Palladium(II) Cage Compounds Based on Diphenylglycoluril

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Abstract: A four-armed tetra-1-imidazolyl ligand (Lig) equipped with the concave framework of diphenylglycoluril (tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-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 = $CH_2(OCH_2CH_2)_2Im$) with $Pd(CH_3CN)_2Cl_2$ results in the formation of a complex with the general formula $[Pd(Lig)]Cl_2$. This complex has a cage 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 $Pd(CH_3CN)_2Cl_2$ to afford cage complexes with the molecular formula [Pd(Lig)Cl]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^{2+} 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.

When catalytic systems are designed, it is particularly intriguing to mimic nature. In this respect, we are interested in synthesizing systems to imitate the behavior of metalloenzymes, which are involved in substrate activation processes.[1] Simplification of the very special three-dimensional structure of a metalloenzyme shows a cavity-containing molecule with binding sites (B) and one or more metal centers (M) in or close to the cavity. The metalloenzyme acts as a metallohost,[2] and because of the special structure of the cavity, it is quite selective in binding a substrate (S); see Figure 1.

In 1970 Breslow and Overman were the first to report a man-made system based on this MSB concept.[3] They combined a naturally occurring α-cyclodextrine with a nickel(II) ion and obtained a metallohost that shows metalloenzyme features. Tabushi's team reported a carbonic anhydrase model in which they also used this cyclodextrine as a host molecule.[4] At this moment examples of fully synthetic metallohosts are scarce.[5]

Study of metallohosts shows that the organic part is a polydentate macroligand that must be able to furnish substrate-binding sites and the framework for a cavity. In this paper we report the design and synthesis of a new family of ligands having these properties. Several Pd(II) cage compounds based on the new macroligands have been prepared, and features of their solution dynamic behavior are described.[6]

Results and Discussion

Strategy. Cram realized that in the design of cavity-containing molecules it is preferable to start from a concave building block.[7] Our design for a ligand, which has to supply the framework for a cavity-containing molecule, starts from such a block, viz. glycoluril (tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (**1a**); Chart I) that has its convex side sterically shielded by two phenyl groups (**1c**).[8] To the ureylene nitrogen atoms can then be attached four chains as spacer units (A), which are furnished with potential substrate-binding sites and terminated with metal-binding groups (L). In this way what may be called a heterotopic tetrapodal ligand or simply a tetrapodand is formed.[9] Coordination of the four ligating groups to a metal center M results in the creation of a metallocage (Figure 2). Thus, in this design the metal center has a dual function. First, it acts as a template facilitating the formation of the desired cavity. Second, it is a potentially reactive site, e.g. a catalytic center.

We have chosen ethylene glycol ether chains, which are known to possess binding properties,[9] as spacer units and imidazolyl groups, which are excellent ligands to a variety of metal ions, as the metal-binding groups. For comparative purposes, tetrapodands containing either 2-oxaalkyl chains or *n*-hexyl chains as spacer units have also been prepared.

Scheme I

Route A:

$$\underset{\mathbf{1c}}{Ph_2\text{-GU-}H_4} \xrightarrow{\text{X-A-X}} \underset{\substack{\mathbf{5c},\ \mathbf{6a} \\ X = Cl,\ Br}}{Ph_2\text{-GU-(A-X)}_4}$$

Route B:

$$\underset{\mathbf{1c}}{Ph_2\text{-GU-}H_4} \xrightarrow[OH^-]{CH_2O} \underset{\mathbf{2}}{Ph_2\text{-GU-}(CH_2OH)_4} \xrightarrow[H^+]{}$$

$$\underset{\mathbf{3b}}{Ph_2\text{-GU-}(CH_2OCH_2)_2} \xrightarrow[p\text{-TsOH}]{\text{HO-A-X}} \underset{\substack{\mathbf{4a},\ \mathbf{4c},\ \mathbf{5a} \\ X = Cl,\ Br}}{Ph_2\text{-GU-(A-X)}_4}$$

Scheme II

$$Ph_2\text{-GU-(A-X)}_4 \xrightarrow[NaH]{ImH} Ph_2\text{-GU-(A-Im)}_4 \qquad X = Cl,\ Br$$

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

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(1) (a) Nolte, R. J. M.; Razenberg, J. A. S. J.; Schuurman, R. *J. Am. Chem. Soc.* **1986**, *108*, 2751-2752. (b) van Esch, J.; Roks, F. M.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1986**, *108*, 6093-6094. (c) Smeets, J. W. H.; Sijbesma, R. P.; Niele, F. G. M.; Spek, A. L.; Smeets, W. J. J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1987**, *109*, 928-929.

(2) Cram, D. J.; Trueblood K. N. *Top. Curr. Chem.* **1981**, *98*, 43-106.

(3) Breslow, R.; Overman, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1075-1077.

(4) Tabushi, I.; Kuroda, Y.; Mochizuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152-1153.

(5) (a) Meade, T. J.; Takeuchi, K. J.; Busch, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 725-728. (b) Hamilton, A.; Lehn, J. M.; Sessler, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5158-5167. (c) Capped porphyrins can be considered as metallohosts, see: Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181-220.

(6) Part of this work has been described in a preliminary communication: Niele, F. G. M.; Zwikker, J. W.; Nolte, R. J. M. *Tetrahedron Lett.* **1986**, *27*, 243-246. In this paper it was erroneously concluded that the two twisted forms of $[Pd(\mathbf{4d})]^{2+}$ do not interconvert rapidly.

(7) Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177-1183.

(8) We propose the general name *dipteranes* for compounds derived from the two-winged diphenylglycoluril unit (from the Greek *διπτεροσ* = two-winged).

