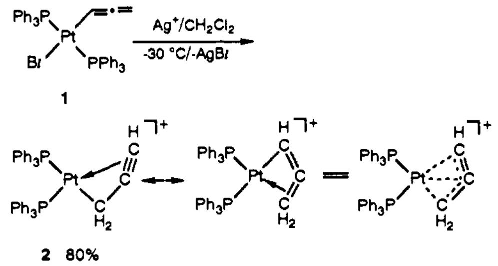
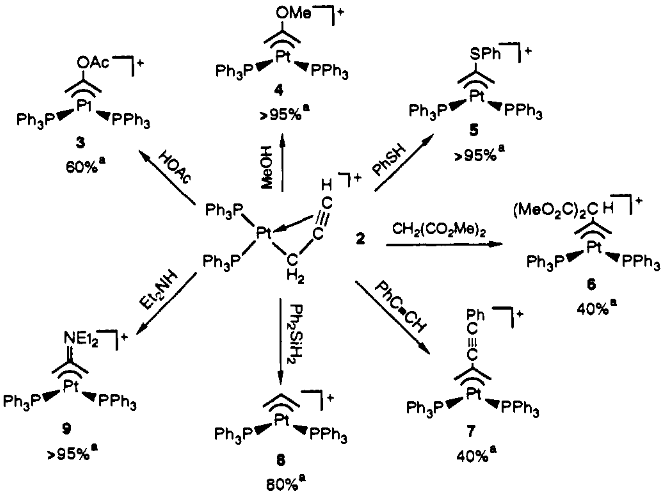
Scheme I



Scheme II



^{a}All product yields were estimated on the basis of ^{31}P NMR measurements.

spectrum of **2**, a doublet at δ 90.6 having J_{CH} = 246 Hz is assigned to the CH of the propargyl terminus and a triplet at δ 51.8 with J_{CH} = 171 Hz is assigned to the propargyl CH_2, the large coupling constant of which suggests the possibility of an η^3-allenyl resonance structure (Scheme I).[6] Such a highly strained η^3-propargyl feature also explains the unusually large values of J_{PtP} (3810 and 4179 Hz) and the unusually small values of $J_{PtC(terminal)}$ (105 and 137 Hz).[6-8]

Complex **2** readily undergoes an addition reaction with a wide range of hard and soft species including weak protic acids (HOAc, MeOH, and PhSH) and weak carbon acids ($H_2C(CO_2Me)_2$ and PhC≡CH) to generate β-substituted π-allyl complexes $[Pt(\eta^3\text{-}CH_2C(Y)CH_2)(PPh_3)_2](BF_4)$ (Y = OAc, **3**; OMe, **4**; SPh, **5**; $CH(COOMe)_2$, **6**; C≡CPh, **7**). In the reaction of **2** with Ph_2SiH_2, only the simple allyl complex (Y = H, **8**) was obtained (Scheme II). While π-allyl products were characterized spectroscopically, the structure of **5** was confirmed by crystallography.[8] The analogous reaction of **2** with Et_2NH yielded platinum η^3-azatrimethylenemethane $[Pt(\eta^3\text{-}CH_2C({=}NEt_2)CH_2)(PPh_3)_2](BF_4)$ (**9**) at a rate exceedingly faster than its formation from the reaction of **1** and the amine.[3b] Note that the other complexes (**3**–**8**) cannot be prepared directly from **1**. Exclusive addition of MeOH, PhSH, or Et_2NH to **2** was complete on mixing the reactants at 0 °C, judging from immediate NMR measurements. The reactions with other reagents are relatively slow.[9]

Although regioselective addition of nucleophiles to the propargyl complex has been known,[11] the reactivity of neutral malonate ester, phenylacetylene, and silane without the assistance of a base is unprecedented. The versatile bond-forming ability of the η^3-propargyl ligand activated by π-interaction with the cationic metal center suggests a rich chemistry. The reaction scope and mechanism of such transformations and application to organic synthesis are certainly worthy of further investigation.

