination sphere within the Pd(4d)Cl₂ complex. The molar conductivity of this complex determined in methanol solution (Table I) is in the range expected for 2:1 electrolytes and suggests that the Cl⁻ anions are not bonded to the palladium center, i.e. [Pd(4d)]Cl₂. Furthermore, the 'H NMR data for this compound (methanol-d₄, 200 MHz) point to all four imidazolyl groups being coordinated to the palladium; compared to the free tetrapodand 4d, the resonances of the NCH₃ imidazole protons in the complex show a large downfield chemical shift (0.55 ppm). The white color of [Pd(4d)]Cl₂ that is typical of complexes with four (substituted) imidazolyl ligands coordinated to Pd(II) is a third indication for the proposed formulation. These results indicate for [Pd(4d)]²⁺ a metallocage structure as depicted in Figure 2. However, this picture is too simple. Whereas the CH₃Im protons H₆ and H₀ (Figure 5a) would be expected to be equivalent, the 'H NMR spectrum shows them not to be so since they give rise to four triplets in the region 4.0–4.15 ppm (Figure 5c). Spin decoupling by irradiation of their vicinal H₅ protons converted the four triplets into an AB quartet, indicating the protons E and D to be chemically nonequivalent. To obtain more detailed information, NOE difference spectroscopy was employed (Table II). Irradiation of the olefinic imidazole proton H₈ caused a NOE enhancement of the H₆ signal, which is typical of complexes with four (substituted) imidazole groups, which all make the same angle with the coordination plane.¹³

In a second NOE experiment, the NCH₂O methylene protons H₈ and H₇ were irradiated. The NOE difference spectrum shows a very remarkable NOE enhancement of the H₇ signal, which implies the presence of a spatial connection between H₈ and H₁₋₁/H₁ (Figure 5b). A CPK model of [Pd(4d)]²⁺ shows that this spatial connection can arise from a collapse of the metallocage via a twisting motion along the z axis (see Figure 6a). The orientation of the CH₃Im methylene protons must be outward since their near proton; the free tetrapodand in comparable experiments showed no such enhancement. The most likely structure of [Pd(4d)]²⁺, therefore, is one having a four-bladed propeller-like conformation of the Pd-coordinated (1-substituted) imidazole groups, which all make the same angle with the xy metal coordination plane.¹³

Finally, we examined the temperature dependence of the normal °H NMR 200-MHz spectrum of [Pd(4d)]Cl₂ in the region 7.5–9.0 ppm. In the range 32–60 °C, the spectrum does not alter noticeably, but lowering the temperature to ~95 °C leads to a splitting of the H₅ signals (Figure 5d). CPK models show that in the twisted compressed conformation two of the imidazolyl groups are situated close to the ureylene carbonyls (Figure 6b, site S), indicating the possibility of a significant anisotropy effect.

Table II. NOEDS Results for [Pd(4d)]Cl₂

<table>
<thead>
<tr>
<th>irradiated proton</th>
<th>NOE effect (intensity, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Pd(4d)]Cl₂ 4d</td>
</tr>
<tr>
<td>D(E)</td>
<td>A (3.5)</td>
</tr>
<tr>
<td>E(D)</td>
<td>C (2.6)</td>
</tr>
<tr>
<td>I(J)</td>
<td>A (2.3)</td>
</tr>
<tr>
<td>B</td>
<td>C (2.9)</td>
</tr>
<tr>
<td>J(J)</td>
<td>A (1.0)</td>
</tr>
<tr>
<td>K</td>
<td>C (&lt;0.1)</td>
</tr>
<tr>
<td>A</td>
<td>B (1.2)</td>
</tr>
<tr>
<td>B</td>
<td>C (7)</td>
</tr>
<tr>
<td>C</td>
<td>B (2.3)</td>
</tr>
<tr>
<td>D</td>
<td>B (&lt;0.1)</td>
</tr>
</tbody>
</table>

on the H\textsuperscript{2} chemical shift. The other two imidazolyl groups are in a different chemical environment (Figure 6b, see T). These variable-temperature \textsuperscript{1}H NMR experiments imply that at room temperature the two sets of imidazolyl protons are involved in a fast exchange process in which the metallocage alternates between the left and right twisted conformations (Figure 6a). The free energy of activation of this conformational change is 30 ± 2 kJ/mol.