(9) For a review on crown-type compounds, see: Weber, E.; Vögtle, F. *Top. Curr. Chem.* **1981**, *98*, 1-41.

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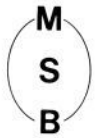


Figure 1. MSB concept.

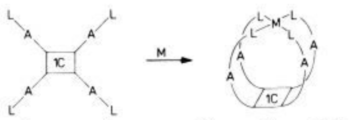
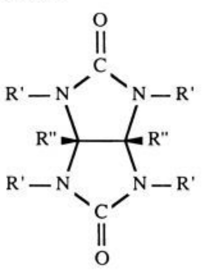


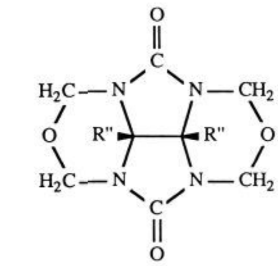
Figure 2. Strategy for preparing a metallocage from diphenylglycoluril.

Chart I

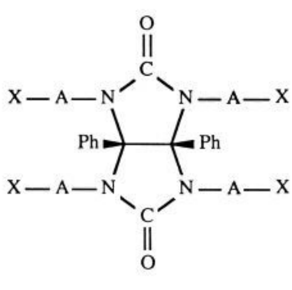


1a, R' = H, R'' = H
1b, R' = H, R'' = CH_3
1c, R' = H, R'' = Ph
2, R' = CH_2OH, R'' = Ph

Short-hand notation:
$(R'')_2$-GU-$(R')_4$



3a, R'' = CH_3
3b, R'' = Ph



	A	X
4a,	$CH_2OCH_2CH_2$	Br
4b,	$CH_2OCH_2CH_2$	Im (= 1-imidazolyl)
4c,	$CH_2(OCH_2CH_2)_2$	Cl
4d,	$CH_2(OCH_2CH_2)_2$	Im
5a,	$CH_2O(CH_2)_4$	Cl
5b,	$CH_2O(CH_2)_4$	Im
5c,	$CH_2O(CH_2)_6$	Cl
5d,	$CH_2O(CH_2)_6$	Im
6a,	$(CH_2)_6$	Br
6b,	$(CH_2)_6$	Im

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 ω-dihalogenide to produce the tetrahalogenides **5c** and **6a**. Route B is a three-step synthesis that starts from **1c** with the formation of the unstable tetrol compound **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 a ω-halogeno alcohol under very stringent water-removal conditions affords the tetrahalogenides **4a**, **4c**, and **5a** (see the Experimental Part). In the final stage the resulting tetrahalogenides from these two routes are then reacted with sodium imidazolate to afford the tetrapodands **4b** and **4d** (containing ethylene glycol spacers), **5b** and **5d** (containing 2-oxaalkyl spacers), and **6b** (containing *n*-hexyl spacers); see Scheme II.

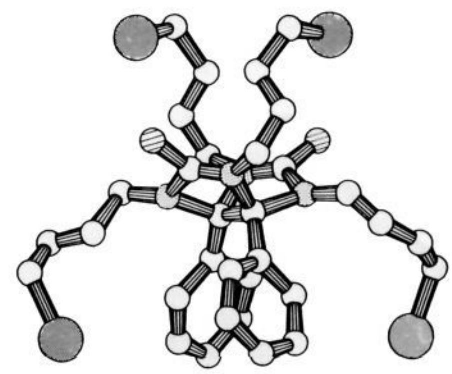


Figure 3. Crystal structure of compound **4a**.

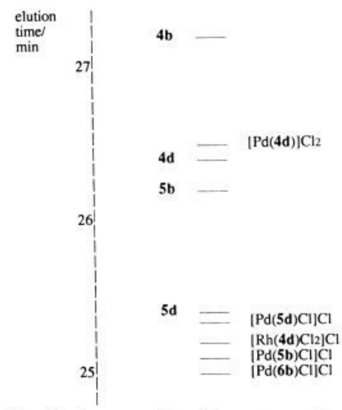


Figure 4. Results of gel permeation chromatography.

Table I. Molar Conductivities of Palladium Complexes[a]

compd	Λ_m, Ω^{-1} cm^2 mol^{-1}	compd	Λ_m, Ω^{-1} cm^2 mol^{-1}
[Pd(**4d**)]Cl_2	170	[Pd(**6b**)Cl]Cl	94
[Pd(**5b**)Cl]Cl	106	TEBA[b]	101
[Pd(**5d**)Cl]Cl	110		

[a] In methanol at 25 °C. [b] TEBA = triethylbenzylammonium chloride.

During these investigations X-ray structural characterization of a tetracyclic either (**3a**) and of a tetrahalogenide (**4a**) has been carried out.[10] 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 $Pd(CH_3CN)_2Cl_2$ 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 $[Pd(\mathbf{4d})]^+$ was detected with an isotope pattern that perfectly matches the one simulated for $C_{48}H_{62}N_{12}O_{10}Pd$.