Acknowledgment. We are grateful to the National Science Council, ROC, for financial support and to the Institute of Chemistry, Academia Sinica, Nangkang, for help in (500 MHz) NMR measurements. J.-T.C. thanks Professor T.-Y. Luh for helpful discussion. Stimulating comments and suggestions as to the structure of **2** and the possible reaction mechanisms from Professor Charles P. Casey, Department of Chemistry, University of Wisconsin, are gratefully acknowledged.

Supplementary Material Available: Experimental and characterization data for complexes **1**–**9** including two NMR spectra of **2** and crystal data and an ORTEP drawing of **5** (7 pages). Ordering information is given on any current masthead page.

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(6) For comparison: ^{1}H-coupled ^{13}C NMR data of $\{Pt[\eta^3\text{-}CH_2CHCH_2](PPh_3)_2\}(BF_4)$ (**8**) δ 69.9 (t, J_{CH} = 161 Hz, C_α); ^{31}P NMR δ 17.02 ($J_{P\text{-}Pt}$ = 3989 Hz).

(7) The value of $J_{P\text{-}Pt}$ for a P trans to a Pt–C(σ) bond is ~2000 Hz; the value of J_{CPt} for a carbon of Pt–C(σ) bond is ~500 Hz.[1]

(8) Selected spectral data for $\{Pt[\eta^3\text{-}(CH_2C(SPh)CH_2)](PPh_3)_2\}(BF_4)$ (**5**): ^{31}P NMR ($CDCl_3$) δ 18.16 ($J_{P\text{-}Pt}$ = 3801 Hz); ^{1}H NMR ($CDCl_3$) δ 3.13 (2 H, J_{HH} = 3.4 Hz, J_{PH} = 8.4 Hz, J_{PtH} = 42.5 Hz, H_{anti}), 3.26 (2 H, J_{HH} = 3.4 Hz, H_{syn}), 7.1–7.5 (m, phenyl H); ^{13}C NMR ($CDCl_3$) δ 63.0 (dd with ^{195}Pt satellites, J_{PC} = 4.7, 37 Hz, J_{PtC} = 98 Hz, C_α), 126–136 (phenyl carbons), 142.3 (t, J_{PC} = 2.6 Hz, C_β). Crystal data of $C_{45}H_{39}P_2SPtBF_4{\cdot}CH_2Cl_2$: $P\bar{1}$, a = 11.285(3) Å, b = 11.615(2) Å, c = 17.946(2) Å, α = 106.57(1)°, β = 91.44(1)°, γ = 106.43(2)°, V = 2148.2(6) Å^3; Mo Kα radiation λ = 0.7107 Å, Z = 2, μ = 3.59 mm^{-1}; 5620 total reflections, 4819 observed reflections ($I > 2.0\sigma(I)$), R = 0.030, R_w = 0.025.

(9) Noting that the overall reactions from **2** to **3**–**9** involve both protonation to a terminal carbon and nucleophilic addition to the central carbon of the propargyl ligand, the mechanism may comprise either (1) leading nucleophilic attack to the central carbon, yielding an intermediate of platinacyclobutene[4,10] followed by protonation, or (2) protonation first, resulting a π-allene complex which then adds a nucleophile to the central carbon.

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Concerning the Formation of Hydrogen in Nuclear Waste. Quantitative Generation of Hydrogen via a Cannizzaro Intermediate

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During the storage of certain nuclear waste, particularly mixtures containing complexing agents like EDTA and HEDTA in highly basic media, mixtures of gases containing large amounts of hydrogen are produced. In order to provide the foundation for control of this potentially dangerous situation, a fundamental understanding of the reactions responsible for the formation of hydrogen is crucial. Since it is known that the photolytic,[1] radiolytic,[2] and thermal[3] degradation of EDTA produces formaldehyde, it is reasonable to assume that formaldehyde is formed during the storage of nuclear waste, and that it could be an important intermediate in the generation of hydrogen. In a study

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(1) Lockhardt, H. B.; Blakeley, R. V. *Environ. Sci. Technol.* **1975**, *9*(12), 1073; *Chem. Abstr.* **1976**, *84*, 196430k.

