long bulk lifetime (>2 ms),[10] (100) oriented, 190-μm thick sample of n-Si in contact with concentrated H_2SO_4. Both sides of this wafer were optically polished, and both sides were in contact with the solution. In agreement with prior work,[7a] the excess carrier concentration decays with a remarkably long time constant in contact with aqueous acid solutions. Using the known expression that $k_{obsd} = k_{bulk} + k_{surf}$,[9] and the knowledge that $k_{bulk} < 5 \times 10^2$ s^{-1} for these samples,[10] we calculate that the surface recombination velocity is 25 cm/s (from $k_{obsd} \approx 2S/L$ where L = 190 μm and S is the surface recombination velocity in cm/s) under our conditions.

The presence of electron donors or acceptors in the solution should decrease the observed lifetime, especially if electron transfer is occurring on a rapid time scale. Figure 1b displays the reflected power decay curves for this same n-Si sample in contact with 0.34 M dimethylferrocene (Me_2Fc), 5 mM Me_2Fc^+, and 0.10 M $LiClO_4$ in CH_3OH. The excess carriers were remarkably long-lived, with excess carrier lifetimes of 0.24 ms, corresponding to a surface recombination velocity of 40 cm/s for this system. At 0.34 M Me_2Fc, this corresponds to an upper limit on the bimolecular hole transfer rate constant of 1.95×10^{-19} cm^4/s. This result has been obtained with both the microwave and the rf conductivity apparatus, confirming that it is not an artifact of the measurement technique.

The reflected power decay profiles have also been investigated as a function of excitation wavelength (Figure 1b). Even with excitation at 355 nm, where the photoexcited carriers have over 2.3 eV of excess unthermalized energy and are initially confined to the 140-Å penetration depth of the incident light,[11] we observed lifetimes of greater than 0.2 ms for these carriers in the presence of the $Me_2Fc^{+/0}$. These long lifetimes were also obtained with the $Me_2Fc^{+/0}$ system in other solvents, including propylene carbonate and acetonitrile.

The large concentration of Me_2Fc donors might be expected to act as effective hole traps, and this should reduce the measured signal by 25% even if all of the electrons remained in the solid (from eq 1 and the fact that $\mu_n/\mu_p \approx 3$ for Si). However, no fast component of the concentration decay was observed even on the nanosecond time scale (Figure 1b inset). We note that, for excitation at 1064 nm, the photon penetration depth in Si is 0.84 mm.[11b] When excess carriers are created uniformly throughout the 190 μm thick Si sample, the half-life for carriers to be captured at a diffusion-limited rate to the surface (with the ambipolar D = 10 cm^2/s)[3] is 7 μs;[9] thus, the time response of the experimental system is more than adequate to observe any fast-decay components associated with the postulated trapping processes. We have also examined the Si surface after a laser flash to see whether an insulating layer was formed that could impede electron transfer, but after exposure to three light pulses (3×10^{13} photons/cm^2 per pulse) in $CH_3OH/Me_2Fc^{+/0}$ at 1064 nm, we observed only Si, adventitious C, and less than 0.25 monolayers of silicon oxide by high-resolution X-ray photoelectron spectroscopy.[12] We therefore conclude that the carrier lifetimes are very long in these Si samples and that no light-induced insulating layer is leading to spuriously low rate constants in these experiments. Our analysis places an upper limit to the interfacial charge transfer rate constant of 40 cm/s, as compared to charge transfer rate constants of 10^7 cm/s observed for semiconductor/metal interfaces.[9]

Taken at face value, these results seem to contradict the impressive current–voltage properties and high energy conversion efficiencies displayed by the n-Si/CH_3OH interface in contact with the $Me_2Fc^{+/0}$ redox system.[13] However, the ratio of the minority carrier injection rate into the electrolyte relative to the minority carrier recombination rate will determine the net photocurrent quantum yield;[1,2,14] therefore, if the surface nonradiative recombination rates are sufficiently small, a slow interfacial charge transfer rate still can produce high net quantum yields in steady-state experiments. Current continuity arguments can be used to place a lower limit on the hole capture velocity of 1 cm/s and an upper limit on the electron capture velocity of 10^4 cm/s in the n-Si/$Me_2Fc^{+/0}$ cell;[13-16] thus, there is no actual contradiction between the real-time data and the steady-state photoelectrochemical efficiency measurements. However, the unexpectedly slow injection rates do underscore the usefulness of real-time techniques in elucidating the magnitude of the charge-transfer kinetics.