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]

(10) The X-ray structures will be published separately. **3a**: Niele, F. G. M.; Kanters J. A.; Nolte, R. J. M., to be submitted for publication in *Acta Crystallogr.* **4a**: Niele, F. G. M.; Spek, A. L.; Smeets, W. J. J.; Nolte, R. J. M., to be submitted for publication in *J. Inclusion Phenom.*

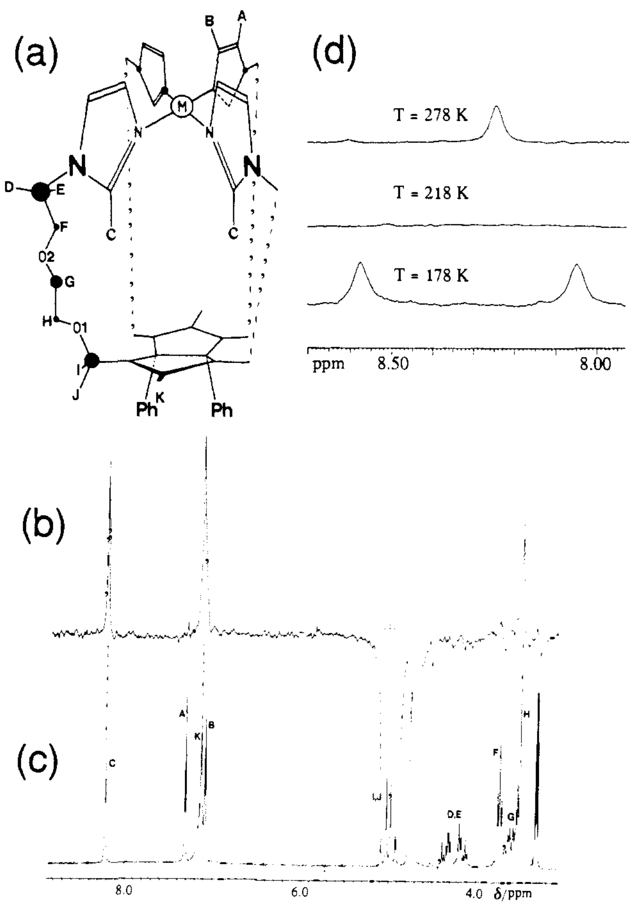


Figure 5. ^1H NMR experiments on $[Pd(\mathbf{4d})]Cl_2$: (a) numbering of protons; (b) NOE difference spectrum; (c) 200-MHz ^1H NMR in CD_3OD; (d) variable-temperature experiment.

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 $Pd(\mathbf{4d})Cl_2$ 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 $Pd(\mathbf{4d})Cl_2$ is monomeric in solution.

The following step was to identify the ligands comprising the coordination sphere within the $Pd(\mathbf{4d})Cl_2$ complex. The molar conductivity of this complex determined in methanol solution (Table I) is in the range expected for 2:1 electrolytes[11] and suggests that the Cl^- anions are not bonded to the palladium center, i.e. $[Pd(\mathbf{4d})]Cl_2$. Furthermore, the ^1H NMR data for this compound (methanol-d_4, 200 MHz) point to all four imidazolyl groups being coordinated to the palladium; compared to the free tetrapodand, the resonances of the NCHN imidazole protons in the complex show a large downfield chemical shift (0.55 ppm). The white color of $[Pd(\mathbf{4d})]Cl_2$ that is typical of complexes with four (substituted) imidazole ligands coordinated to Pd(II)[12] is a third indication for the proposed formulation. These results indicate for $[Pd(\mathbf{4d})]^{2+}$ a metallocage structure as depicted in Figure 2. However, this picture is too simple. Whereas the CH_2Im protons H^E and H^D (Figure 5a) would be expected to be equivalent, the ^1H 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 H^F 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

(11) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(12) (a) For a discussion of alkylated imidazole Pd(II) complexes, see: Hazarika, T. N.; Bora, T. *Transition Met. Chem.* (*Weinheim, Ger.*) **1982**, *7*, 210–212. (b) Camazõn, M. J.; Alvarez-Valdés, A.; Masaguer, J. R.; Navarro-Ranninger, M. C. *Transition Met. Chem.* (*Weinheim, Ger.*) **1986**, *11*, 226–229.

Table II. NOEDS Results for $[Pd(\mathbf{4d})]Cl_2$

	NOE effect (intensity, %)	
irradiated proton	$[Pd(\mathbf{4d})]Cl_2$	**4d**
D(E)	A (3.5)	
	C (2.6)	
E(D)	A (2.3)	
	C (2.9)	
I(J)	C (1.0)	C (<0.1)
	K (1.2)	K (<0.1)
A	B (12.5)	
B	A (7)	
	C (2.3)	C (<0.1)
C	B (2.7)	B (<0.1)

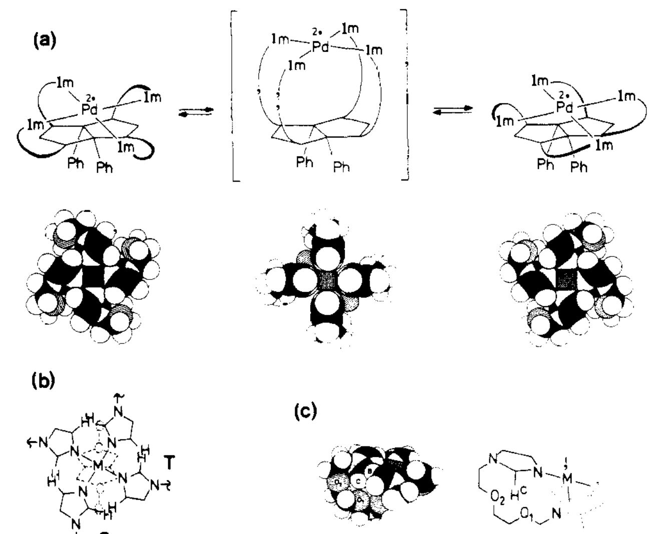


Figure 6. (a) Twisting motion in $[Pd(\mathbf{4d})]^{2+}$ (top, schematic representation; bottom, CPK models, view from above). (b) Top view of $[Pd(\mathbf{4d})]^{2+}$, for a discussion see text. (c) Hydrogen-bond interaction between imidazole group and oxygen atoms of spacer unit $[Pd(\mathbf{4d})]^{2+}$ (left, side view picture of the CPK model; right, structure formula).