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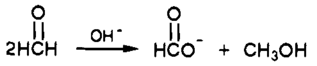
Table I. Stoichiometry of the Reaction of Formaldehyde with NaOH in Water[a]

T, °C	[CH_2O], M	[NaOH], M	% H_2	% $HCOO^-$	% CH_3OH
28	4×10^{-4}	19	102.4	97.0	0
90	2×10^{-2}	17	41.1	71.3	27.0

[a] All reactions were carried out until hydrogen was no longer produced.

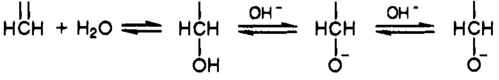
of the Cannizzaro reaction in 1887, it was reported that the interaction of aqueous solutions of formaldehyde and NaOH produced a very small quantity of hydrogen.[4] A mechanistic explanation of hydrogen evolution from formaldehyde in the presence of base has not been presented until now, nor has the formation of H_2 in high yield been previously reported. Additionally, there has been no explanation from any source as to the origin of hydrogen produced from nuclear waste except for the amount produced by the radiolysis of water.

The reaction in which two aldehyde molecules, in the presence of base, are transformed into the corresponding alcohol and carboxylic acid is known as the Cannizzaro reaction (eq 1). This

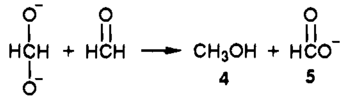


$$2\,\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} \xrightarrow{\mathrm{OH}^-} \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}^- + \mathrm{CH_3OH} \qquad (1)$$

reaction is characteristic of aldehydes that do not possess an α hydrogen atom, and the simplest of these aldehydes is formaldehyde. When allowed to react with excess base, formaldehyde generates the Cannizzaro intermediate (**3**) (eq 2). Intermediate **3** serves as a hydride ion donor to reduce another formaldehyde molecule to form CH_3OH (**4**) and $HCOO^-$ (**5**) (eq 3).[5] On the other hand, it seems reasonable to assume that the Cannizzaro intermediate (**3**) could also react with water to form $HCOO^-$ and H_2 (eq 4) since **3** is a hydride ion donor.

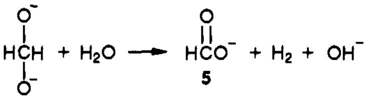


$$\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} + \mathrm{H_2O} \rightleftharpoons \underset{\mathbf{1}}{\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{HCH}}}} \underset{}{\overset{\mathrm{OH}^-}{\rightleftharpoons}} \underset{\mathbf{2}}{\overset{\mathrm{OH}}{\underset{\mathrm{O}^-}{\mathrm{HCH}}}} \overset{\mathrm{OH}^-}{\rightleftharpoons} \underset{\mathbf{3}}{\overset{\mathrm{O}^-}{\underset{\mathrm{O}^-}{\mathrm{HCH}}}} \qquad (2)$$



3 **4** **5**

$$\underset{\mathbf{3}}{\overset{\mathrm{O}^-}{\underset{\mathrm{O}^-}{\mathrm{HCH}}}} + \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} \longrightarrow \underset{\mathbf{4}}{\mathrm{CH_3OH}} + \underset{\mathbf{5}}{\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}^-} \qquad (3)$$



3 **5**

$$\underset{\mathbf{3}}{\overset{\mathrm{O}^-}{\underset{\mathrm{O}^-}{\mathrm{HCH}}}} + \mathrm{H_2O} \longrightarrow \underset{\mathbf{5}}{\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}^-} + \mathrm{H_2} + \mathrm{OH}^- \qquad (4)$$

One of the simplest ways of establishing the integrity of eq 4 is to allow formaldehyde (CH_2O) to react with NaOD in D_2O and determine if HD is formed. Indeed, HD was formed; however, due to exchange of HD in D_2O/OD^- to produce D_2, this method did not provide reproducible data.[6] In view of the above, a number of other studies were carried out in order to establish the sequence of reactions, eqs 2–4.