A second phenomenon noted in the \textsuperscript{1}H NMR spectra on lowering the temperature was the downfield shift of the weighted average of the signals of the NCHN protons. This suggests that these protons are participating in a hydrogen bond;\textsuperscript{14} a CPK model of the twisted cage conformation does show that a NCHN hydrogen atom can approach both oxygen atoms of its own spacer unit (Figure 6c).

To discover what would happen when one or both oxygen atoms in the spacer units were omitted, the tetrapodands 5b, 5d, and 6b were reacted with Pd(CH\textsubscript{3}CN)\textsubscript{2}Cl\textsubscript{2}. In all three cases, the elemental analysis of the product corresponded to the molecular formula Pd(tetrapodand)Cl\textsubscript{2}. The molar conductivities of solutions of the three Pd(tetrapodand)Cl\textsubscript{2} compounds fall in the range for 1:1 electrolytes (Table 1). This means that only one chloride ion is dissociated from the palladium center, whereas the other one is still bonded; i.e., the compounds are more accurately formulated as [Pd(tetrapodand)Cl]\textsuperscript{2+}.

To check whether we dealt with monomeric or oligomeric aggregates, we performed gel permeation chromatography. From the results (Figure 4), we see that the three Pd complexes have sizes of the same order of magnitude as the largest tetrapodand 5d. As another reference compound, we used the [Rh(4d)Cl\textsubscript{2}]\textsuperscript{2+} metallocage (see Figure 7). This compound cannot collapse in the way the [Pd(4d)]\textsuperscript{2+} complex does, because of the presence of a metal-bonded chloride ligand within the cage. Since the sizes of three [Pd(tetrapodand)Cl]\textsuperscript{2+} systems are also found to be similar to that of this rhodium cage, it is clear that we are dealing with monomeric species.

The \textsuperscript{1}H NMR spectra of the palladium complexes of tetrapodands 5b, 5d, and 6b (methanol-\textit{d}\textsubscript{4}, 80 MHz) showed very broad signals. Lowering the temperature to -70 °C (200 MHz) in the case of [Pd(6b)Cl]Cl resulted in an even greater broadening, whereas an increase in temperature (to 60 °C) caused a little broadening of the other two imidazolyl groups. Lowering the temperature to -70 °C (200 MHz) in the case of [Pd(6b)Cl]Cl. The molar conductivities of solutions of the three Pd(tetrapodand)Cl\textsubscript{2} compounds fall in the range for 1:1 electrolytes (Table 1). This means that only one chloride ion is dissociated from the palladium center, whereas the other one is still bonded; i.e., the compounds are more accurately formulated as [Pd(tetrapodand)Cl]\textsuperscript{2+}.

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water, and dried (P205) under vacuum: yield 514 mg (40%) of white 6a.

The residue was dissolved in diethyl ether, filtered, evaporated under water vapor pressure (65°C). The mixture was refluxed for 16 h, filtered and dried under vacuum; yield 350 mg (11%) of white 6a.

1.3.4.6-Tetrakis(7-chloro-2,5-dioxoheptyl)tetrahydro-3a,6a-diphenylimidazo[4,5-j]imidazo[2,5,1(f,h,3f)-dione (4c). Compound 2 (20.8 g, 50 mmol), 2-bromoethanol-water, and dried (P205) under vacuum: yield 514 mg (40%) of white 6a.

The mixture was extracted with a saturated aqueous solution of NaHCO3 and filtered and dried under vacuum; yield 38.7 g (92%) of white 6a.

Yield: 12.8 g (79%) of white 6a.