difference spectroscopy was employed (Table II). Irradiation of the olefinic imidazole proton H^B caused a NOE enhancement of the NCH^CN imidazole proton signal, indicating that H^C is a nearby proton; the free tetrapodand in comparable experiments showed no such enhancement. The most likely structure of $[Pd(\mathbf{4d})]^{2+}$, 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]

In a second NOE experiment, the NCH_2O methylene protons H^I and H^J were irradiated. The NOE difference spectrum shows a very remarkable NOE enhancement of the H^C signal, which implies the presence of a spatial connection between H^C and H^I/H^J (Figure 5b). A CPK model of $[Pd(\mathbf{4d})]^{2+}$ 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 CH^IH^J methylene protons must be outward since their irradiation also induced NOE effects on their neighboring methylene protons H^H and some (most likely ortho) phenyl protons H^K.

Finally, we examined the temperature dependence of the normal ^1H NMR 200-MHz spectrum of $[Pd(\mathbf{4d})]Cl_2$ 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 H^C 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

(13) For the structure of the related $[Pt(1\text{-MeIm})_4]^{2+}$ complex, see: Cingi, M. B.; Lanfredi, A. M. M.; Tiripicchio, A.; van Kralingen, C. G.; Reedijk, J. *Inorg. Chim. Acta* **1980**, *39*, 265–270.

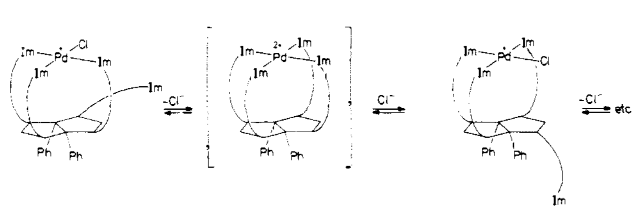


Figure 7. Fluxional behavior of the Pd(II) compounds derived from **5b**, **5d**, and **6b**.

on the H^C chemical shift. The other two imidazolyl groups are in a different chemical environment (Figure 6b, site T). These variable-temperature ^1H 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 ^1H 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;[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 $Pd(CH_3CN)_2Cl_2$. In all three cases, the elemental analysis of the product corresponded to the molecular formula Pd(tetrapodand)Cl_2. The molar conductivities of solutions of the three Pd(tetrapodand)Cl_2 compounds fall in the range for 1:1 electrolytes (Table I). This means that only one chloride anion 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]Cl.

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 $[Rh(\mathbf{4d})Cl_2]^+$ metallocage, details of which are published elsewhere.[15] This compound cannot collapse in the way the $[Pd(\mathbf{4d})]^{2+}$ complex does, because of the presence of a metal-bonded chloride ligand within the cage. Since the sizes of three [Pd(tetrapodand)Cl]Cl systems are also found to be similar to that of this rhodium cage, it is clear that we are dealing with monomeric species.

The ^1H NMR spectra of the palladium complexes of tetrapodands **5b**, **5d**, and **6b** (methanol-d_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 sharpening, but no fine structure came up. The NCHN imidazole protons appear as an unsymmetrical pattern shifted downfield with respect to their free tetrapodand. This indicates that the four imidazolyl groups are in the coordination sphere of the Pd(II) ion, but it suggests also that a symmetrical, five-coordinated square-pyramidal Pd(II) surrounding is not the predominant form. We believe therefore that in the three [Pd(tetrapodand)Cl]Cl complexes a scrambling process is operative involving the four imidazole units and the two chloride ions at the metal center such that, at any given moment, the Pd ion has a square-planar arrangement containing only three imidazolyl groups and one halide ion. An intermediate in this scrambling process is probably the $[Pd(tetrapodand)]^{2+}$ metallocage (see Figure 7).

(14) (a) el Basyony, A.; Klimes, J.; Knögel, A.; Oehler, J.; Rudolph, G. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1192–1200. (b) de Boer, J. A. A.; Reinhoudt, D. N.; Harkema, S.; Van Hummel, G. J.; De Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073–4076. (c) For a review on complexes between polar CH bond-containing guests and crown-type hosts, see: Vögtle, F.; Sieger, H.; Müller, W. M. *Top. Curr. Chem.* **1981**, *98*, 107–161.

(15) Niele, F. G. M.; Nolte, R. J. M., to be submitted for publication.

Conclusion

The above results concerning the palladium compounds clearly show the great importance of the spacer composition of the tetrapodand in determining the type of palladium–tetrapodand complex that is formed. In the case of $[Pd(\mathbf{4d})]^{2+}$, the metallocage is unstable and collapses via a twisted motion, most likely as a consequence of intramolecular H bonding between the polar C(2)H bond of the imidazolyl groups and the CH_2OCH_2 functions in the spacers. However, in the three $[Pd(tetrapodand)Cl]^+$ cage compounds, where there are fewer ether functions, metal coordination fluxionality is observed.

Experimental Part

General Procedures. ^1H NMR spectra were recorded on Varian EM-360, Bruker AW-80, and Bruker WP-200 instruments. Chemical shifts (δ) are reported downfield from internal $(CH_3)_4Si$. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared and UV-vis spectra were taken on Perkin-Elmer 283 and Perkin-Elmer 555 spectrophotometers, respectively. FAB mass spectra were recorded on a VG ZAB 2F spectrometer (matrix: glycerol, thioglycerol). Conductivity measurements were carried out at 25.0 °C with a Philips PW 9501 conductivity meter. Molecular weights were determined with a modified Gallenkamp ebulliometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry TNO Zeist, The Netherlands. Melting points were determined on a Mettler FP5/FP51 photoelectric melting apparatus. Gel permeation chromatography was performed on a Sephadex LH-60 column (length 21.5 cm, diameter 1 cm) with methanol as eluent at a flow rate of 31 mL/h.