These results, in conjunction with those obtained for CdS,[5] imply that a wide range of electron-transfer rate constants may be found at semiconductor/liquid interfaces. They also demonstrate that these rate constants may be over 6 orders of magnitude slower than previously postulated for semiconductors and still be consistent with established steady-state voltammetric experiments. The real-time methods described above can be used to obtain rate constant information in aqueous media and for a variety of other redox systems, and such work is in progress at present.

Acknowledgment. We thank B. J. Tufts for running the XPS experiments, P. G. Santangelo and A. Kumar for experimental assistance, and E. Yablonovitch, T. Gmitter, M. Kunst, J. Warman, and H. Tributsch for helpful discussions regarding the experimental setup. We are also grateful to R. Swanson and R. Sinton of Stanford University for providing the Si samples. M.D.E.F. is grateful for financial support from the National Science Foundation through its Postdoctoral Fellowship Program in Chemistry. This work was supported by Grant No. CHE-8814263 from the National Science Foundation.

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[14] (a) Evenor, M.; Huppert, D.; Gottesfeld, S. *J. Electrochem. Soc.* **1986**, *133*, 296. (b) Tufts, B. J.; Abrahams, I. L.; Casagrande, L. G.; Lewis, N. S. *J. Phys. Chem.* **1989**, *93*, 3260.

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Palladium-Catalyzed Stereocontrolled Intramolecular 1,4-Additions to Cyclic 1,3-Dienes Involving Amides as Nucleophiles

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Regioselective metal-mediated additions to conjugated dienes have attracted considerable interest recently.[1] In the palladium-catalyzed oxidation of conjugated dienes, two nucleophiles are added in a regio- and stereospecific manner across the diene (Scheme I).[1-3] The latter type of reaction occurs in the presence of an acid with benzoquinone being used as electron-transfer catalyst or oxidant. Nucleophiles that can be used include carboxylates, alcohols, and halides. It would be of great synthetic interest to extend these selective 1,4-oxidations to other nucleophiles, such as carbon and nitrogen nucleophiles. In this communication, we report for the first time the use of nitrogen nucleophiles in the palladium-catalyzed 1,4-oxidation of 1,3-dienes.

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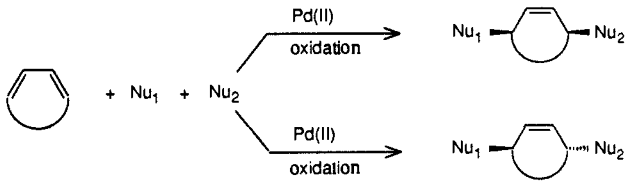
[1] Bäckvall, J. E. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1989; Vol. 1, pp 135–175.

[2] (a) Bäckvall, J. E.; Nyström, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676. (b) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619.

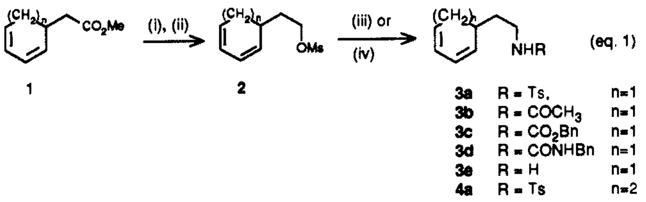
[3] (a) Bäckvall, J. E.; Vågberg, J. O. *J. Org. Chem.* **1988**, *53*, 5695. (b) Bäckvall, J. E.; Andersson, P. G.; Vågberg, J. O. *Tetrahedron Lett.* **1989**, *30*, 137.

