

separating polarity and direct coordination properties of ethereal solvents.

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Binuclear Ruthenium(II) Porphyrins: Reinvestigation of Their Preparation, Characterization, and Interactions with Molecular Oxygen

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Ruthenium porphyrins have recently shown some promise in understanding the reactions of iron hemes with molecular oxygen.¹ Although reports of ruthenium porphyrins first appeared 10 years ago,² surprisingly little is known about their properties and reactivity.³ In view of the rich chemistry exhibited by closely related iron porphyrins,⁴ we have begun a general investigation of the properties of ruthenium-porphyrin complexes.

In 1975 Whitten and co-workers⁵ reported an interesting binuclear ruthenium(II)-porphyrin complex and suggested that a metal-metal bond exists between the two ruthenium centers constraining the two porphyrin macrocycles in a cofacial orientation. In our own studies⁶ we have found that the complexes originally characterized by Whitten were μ -oxido-bridged dimers formed from the oxidation of the metal-metal bonded dimers by molecular oxygen. Here we report the results of our investigations into this area.

Dipyridine complexes of several ruthenium porphyrins, Ru(P)py₂ (P = OEP, **1**; TPP, **2**; TTP, **3**),⁷ were synthesized by literature methods.⁸ Vacuum pyrolysis (10⁻⁵ torr, 190–210 °C, 5 h) of polycrystalline samples of **1** caused the red solid to turn dark green. The ¹H NMR spectrum (Figure 1A)⁹ of the product,

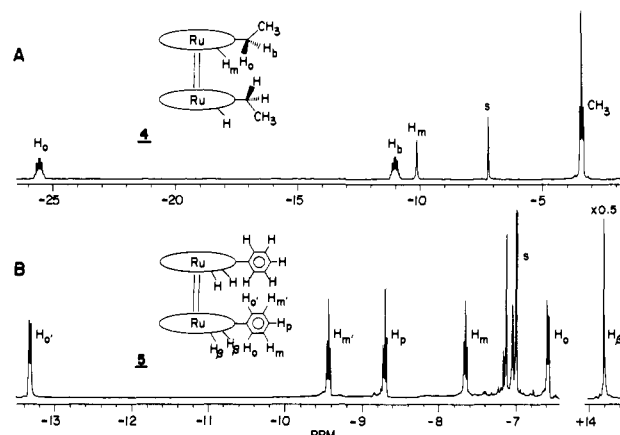


Figure 1. (A) ¹H NMR (100 MHz) of **4** in oxygen-free benzene-*d*₆ (s = residual solvent protons) at 30 °C. Ethyl group (AMX₃ system) coupling constants: ²J_{H_a-H_b} = 14.7 Hz, ³J_{H_a-CH₃} = ³J_{H_b-CH₃} = 7.0 Hz. (B) ¹H NMR (360 MHz) of **5** in oxygen-free toluene-*d*₆ (s = residual solvent protons) at 25 °C. Absorptions for the phenyl protons were assigned on the basis of observed splitting patterns, decoupling, and comparison with the spectrum of the analogous TTP complex, **6**. The relative assignments between pairs of protons o, o' and m, m' are tentative.¹⁷

dissolved in benzene-*d*₆ with the careful exclusion of oxygen or other potential ligands,¹⁰ is indicative of a single *paramagnetic* OEP complex, **4**.

Assignment of the resonances is greatly facilitated by the observation of all proton spin-spin splittings.¹¹ Decoupling irradiation of the methyl triplet causes the two downfield multiplets (-11.1 and -25.6 ppm) to collapse into a pair of doublets exhibiting a 14.7-Hz geminal coupling constant. The two multiplets can thus be assigned to the diastereotopic methylene protons.¹² The porphyrin meso proton appears as a sharp singlet, exhibiting only a small (<1 ppm) paramagnetically induced shift.