Unless otherwise indicated, commercial chemicals were used as received. DMSO, DMF, and methanol were dried over 3-Å sieves prior to use. Diethyl ether and chloroform were distilled from benzophenone ketyl and $CaCl_2$, respectively.

Tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (1a). This compound was synthesized as described in literature.[16]

Tetrahydro-3a,6a-dimethylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (1b). This compound was synthesized according to a literature procedure.[17]

Tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (1c). This compound was synthesized according to a literature procedure.[18]

1,3,4,6-Tetrakis(hydroxymethyl)tetrahydro-3a,6a-diphenylimidazo-[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione(2). In a nitrogen atmosphere compound **1c** (1 g, 3.4 mmol) and paraformaldehyde (0.5 g, 16.7 mmol) were mixed in DMSO (5 mL). The mixture was adjusted to pH 9 with 1 M aqueous NaOH. The reaction mixture was stirred at ambient temperature for 16 h, filtered over infusorial earth, and added dropwise, with vigorous stirring, to a mixture of 35 mL of doubly distilled water and 3.5 mL of acetone. The precipitate was filtered, washed with water and acetone, and dried under vaeuum: yield 1.2 g (82%) of white **2**; mp >300 °C dec; FABMS $(M + H)^+$ *m/e* 415; IR (KBr) 3510–3300 (OH), 1730 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.0 (m, br, 10 H, ArH), 6.30 and 6.20 (2 d, ^3J = 6 Hz, 4 H, OH), 5.05 and 4.50 (dd, J_{gem} = 12 Hz, 8 H, CH_2).

1,3:4,6-Bis(2-oxapropylene)tetrahydro-3a,6a-dimethylimidazo[4,5-*d*]-imidazole-2,5(1*H*,3*H*)-dione (3a). Compound **1b** (1 g, 5.9 mmol) and formaldehyde (37 wt% solution in water; 2.2 g, 26.6 mmol) were mixed in 20 mL of water. The solution was adjusted to pH 1 with concentrated HCl, and the mixture was boiled for 4 h. The precipitate was filtered, washed with water and diethyl ether, and dried under vacuum; yield 1.4 g (92%) of white **3a**. A sample was recrystallized from DMSO: mp > 300 °C dec; FABMS $(M + H)^+$ *m/e* 255; IR (KBr) 1728 (C=O), 1120, 1027 (COC) cm^{-1}; ^1H NMR δ (DMSO-d_6) 5.30 (AB q, J_{gem} = 18 Hz, 8 H, CH_2) 1.80 (s, 6 H, CH_3). Anal. Calcd for $C_{10}H_{14}N_4O_4$: C, 47.24; H, 5.51; N, 22.05; O, 25.20. Found: C, 47.32; H, 5.62; N, 22.07; O, 25.02.

1,3:4,6-Bis(2-oxapropylene)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]-imidazole-2,5(1*H*,3*H*)-dione (3b). In a nitrogen atmosphere, compound **1c** (1 g, 3.4 mmol) and paraformaldehyde (0.5 g, 16.7 mmol) were mixed in DMSO (5 mL). The mixture was adjusted to pH 9 with 1 M aqueous NaOH. The reaction mixture was stirred at ambient temperature for 16 h. The pH was brought to 1 with concentrated HCl, and the mixture was stirred at 100 °C for 2 h. The precipitate was filtered, washed with

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water, and dried (P_2O_5) under vacuum: yield 514 mg (40%) of white **3b**; mp >300 °C dec; FABMS $(M + H)^+$ m/e 379; IR (KBr) 1728 (C=O), 1122, 1027 (COC) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (s, 10 H, ArH), 5.70 and 4.60 (AB q, J_{gem} = 12 Hz, 4 H, CH_2).

1,3,4,6-Tetrakis(4-bromo-2-oxabutyl)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (4a). Compound **2** (20.8 g, 50 mmol), 2-bromoethanol (250 g, 2 mol), and *p*-toluenesulfonic acid monohyrate (0.51 g, 2.7 mmol) were dissolved in 400 mL of toluene, and the solution was refluxed under N_2 for 48 h with a Soxhlet extraction apparatus filled with 3-Å sieves as a water remover. The reaction mixture was extracted with a saturated aqueous solution of $NaHCO_3$ and with water, respectively, dried ($MgSO_4$), and evaporated under vacuum. The residue was dissolved in a minimum of $CHCl_3$ and added dropwise, with vigorous stirring, to 500 mL of diethyl ether. The precipitate was filtered and dried under vacuum; yield 38.7 g (92%) of white **4a**. A sample was recrystallized from 2-bromoethanol–water: mp 125 °C; FABMS $(M - H)^+$ m/e 841; IR (KBr) 1730 (C=O), 1090, 1030 (CO-C), 690 (CBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (m, 10 H, ArH), 4.93 (AB q, J_{gem} = 9 Hz, 8 H, NCH_2O), 4.00 (m, 8 H, CH_2CH_2Br), 3.52 (m, 8 H, CH_2Br). Anal. calcd for $C_{28}H_{34}Br_4N_4O_6$: C, 39.93; H, 4.07; Br, 37.95; N, 6.65. Found: C, 40.03; H, 4.19, Br, 37.93; N, 6.67.