0002-7863/90/1512-3683$02.50/0

Scheme I



Scheme II[a]



[a] (i) DIBAL, hexane. (ii) MsCl, Et_3N. (iii) RNHNa, for R = Ts and R = $COCH_3$. (iv) For R = CO_2Bn and R = CONHBn: (a) potassium phthalimide, DMF, 18-crown-6; (b) NH_2NH_2, EtOH, H^+; (c) $ClCO_2Bn$, Et_3N (or OCNBn, Et_3N).

Scheme III

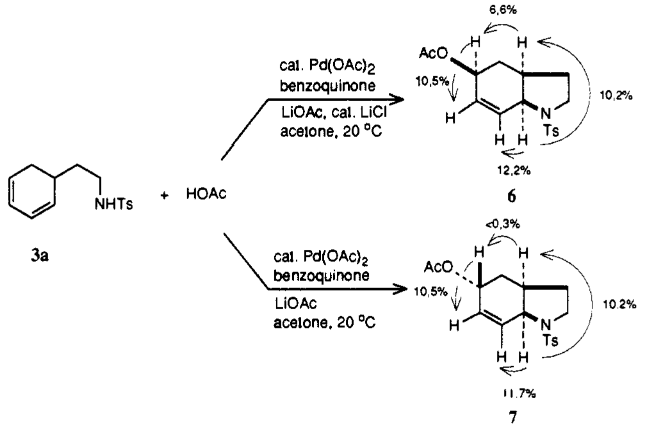
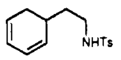
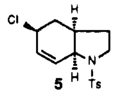
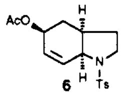
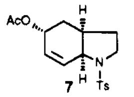
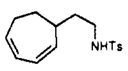
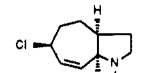
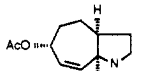
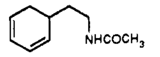
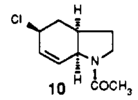
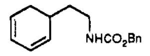
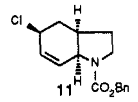
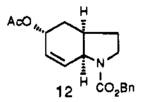
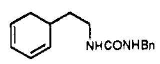
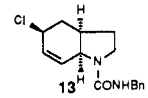


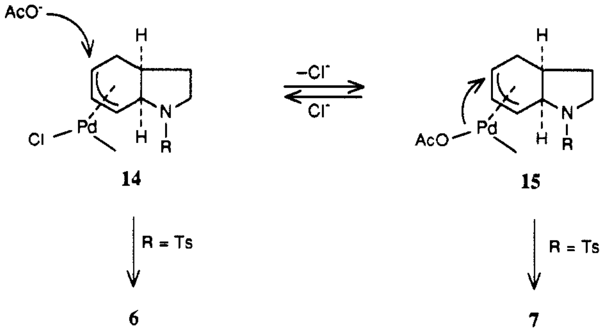
Table I. Palladium-Catalyzed Intramolecular 1,4-Chloro- and 1,4-Oxyamidation of Conjugated Dienes[a]

Diene amide[b]	reaction time	method	product	% yield[c]	stereo-chem.[d]
 **3a**	8h	A	 **5**	90	>98% cis
3a	48h	B	 **6**	65	>96% cis
3a	16h	C[e]	 **7**	82	>93% trans
 **4a**	16h	A	 **8**	86	>98% cis
4a	72h	C[f]	 **9**	92	trans : cis = 80 : 20
 **3b**	2h	A	 **10**	94	>98% cis
 **3c**	2h	A	 **11**	97	>98% cis
3c	16h	C[f]	 **12**	85	>98% trans
 **3d**	2h	A	 **13**	88	>98% cis

[a] Unless otherwise noted, the reactions were performed in acetone–acetic acid (4:1) at room temperature, with 0.1–0.2 mmol of substrate/mL, using 5 mol % of $Pd(OAc)_2$ and 2 equiv of *p*-benzoquinone. Method A: 2 equiv of LiCl. Method B: 0.2 equiv (20 mol %) of LiCl and 2 equiv of $LiOAc{\cdot}2H_2O$. Method C: in the absence of LiCl. [b] Ts = SO_2-*p*-$C_6H_4CH_3$, Bn = benzyl. [c] Isolated yield of pure product. [d] Refers to the addition across the diene system. The bridgehead protons are always cis to one another (>99%). (Determined by ^1H NMR spectroscopy.) [e] In the presence of 1 equiv of $LiOAc{\cdot}2H_2O$. [f] Without $LiOAc{\cdot}2H_2O$.