In a nitrogen atmosphere, compound 4c (5.9 g, 20 mmol) and NaH (from a 80% dispersion in mineral oil, washed with hexane; 408 mg, 17 mmol) were mixed in 80 mL of DMF. The mixture was stirred at ambient temperature until gas production stopped. After this period 1,8-dichloro-2-oxaoctane (19.2 g, 100 mmol) was added dropwise, with vigorous stirring, to 100 mL of diethyl ether. The precipitate was filtered, washed with cold diethyl ether, and dried under vacuum: yield 10.9 g (56%) of white 6c.

The mixture of 6c was dissolved in 8 mL of CH2Cl2, washed (2X), decanted, and the residue was dried under vacuum: yield 350 mg (11%) of 6a as a colorless syrup; IR (NaCl disks) 1722 (C=O), 689 (CBr) cm-1; 1H NMR (CDCl3) 6 7.0-6.8 (m, 10 H, ArH), 3.3 (t, 8 H, CH2Br), 3.5-2.5 (br, 8 H, CH2), 1.1-2.1 (br, 32 H, CH2(C6H5)2CH2).

Compound 6a was converted into the corresponding tetra-1-imidazolyl compound.

1.3.4.6-Tetrakis(7-(1-imidazolyl)-2,5-dioxoheptyl)tetrahydro-3a,6a-diphenylimidazo[4,5-j]imidazo[2,5,1(f,h,3f)-dione (4b): white solid; mp 87°C; FABMS (M + H)+ m/z 997; 1H NMR (CDCl3) 6 7.67 (pseudo s, 4 H, NCHN), 7.18 (dd, Jgem = 11 Hz, 4 H, N(1)CHN(3)), and 6.92 (dd, 4 H, N(1)CHN(3)); 4.2 (pseudo t, 8 H, remaining Jgem = 11 Hz, 8 H, NCH2).

Acknowledgment. We thank R. H. Fokkens and Prof. N. M. Nibbering for measuring the FAB mass spectra. R. P. Sybesma for carrying out the NOE experiments, C. J. Witmans and Dr. J. W. Zwicker for synthesizing compounds 5, and Dr. M. Grove
Selective Molecular Oxygen Oxidation of Thioethers to Sulfoxides Catalyzed by Ce(IV)

D. P. Riley,*† M. R. Smith,* and P. E. Correa†

Contribution from the Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, Missouri 63167, and The Procter and Gamble Company, Miami Valley Laboratories, P.O. Box 39175, Cincinnati, Ohio 45247. Received June 15, 1987

Abstract: The selective molecular oxygen conversion of thioethers to sulfoxides is catalyzed by ceric ammonium nitrate (CAN) with rate enhancements that are at least three orders of magnitude greater than the uncatalyzed autoxidation of thioethers. Mechanistic studies (including spectroscopic, labeling, uptake, mixed reactant, and autocatalysis studies) of this novel reaction reveal that both atoms of dioxygen are incorporated into product sulfoxide, that a novel oxygen-driven Ce(IV)/Ce(III) redox cycle gives rise to the catalysis, and that molecular oxygen efficiently traps a sulfur-centered radical cation of the thioether (produced by Ce(IV) oxidation of thioether) to yield the oxygenated radical cation R₂SOO⁺, which, it is proposed, reoxidizes Ce(III) to Ce(IV). The zwitterionic R₂SOO⁺ intermediate (persulfide) reacts with thioether to yield two sulfoxide product molecules.

The ability to selectively convert a particular molecule via an oxidation utilizing the abundant and cheap oxidant oxygen often represents a desirable low-cost method for upgrading the value of a raw material. The goal of much of our research in recent years has been directed toward the utilization of oxygen as a cheap and selective oxidant. During our research into better methods of selectively oxidizing waste thioethers (e.g., Me₂S) to their more valuable sulfoxides, we discovered that thioethers are subject to a novel autoxidation process that under high oxygen concentration, elevated temps., and polar solvents yields almost exclusively the sulfoxide product.† The mechanism of this unusual autooxidation most likely involves an initial unfavorable electron transfer step (eq 1), followed by triplet oxygen (in high concentration) trapping of the resultant radical cation (eq 2). Back-

R₂S + 3O₂ → R₂S⁺ + O₂⁻ (1)

R₂S⁺ + 3O₂ → O₂ (2)

...