1,3,4,6-Tetrakis(7-chloro-2,5-dioxaheptyl)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (4c). Compound **2** (9.57 g, 23.1 mmol), 2-(2-chloroethoxy)ethanol (115.1 g, 924 mmol), and *p*-toluenesulfonic acid monohydrate (666 mg, 3.5 mmol) were refluxed in 250 mL of toluene under N_2 for 60 h with a Soxhlet extraction apparatus filled with 4-Å sieves as a water remover. The reaction mixture was neutralized (Na_2CO_3) and evaporated at water vapor pressure. The residue was washed with 300 mL of water (3×), dissolved in diethyl ether (2× its own volume), and cooled to −30 °C. The precipitate was filtered, washed with cold diethyl ether, and dried under vacuum: yield 10.9 g (56%) of white **4c**; mp 45–55 °C; FABMS $(M - H)^+$ m/e 837; IR (KBr) 1730 (C=O), 1130–1000 (COC), 724 (CCl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–6.8 (m, 10 H, ArH), 4.8 (AB q, J_{gem} = 12 Hz, NCH_2O), 3.7–3.1 (m, 32 H, $OCH_2CH_2OCH_2CH_2Cl$).

1,3,4,6-Tetrakis(6-chloro-2-oxahexyl)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5a). This compound was prepared from **2** (10.8 g, 26 mmol) and 4-chloro-1-butanol (56.5 g, 520 mmol) as described for **4c**. The product was recrystallized from methanol. Yield: 12.8 g (79%) of white **5a**; mp 56 °C; FABMS $(M - H)^+$ m/e 773; IR (KBr) 1720 (C=O), 1100–1050 (COC), 725 (CCl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 10 H, ArH), 4.87 (AB q, J_{gem} = 11 Hz, 8 H, NCH_2O), 3.6 (m, 16 H, $OCH_2CH_2CH_2CH_2Cl$). Anal. Calcd for $C_{36}H_{50}Cl_4N_4O_6$: C, 55.67; H, 6.44; Cl, 18.30; N, 7.22; O, 12.37. Found: C, 55.95; H, 6.59; Cl, 17.89; N, 6.97; O, 12.55.

1,3,4,6-Tetrakis(8-chloro-2-oxaoctyl)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5c). In a nitrogen atmosphere compound **1c** (5.9 g, 20 mmol) and NaH (from a 80% dispersion in mineral oil, washed with hexane; 2.4 g, 100 mmol) were mixed with 100 mL of DMF, and the solution was stirred at ambient temperature until gas production stopped. After this period 1,8-dichloro-2-oxaoctane[19] (19.2 g, 104 mmol) was added dropwise while the reaction mixture was kept at 15–20 °C. The mixture was stirred for 16 h at ambient temperature, filtered, and evaporated [70 °C (0.01 mmHg)]. The residue was dissolved in diethyl ether, filtered, evaporated under reduced pressure, and chromatographed on silica gel (particle size 0.040–0.063 mm, 230–400 mesh, ASTM) with chloroform–ethyl acetate (10:1 v/v) as eluent: yield 6.4 g (36%) of **5c** as a colorless syrup; FABMS $(M - H)^+$ m/e 885; IR (NaCl disks) 1720 (C=O), 1100–1050 (COC), 728 (CCl) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 10 H, ArH), 4.83 (AB q, J_{gem} = 11 Hz, 8 H, NCH_2O), 3.5 (m, 16 H, $OCH_2(CH_2)_4CH_2Cl$), 1.7 (m, 32 H, $OCH_2(CH_2)_4CH_2Cl$). Anal. Calcd for $C_{44}H_{66}Cl_4N_4O_6$: C, 59.46; H, 7.43; Cl, 15.99; N, 6.31; O, 10.81. Found: C, 59.25; H, 7.48, Cl, 15.72; N, 6.00; O, 10.40.

1,3,4,6-Tetrakis(6-bromohexyl)tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (6a). In a nitrogen atmosphere compound **1c** (1 g, 3.4 mmol), 1,6-dibromohexane (33.2 g, 136 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 90 °C for 1 h. The DMF was evaporated under water vapor pressure. Hexane (80 mL) was added to the residue. The solution was separated from the solid material and placed in a refrigerator at −20 °C for 48 h. The underlayer was washed first with 10 mL and subsequently with 30 mL of hexane and concentrated under vacuum. The residue was vigorously stirred for 1 h with 30 mL of refluxing hexane. The hexane was 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 ($CDCl_3$) δ 7.1–6.5 (m, 10 H, ArH), 3.3 (t, 8 H, CH_2Br), 3.5–2.5 (br m, 8 H, NCH_2), 1.1–2.1 (br m, 32 H, $CH_2(CH_2)_4CH_2$). Compound **6a** was converted into **6b** without further purification.

Tetrakis-1-imidazolyl Compounds. The tetrahalogenides **4a**, **4c**, **5a**, **5c**, and **6a** were converted into the corresponding tetra-1-imidazolyl compounds **4b**, **4d**, **5b**, **5d**, and **6b** by the following general procedure. In a nitrogen atmosphere the tetrahalogenide (1 mmol) was mixed with a solution of sodium imidazolate (8 mmol) in 10 mL of DMF and the solution stirred at 80 °C for 16 h. The reaction mixture was treated with 0.2 mL of water and evaporated under water vapor pressure (65 °C). The residue was dissolved in 8 mL of $CHCl_3$, washed (4×) with 8 mL of basic water (adjusted to pH 12 with Na_2CO_3) and with 8 mL of water (2×), dried ($MgSO_4$), and evaporated under vacuum; yield ≈100% of the tetraimidazolyl compound.