During previous work on 1,4-oxidations of conjugated dienes involving intramolecular reactions, it occurred to us that amides might be able to serve as nucleophiles. The required dienic amides were prepared from readily available ester **1**,[3b,4] according to eq 1 (Scheme II). Amides **3a**, **4a**, and **3b** were obtained via direct displacement of the mesylate by the corresponding amide anion ($TsNH^-$ or CH_3CONH^-). In the case of amides **3c** and **3d**, mesylate **2** was converted to primary amine **3e**[5] followed by reaction with benzyl chloroformate or benzyl isocyanate, respectively.

Palladium-catalyzed reaction of amido dienes **3a** and **4a** in the presence of LiCl (2 equiv) and acetic acid in acetone using benzoquinone as the oxidant afforded adducts **5** and **8**, respectively, in good yield (Table I, entries 1 and 4). By a slight change in reaction conditions, it was possible to obtain a stereocontrolled oxyamidation (Scheme III). Thus, reaction of **3a** in the presence of lithium acetate and a catalytic amount of lithium chloride but otherwise maintaining the usual reaction conditions resulted in a cis-1,4-oxyamidation to give **6**. Reaction of **3a** in the absence of lithium chloride gave **7** via a trans-1,4-oxyamidation. The stereochemistry of products **6** and **7** was determined by NOE experiments,[6] which also confirmed the 1,4-relation between nitrogen and oxygen. The explanation for this dual stereocontrol, which has been discussed previously,[1,2b] is that chloride blocks the coordination of acetate to palladium in the catalytic intermediate, thus suppressing the cis migration of acetate. Thus, intermediate **14** would react only with an external acetate to give product **6** whereas **15** would produce **7** via a cis migration.



The intramolecular amidation reaction also worked well for acetamides, carbamates, and ureas. Thus, **3b**, **3c**, and **3d** afforded chloroamidation products in high yield (entries 6, 7, and 9, Table

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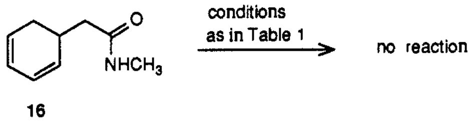
(4) (a) Bäckvall, J. E.; Vågberg, J. O.; Zercher, C.; Genêt, J. P.; Denis, A. *J. Org. Chem.* **1987**, *52*, 5430. (b) Ester **1** was prepared according to refs 3b and 4a. An alternative preparation of **1** (*n* = 2) has been described by Pearson: Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

(5) Primary amine **3e** was also obtained by transforming ester **1** to amide followed by reduction ($LiAlH_4$).

(6) The NOE experiments were run in degassed $CDCl_3$ (10 mg/mL) under nitrogen at 300 MHz.

I). In several of these cases, the catalytic intermediates related to **14** were observed by ^{1}H NMR.[7] Nucleophilic attack by chloride on these intermediates gives the products observed. In one case, the chloride dimer of **14** (R = $COCH_3$) was isolated and characterized.[8]

Amides have previously been utilized as nucleophiles in palladium-catalyzed additions to monoolefins.[9,10] For example, carbamates and sulfonamides were applied in palladium-catalyzed intramolecular reactions to produce heterocycles,[9] and various amides were used in palladium-catalyzed intramolecular amidocarbonylations.[10] The results here are the first-described selective oxidations of conjugated dienes where amides serve as nucleophiles. It is remarkable that the amide nitrogen can act as a nucleophile under the slightly acidic conditions.[11] Dienic amides such as **16**, which on cyclization would give γ-lactams, did not give the desired amidation products. Attempts to cyclize **16**, readily available from **1**,[12] gave only recovered starting material. Apparently the ring strain caused by the carbonyl group makes the rate too slow to be synthetically useful.