When dilute solutions[7] of CH_2O (4×10^{-4} M) were allowed to react with concentrated NaOH (19 M) at room temperature, it was surprising to find that H_2 was produced in quantitative yield (Table I). The literature reports[4] only trace amounts of H_2 for this reaction; however, it should be emphasized that the conditions reported in the literature involved higher concentrations of formaldehyde and lower concentrations of base. The data in Table I show that at room temperature and at low concentrations of formaldehyde, one molecule of formate was produced per molecule of hydrogen evolved and no methanol was observed. When the concentration of formaldehyde was increased, some methanol was produced (eq 3). When the amount of methanol produced (27.0%) was subtracted from the total yield of formate (71.3%), the yield of formate produced by the hydrogen-producing reaction was obtained and was approximately equal to the hydrogen yield (41.1%). These results suggest that one hydrogen atom originates from formaldehyde and the other from water in the formation of H_2. If both hydrogen atoms came from formaldehyde, then the ratio of H_2 to $HCOO^-$ would be 0.5.

Table II. Order in Formaldehyde on Reaction with NaOH at Different Temperatures[a]

[NaOH], M	[CH_2O], M	T, °C	order[b]	k, M^{-1} hrs^{-1}
18	0.02–1	28 ± 1	1.1	7×10^{-5}
7	0.02–0.1	90 ± 1	0.9	3×10^{-2}

[a] All reactions were carried out to 5–10% conversion. [b] These values were calculated from the initial rates of H_2 evolution at different [CH_2O], taking the slope of the line from the plot of ln(initial rate) vs ln([CH_2O]). H_2 was measured by GC, using a 5-Å molecular sieve (60/80 mesh) column at room temperature.

Table III. Order in Hydroxide and Effect of Base Concentration on the Hydrogen Yield

[CH_2O], M	[NaOH], M	% H_2[a]	order[b]
1.5×10^{-3}	4	31.1	1.0
1.5×10^{-3}	8	57.5	
1.5×10^{-3}	16	97.9	

[a] All reactions were carried out at 60 °C until hydrogen was no longer produced. [b] This value was calculated from the initial rates of H_2 evolution at different [NaOH], taking the slope of the line from the plot of ln(initial rate) vs ln(activity OH^-). H_2 was measured as stated in Table II.

Table IV. Yield of Hydrogen at Different Concentrations of CH_2O[a]

[CH_2O], M	2×10^{-1}	2×10^{-2}	2×10^{-3}	4×10^{-4}	4×10^{-5}
% H_2[b]	1.4	8.2	34.5	61.1	103.8
% H_2[c]	6.5	30.8	75.7	102.4	99.0

[a] All reactions were carried out until hydrogen was no longer produced. [b] T = 60 °C, [NaOH] = 11 M. [c] T = room temperature, [NaOH] = 19 M.

The kinetic order with respect to formaldehyde was determined from initial rate studies (Table II) and was found to be approximately 1, indicating that only one molecule of formaldehyde is participating in the rate-determining step of the reaction. The kinetic order with respect to OH^- was determined from initial rate studies (Table III). The order obtained from the slope of a plot of ln(initial rate) vs ln(activity OH^-)[8] was found to be 1.0. It is known that the equilibrium between CH_2O and $CH_2(OH)_2$ is strongly in favor of the *gem*-diol (**1**),[9] which is mainly in the form of the $CH_2(OH)O^-$ ion at these base concentrations.[10,11] It may be concluded from the first-order dependence on OH^- that $CH_2(O^-)_2$ is the intermediate that acts as the hydride donor. Additionally, the rate of hydrogen generation for CH_2O at room temperature was found to be 5 times faster than that for CD_2O, indicating that the rate-determining step involves cleavage of the C–H bond.