1,3,4,6-Tetrakis[4-(1-imidazolyl)-2-oxabutyl]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (4b): white solid; mp 87 °C; FABMS $(M + H)^+$ m/e 791; ^1H NMR ($CDCl_3$) δ 7.67 (pseudo s, 4 H, NCHN), 7.18 (dd, $^3J \approx {}^4J$ = 1.5 Hz, 4 H, N(1)C*H*CHN(3)), and 6.92 (dd, 4 H, N(1)CHC*H*N(3)); 4.2 (pseudo t, 8 H), remaining resonances within 0.1 ppm as for **4a**.

1,3,4,6-Tetrakis[7-(1-imidazolyl)-2,5-dioxaheptyl]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (4d): light yellow syrup; FABMS $(M + H)^+$ m/e 967; ^1H NMR ($CDCl_3$) as for **4b** and **4c** within 0.1 ppm.

1,3,4,6-Tetrakis[6-(1-imidazolyl)-2-oxahexyl]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5b): light yellow syrup; FABMS $(M + H)^+$ m/e 903; ^1H NMR ($CDCl_3$) as for **4b** and **5a** within 0.1 ppm.

1,3,4,6-Tetrakis[8-(1-imidazolyl)-2-oxaoctyl]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5d): light yellow syrup; FABMS $(M + H)^+$ m/e 1015; ^1H NMR ($CDCl_3$) as for **4b** and **5c** within 0.1 ppm.

1,3,4,6-Tetrakis[6-(1-imidazolyl)hexyl]tetrahydro-3a,6a-diphenylimidazo[4,5-*d*]imidazole-2,5-(1*H*,3*H*)-dione (6b): light yellow syrup; FABMS $(M + H)^+$ m/e 895; ^1H NMR ($CDCl_3$) as for **4b** and **6a** within 0.1 ppm.

[Pd(4d)]Cl$_2$. $Pd(CH_3CN)_2Cl_2$ (628 mg, 2.4 mmol) was added to a solution of compound **4d** (2.34 g, 2.4 mmol) in 50 mL of methanol. The mixture was refluxed for 16 h and filtered over infusorial earth. After reduction of the volume to 3–5 mL, the mixture was added dropwise, with vigorous stirring, to 100 mL of diethyl ether. The precipitate was filtered and dried under vacuum: yield 2.14 g (78%) of white [Pd(**4d**)]Cl_2; mp >90 °C dec; FABMS $(M - Cl)^+$ m/e 1107, $(M - 2Cl)^+$ m/e 1072; IR (KBr) 1720 (C=O), 1110–1000 (COC) cm^{-1}; ^1H NMR (CD_3OD) δ 8.22 (pseudo s, 4 H, NCHN), 7.30 (dd, $^3J \approx {}^4J$ = 1.5 Hz, 4 H, N(1)-C*H*CHN(3)), 7.1 (br s, 10 H, ArH), 7.08 (dd, 4 H, N(1)CHC*H*N(3)), 4.99 (AB q, J_{gem} = 11.6 Hz, 8 H, NCH_2O), 4.25 (t of AB q, J_{gem} = 15.1 Hz, $J_{vic} \approx$ 4–5 Hz, 8 H, CH_2Im), 3.72 (2 × d, 8 H, CH_2CH_2Im), 3.68–3.45 (m, 16 H, OCH_2CH_2O). Anal. Calcd for $C_{48}H_{62}Cl_2N_{12}O_{10}Pd\cdot 2.3H_2O$: C, 48.62; H, 5.66; Cl, 5.98; N, 14.17; O, 16.59. Found: C, 48.31; H, 5.65; Cl, 6.82; N, 14.02; O, 16.59.

[Pd(5b)Cl]Cl, Y[Pd(5d)Cl]Cl, and [Pd(6b)Cl]Cl. General Procedure. $Pd(CH_3CN)_2Cl_2$ (1 mmol) was added to a solution of the tetrapodand (1 mmol) in 20 mL of methanol. The mixture was refluxed for 16 h, filtered over infusorial earth, and evaporated under vacuum; yield 80–90% of a glassy yellow compound. Attempts to take FAB mass spectra of the complexes were unsuccessful. The UV–vis spectra (methanol) show intensive bands of the tetrapodands masking the ligand field ones.

[Pd(5b)Cl]Cl: mp >100 °C dec; ^1H, NMR (CD_3OD) δ 8 (br, 4 H, NCHN), 7.4–6.5 (br, 18 H, ArH + NCHCHN), 5.5–3 (br, 24 H, $NCH_2OCH_2(CH_2)_2CH_2Im$), 1.1–2.2 (br, 16 H, $OCH_2(CH_2)_2CH_2Im$). Anal. Calcd for $C_{48}H_{62}Cl_2N_{12}O_6Pd\cdot 4.2H_2O\cdot 1.1CH_3OH$: C, 49.46; H, 6.19; N, 14.10; O, 15.18. Found: C, 49.70; H, 6.12; N, 14.08; O, 16.46.

[Pd(5d)Cl]Cl: mp >90 °C dec; ^1H NMR (CD_3OD) δ 8 (br, 4 H, NCHN), 7.4–6.5 (br, 18 H, ArH + NCHCHN), 5.5–3 (br, 24 H, $NCH_2OCH_2(CH_2)_4CH_2Im$), 1.1–2.2 (br, 32 H, $OCH_2(CH_2)_4CH_2Im$). Anal. Calcd for $C_{56}H_{78}Cl_2N_{12}O_6Pd\cdot 4.0H_2O\cdot 1.0CH_3OH$: C, 52.75; H, 6.71; N, 12.96; O, 13.57. Found: C, 52.95; H, 6.94; N, 13.15; O, 13.86.