16

In conclusion, these 1,4-oxidations in which one nitrogen nucleophile and one oxygen or halide nucleophile are added across the diene should make a number of nonaromatic nitrogen heterocycles available from amino dienes. The fact that the chloro group can be subsequently regioselectively substituted with either retention or inversion[1,2a,13] should make the present methodology useful in the synthesis of natural products.[14]

Acknowledgment. We are grateful to the Swedish Natural Science Research Council for financial support and to Johnson Matthey for a loan of palladium chloride. We also thank Dr. Adolf Gogoll for assistance with the NOE experiments.

Registry No. 1 (*n* = 1), 125974-25-6; **1** (*n* = 2), 125974-26-7; **2** (*n* = 1), 125974-27-8; **2** (*n* = 2), 125974-28-9; **3a**, 125974-29-0; **3b**, 125974-30-3; **3c**, 125974-31-4; **3d**, 125974-32-5; **3e**, 125974-33-6; **4a**, 125974-34-7; **5**, 125974-35-8; **6**, 125974-36-9; **7**, 125974-37-0; **8**, 125974-38-1; *trans*-**9**, 125974-39-2; *cis*-**9**, 126060-07-9; **10**, 125974-40-5; **11**, 125974-41-6; **12**, 125974-42-7; **13**, 125974-43-8; **14** (R = $COCH_3$), 125995-62-2; **16**, 125995-63-3; $TsNH_2$·Na, 18522-92-4; $AcNH_2$·Na, 2620-30-6; benzyl chloroformate, 501-53-1; benzyl isocyanate, 3173-56-6.

Supplementary Material Available: Experimental details of the preparation of **5** and spectroscopic (^{1}H and ^{13}C NMR, IR, and MS) and analytical data for **5**–**13** (4 pages). Ordering information is given on any current masthead page.

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[7] For the mechanistic studies, the reactions were run in acetone-d_6 and CD_3COOD (4:1) in an NMR tube. ^{1}H NMR spectra were then recorded periodically. The catalytic intermediate π-allyl complex was observed at a steady-state concentration close to that of the catalyst, indicating that the first step is rapid. The spectrum of the π-allyl complex was very similar to that of the isolated dimer.[8]

[8] $[C_{10}H_{14}OPdCl]_2$ (**14**, R = $COCH_3$). This π-allyl complex consisted of two rotamers (2:1 ratio) due to hindered rotation around the acyl–nitrogen bond. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major rotamer) 5.55 (dd, *J* = 7.0 and 6.0 Hz, 1 H, CH of π-allyl), 5.10 (dd, *J* = 6.5 and 6.0 Hz, 1 H, CH of π-allyl), 4.67 (d, *J* = 7.0 Hz, 1 H, CH of π-allyl), 4.36 (d, *J* = 7.8 Hz, 1 H, CHN bridgehead), 3.53 (br q, 1 H, one of CH_2N), 3.36 (br q, 1 H, one of CH_2N), 3.41 (m, 1 H, CH bridgehead), 2.20 (s, 3 H, CH_3CO), 2.02 (br s, 2 H), 1.95–1.65 (m, 2 H); δ (minor rotamer) 5.48 (dd, *J* = 6.0 and 5.4 Hz, 1 H, CH of π-allyl), 5.21 (d, *J* = 5.4 Hz, H2, 1 H, CH of π-allyl), 4.99 (dd, *J* = 6.0 and 5.4 Hz, 1 H, CH of π-allyl), 4.52 (d, *J* = 7.2 Hz, 1 H, CHN bridgehead), the rest of the shifts coincide with the major rotamer.

[9] Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444.

[10] (a) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1988**, *110*, 3994. (b) Tamaru, Y.; Hojo, M.; Yoshida, Z. *J. Org. Chem.* **1988**, *53*, 5731.