The effect of the concentration of formaldehyde on hydrogen yield was studied at room temperature and at 60 °C (Table IV). The hydrogen yield increased as the formaldehyde concentration decreased, which is consistent with the hydrogen-producing reaction (eq 4) being unimolecular with respect to formaldehyde

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[4] Loew, O. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 144.

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[6] We are indebted to Dr. Dan Meisel of Argonne National Laboratories for bringing to our attention references concerning studies of hydrogen–water exchange. Wilmarth, W. K.; Dayton, J. C.; Flournoy, J. M. *J. Am. Chem. Soc.* **1953**, *75*, 4549. Flournoy, J. M.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 2257.

[7] Formaldehyde was prepared by decomposing solid paraformaldehyde at 180 °C. The gas was collected by bubbling it through water, and the concentration of the solution was determined by ^{1}H-NMR using an external standard. H_2 was quantified by GC (see Table II). CH_3OH and $HCOO^-$ were quantified by ^{1}H-NMR using an external standard. $HCOO^-$ was also quantified by IC.

[8] Activities were calculated from data in the following: Åkerlöf, G.; Kegeles, G. *J. Am. Chem. Soc.* **1940**, *62*, 620.

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[10] von Euler, H.; Lövgren, T. *Z. Anorg. Allg. Chem.* **1925**, *147*, 123.

[11] Bell, R. P.; Onwood, D. P. *Trans. Faraday Soc.* **1962**, *58*, 1557.

and thus competing more favorably at low $[CH_2O]$ with the Cannizzaro (bimolecular) reaction. It was also determined that as the concentration of base increases, the hydrogen yield increases (Table III). These results are attributed to the fact that when $[OH^-]$ increases, the concentration of free aldehyde (which is necessary for the Cannizzaro reaction) decreases (eqs 2, 3), thus allowing the hydrogen-producing reaction (eq 4) to compete even at high formaldehyde concentration.

It is interesting to note that other aldehydes that do not possess α hydrogen atoms (e.g., benzaldehyde, glyoxylic acid, pivalaldehyde) produced hydrogen in 17, 29, and 30% yield, respectively, under the same conditions (Table I, second entry) reported for formaldehyde (41% H_2).

Proposed Mechanism. The proposed mechanism for the formation of H_2 involves the formation of the Cannizzaro intermediate **3** (eq 2), which reacts as a hydride ion donor with a water molecule, to produce hydrogen and sodium formate (eq 4).[12] When the concentration of base is high and the concentration of formaldehyde is low, the probability of a bimolecular reaction of the Cannizzaro intermediate with a formaldehyde molecule (eq 3) is small. Instead, intermediate **3** reacts with water to produce H_2 (eq 4). These latter conditions are those believed to be present in nuclear waste storage tanks where small, steady-state concentrations of formaldehyde can form by radiolysis or thermal decomposition of organic complexants and other decomposition products.

Conclusions. Formaldehyde and other aldehydes that do not possess α hydrogen atoms are very likely intermediates for the generation of H_2 during the storage of alkaline nuclear waste. The data reported herein suggests that formaldehyde and water each provide one hydrogen atom in the formation of H_2.

Acknowledgment. We wish to thank Westinghouse-Hanford and the Department of Energy for support of this work.

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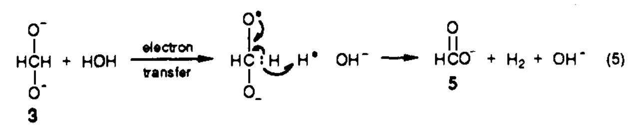
[12] The transfer of hydrogen from the Cannizzaro intermediate (**3**) to H_2O can take place as a hydride ion (H^-) or a hydrogen atom ($H^\bullet$) (eq 5).