[Pd(6b)Cl]Cl: mp >130 °C dec; ^1H NMR (CD_3OD) δ 8.3–8 (br, 4 H, ArH), 4.4–3.8 (br, 8 H, CH_2Im), 3.5–2.6 (br, 8 H, NCH_2), 2.2–1.1 (br, 32 H, $CH_2(CH_2)_4CH_2Im$). Anal. Calcd for $C_{52}H_{70}Cl_2N_{12}O_6Pd\cdot 3.8H_2O\cdot 0.8CH_3OH$: C, 54.32; H, 6.86; N, 14.40; O, 9.05. Found: C, 54.76; H, 6.86; H, 14.11; O, 10.25.

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and Prof. W. Drenth for helpful discussions.

Registry No. 1a, 496-46-8; **1b**, 68374-68-5; **1c**, 101241-21-8; **2**, 101241-22-9; **3a**, 111380-74-6; **3b**, 111380-75-7; **4a**, 111380-76-8; **4b**, 111380-77-9; **4c**, 111380-78-0; **4d**, 101241-23-0; [Pd(**4d**)]Cl_2, 102258-15-1; **5a**, 111380-79-1; **5b**, 111380-80-4; [Pd(**5b**)Cl]Cl, 111380-85-9; **5c**, 111380-81-5; **5d**, 111380-82-6; [Pd(**5d**)Cl]Cl, 111380-86-0; **6a**, 111380-83-7; **6b**, 111380-84-8; [Pd(**6b**)Cl]Cl, 111380-87-1; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; paraformaldehyde, 30525-89-4; 2-bromoethanol, 540-51-2; 2-(2-chloroethoxy)ethanol, 628-89-7; 4-chloro-1-butanol, 928-51-8; 1,8-dichloro-2-oxaoctane, 72418-57-6; 1,6-dibromohexane, 629-03-8; sodium imidazolate, 5587-42-8.

Selective Molecular Oxygen Oxidation of Thioethers to Sulfoxides Catalyzed by Ce(IV)

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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 radial cation of the thioether (produced by Ce(IV) oxidation of thioether) to yield the oxygenated radical cation $R_2S^+OO^\bullet$, which, it is proposed, reoxidizes Ce(III) to Ce(IV). The zwitterionic $R_2S^+OO^-$ intermediate (persulfoxide) 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., Me_2S) to their more valuable sulfoxides, we discovered that thioethers are subject to a novel autoxidation process that under high oxygen concentrations, elevated temps., and polar solvents yields almost exclusively the sulfoxide product.[1] The mechanism of this unusual autoxidation 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).[2] Back-

$$R_2S + {}^3O_2 \rightarrow R_2\overset{+}{S}{}^\bullet + O_2^{\bullet-} \quad (1)$$

$$R_2\overset{+}{S}{}^\bullet + {}^3O_2 \rightarrow R_2\overset{+}{S}OO^\bullet \quad (2)$$

donation of an electron from superoxide to the oxygenated radical cation yields the zwitterionic species (eq 3) whose chemistry is known to yield sulfoxide upon exposure to additional thioether (eq 4).[3]

$$R_2\overset{+}{S}O{-}O^\bullet + O_2^{\bullet-} \rightarrow R_2\overset{+}{S}O{-}O^- + O_2 \quad (3)$$

$$R_2\overset{+}{S}O{-}O^- + R_2S \xrightarrow{k_4} 2R_2\overset{O}{\overset{\uparrow}{S}} \quad (4)$$

Given that the initial unfavorable electron-transfer step is rate-determining in this slow autoxidation reaction, we believed that the use of a suitable one-electron oxidant would possibly be capable of catalyzing or initiating the desired oxygen oxidation of R_2S to sulfoxide. We have communicated our preliminary successful attempts to catalyze this reaction using Ce(IV),[4] and in this paper we present additional examples and mechanistic studies of the novel Ce(IV)-catalyzed molecular oxygen oxidation of thioethers to sulfoxides.

Experimental Section

All of the thioethers used in these studies were purchased from Aldrich Chemical Co. and distilled before use. Sulfoxide standards were prepared by standard procedures with H_2O_2,[5] and $(NH_4)_2Ce(NO_3)_6$ and $Ce(NO_3)_3 \cdot 6H_2O$ and purchased from Alfa-Ventron. HPLC grade acetonitrile was distilled before use and distilled, de-ionized water was used in all cases.

Electronic spectra were monitored by using matched quartz cells in a Hitachi 110A UV-VIS spectrophotometer over the range 200–500 nm. All high-pressure catalytic runs used an apparatus analogous to that reported previously.[6] In general reactions were carried out with a reaction volume of 10 mL in an all glass/Teflon reactor. This small volume also minimized the potential risks inherent in running reactions with oxygen in an explosive regime. *Caution* must be exercised in such studies. In our system the reactor head-space (or gas) volume was kept very small; thus, only a small amount of O_2 is present in the reactor at any time. This reduces the possibility of extensive deflagration. Gas uptake measurements were made by utilizing a pressurized external calibrated steel tube connected directly to the reactor. Pressure drop in this calibrated external tube could be correlated to moles of O_2 consumed during the reaction. Reactions were monitored by gas chromatography on a Varian Model 3400 GC with a flame ionization detector and analyzed on a 15 M OV101 capillary column. Yields were determined by utilizing dodecane as an internal standard and by comparison to calibrated solutions. Electrochemical studies were performed on a Bioanalytical Systems CV-1B cyclic voltammograph, and voltammograms were recorded on a Houston Instruments 100 XY recorder. All cyclics were recorded in dry methylene chloride with 0.5 M tetra-*n*-butylammonium tetrafluoroborate

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