[11] A similar reactivity of amides under acidic conditions was observed by Tamaru et al. in palladium-catalyzed intramolecular amidocarbonylation of olefins.[10a]

[12] Högberg, T.; Ström, P.; Ebner, M.; Rämsby, S. *J. Org. Chem.* **1987**, *52*, 2033.

[13] Bäckvall, J. E. *Bull. Soc. Chim. Fr.* **1987**, 665.

[14] (a) Preliminary experiments showed that *N*-((benzyloxy)carbonyl)- and *N*-((benzylamino)carbonyl)- protected 1-(4-aminobutyl)-1,3-cyclohexadiene resulted in a palladium-catalyzed spiroamidocyclization under the reaction conditions of Table I. These products are of potential interest for the synthesis of histrionicotoxins.[14b,c] (b) Daly, J. W. In *Progress in the Chemistry of Organic Natural Products*; Springer: Berlin, 1982; Vol. 41, p 205. (c) Tanner, D.; Sellén, M.; Bäckvall, J. E. *J. Org. Chem.* **1989**, *54*, 3374.

Stereoelectronic Effects in Cyclization Reactions

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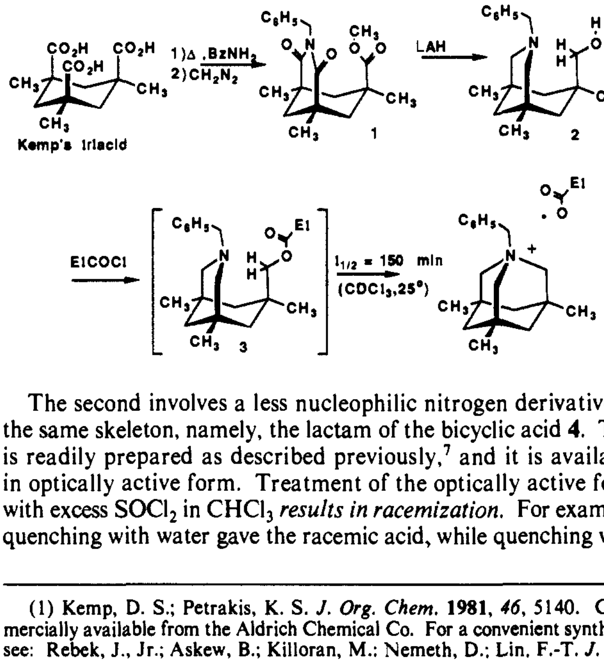
Derivatives of the Kemp Triacid[1] are useful as scaffolds for molecular recognition[2] and as probes for stereoelectronic effects at carboxyl oxygen.[3] The diaxial relationship enforced between any two carboxyl groups encourages neighboring-group participation, leading to enormous rate enhancements in amide hydrolysis.[4] We report here some other unusual manifestations of this unique skeleton as they apply to stereoelectronic effects in cyclization reactions.

The first involves the peculiar behavior of the bicyclic ester **3**. This is readily prepared from the imide methyl ester **1**[5] by LAH reduction followed by acylation[6] (eq 1). Despite the poor leaving group and the nonlinear arrangement of nucleophile, carbon, and the leaving group, the intermediate **3** cyclizes rapidly to the azaadamantane salt. Specifically, the half-life for the cyclization in $CDCl_3$ at room temperature is 150 min. There is no obvious bimolecular counterpart for this reaction.



(1)

The second involves a less nucleophilic nitrogen derivative of the same skeleton, namely, the lactam of the bicyclic acid **4**. This is readily prepared as described previously,[7] and it is available in optically active form. Treatment of the optically active form with excess $SOCl_2$ in $CHCl_3$ *results in racemization*. For example, quenching with water gave the racemic acid, while quenching with

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[1] Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140. Commercially available from the Aldrich Chemical Co. For a convenient synthesis, see: Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426–2431.

[2] Rebek, J., Jr. *Pure Appl. Chem* **1989**, *61*, 1517–1522.

[3] Tadayoni, B. M.; Parris, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 4503.

[4] Menger, F. M.; Ladika, M. *J. Am. Chem. Soc.* **1988**, *110*, 6794.

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