[2.2]Orthoparacyclophane: The Last and Most Strained [2.2] Cyclophane

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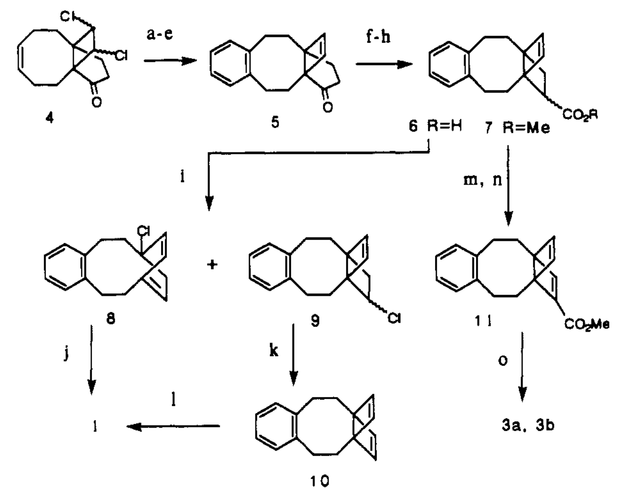
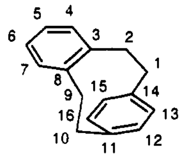
[2.2] cyclophanes can be regarded as prototype members of the cyclophane class and can serve as a good basis for developments in this field.[1] Of the six conceivable [2.2] cyclophane isomers, four relatively unstrained members are known.[2] The highly strained [2.2]orthometacyclophane was recently synthesized by Hopf and co-workers.[3] The last member of this family of compounds, [2.2]orthoparacyclophane (**1**), has been estimated from MM2 calculations to be the most strained[1b,4] and until now has eluded synthesis.[5]

Scheme I[a]



[a] Conditions: (a) LAH, Et_2O, 98%; (b) tetrachlorothiophene dioxide, toluene, 120 °C, 2 h, 91%; (c) Na, NH_3, Et_2O; (d) Na, *t*-BuOH, THF, 52% for two steps; (e) CrO_3, pyridine, 64%; (f) HCO_2Et, NaOEt, benzene; (g) TsN_3, Et_3N, CH_2Cl_2; (h) $h\nu$, H_2O/THF for **6** (34% from **5**) or $h\nu$, MeOH for **7** (40% from **5**); (i) $Pb(OAc)_4$, LiCl, DMSO, room temperature; (j) *t*-BuOK (3 equiv), DMSO, room temperature, 44%; (k) *t*-BuOK (50 equiv), DMSO, room temperature, 100%; (l) heat (50 °C), $CDCl_3$; (m) LDA, Ph_2Se_2, HMPA, THF, −78 °C, 73%; (n) H_2O_2, pyridine, CH_2Cl_2, 88%; (o) heat (40 °C), 1,2-dichloroethane, 47%.

We envision **1** as a benzo-fused homologue of (*Z*)-[6]paracycloph-3-ene (**2**), which was previously prepared in this laboratory.[6] However, in view of the foregoing work on **1**[5] and [3.2]orthopara-,[7] [3.3]orthopara-,[8] and [2.2]orthometacyclophane,[3] the incorporation of two ethylene bridges in the orthopara system should greatly enhance the propensity of the ethylene bond toward homolytic cleavage, generating a pair of benzyl radicals. With those precautions in mind, extension of the synthetic methodology that we used for **2** (thermal or cationic cleavage of the central bond in [6.2.2]propellanes) has led to the synthesis of **1** and its methoxycarbonyl derivatives **3a** and **3b**.



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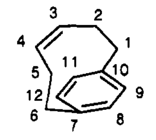
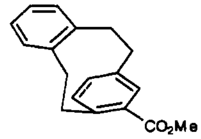
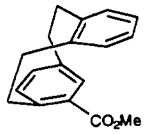


2



3a



3b

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† Faculty of Engineering Science.

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(2) See refs 2-7 in ref 5.

(3) Bodwell, G.; Ernst, L.; Haenel, M. W.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 455.

(4) MM3 calculations reveal that **1** is the most strained isomer. The ranking of the strain energies of the parapara and orthometa isomers is reversed in the MM3 calculations from the order obtained by the MM2 calculations (Hopf, H.; Marquard, C. Unpublished results). We are grateful to Professor Hopf for informing us of the results of the MM3 calculations.

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