Compound **2** was pyrolyzed by using a similar procedure¹³ to give an air-sensitive complex, **5**, whose proton NMR spectrum is shown in Figure 1B. The phenyl proton resonances are completely resolved due to paramagnetic shifts both up- and downfield from the estimated diamagnetic positions. The β -pyrrolic protons experience a large upfield shift to +14.2 ppm.¹⁴

Elemental analyses of **4** and **5** are consistent with the molecular formulas (RuOEP)_n and (RuTPP)_n, respectively.¹⁵ Addition of 2 equiv of pyridine per ruthenium atom to benzene solutions of

(9) The paramagnetic convention is used in the discussions of all NMR spectra. Signals downfield from Me₄Si are referred to as negative and those upfield are positive.

(10) All manipulations of these air-sensitive compounds were performed in an inert atmosphere box or directly on a vacuum line. NMR solvents were vacuum distilled from benzophenone ketyl.

(11) Electron relaxation times in these binuclear complexes are estimated to be 10⁻¹³ s. La Mar, G. N.; Walker (Jenson), F. A. In "The Porphyrins"; Dolphin, D. H., Ed.; Academic Press: New York, 1978; Vol. 4, p 61. Swift, T. J. In "NMR of Paramagnetic Molecules: Principles and Applications"; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. J., Eds; Academic Press: New York, 1973; p 53.

(12) (a) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63. (b) Busby, C.; Dolphin, D. H. *J. Magn. Reson.* **1976**, *23*, 211. (c) The tremendous chemical-shift difference between the diastereotopic protons originates from differential π -spin density transfer from the porphyrin system to each of the protons. Similar effects have been observed for ferric porphyrin systems. See: Walker, F. A.; La Mar, G. N. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 328. La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1782.

(13) The pyrolysis of **2** requires completely *noncrystalline* solid samples. A convenient method of preparing such amorphous samples is to freeze benzene solutions of the ruthenium porphyrin and sublime the solvent away under vacuum at room temperature.

(14) Comparison of the shifts for **4** and **5** indicates large π -spin density in the pyrrole rings and little to none at the meso positions. Such a pattern of contact shifts is consistent with a spin transfer via $3e(\pi)P \rightarrow Ru(d_{xy}d_{yz})$ charge transfer. A detailed analysis of the NMR spectra and magnetic properties of these complexes is in progress.

(15) (RuOEP)_n = C₃₆H₄₄N₄Ru. Anal. Calcd: C, 68.10; H, 6.99; N, 8.84. Found: C, 67.90; H, 7.00; N, 8.75. (RuTPP)_n = C₄₅H₅₂N₄Ru. Anal. Calcd: C, 74.10; H, 3.89; N, 7.72. Found: C, 74.59; H, 3.90; N, 7.63.

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(2) Fleischer, E. B.; Thorp, R.; Venerable, D. *J. Chem. Soc., Chem. Commun.* **1969**, 475. But see also: Chow, B. C.; Cohen, I. A. *Bioinorg. Chem.* **1979**, *1*, 57.

(3) (a) Eaton, S. S.; Eaton, G. R.; Holm, R. H. *J. Organomet. Chem.* **1972**, *39*, 179. (b) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141. (c) Brown, G. M.; Hopf, F. R.; Meyer, T. J.; Whitten, D. G. *Ibid.* **1975**, *97*, 5385. (d) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *Ibid.* **1981**, *103*, 2199.

(4) (a) James, B. R. In "The Porphyrins"; Dolphin, D. H., Ed.; Academic Press: New York, 1979; Vol. 5, Chapter 6. (b) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265. (c) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

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(6) Collman, J. P.; Collins, T. J.; Barnes, C. E.; Brothers, P. J.; Gallucci, J.; Ibers, J. A., manuscript in preparation.

(7) Abbreviations used: RuP = ruthenium porphyrin in general; RuOEP = ruthenium octaethylporphyrin; RuTPP = ruthenium *meso*-tetraphenylporphyrin; RuTTP = ruthenium *meso*-tetra-*p*-tolylporphyrin; py = pyridine; H_m = meso proton of OEP ligand. L = coordinated axial ligand.

(8) Antipas, A.; Buckler, J.; Gouterman, M.; Smith, P. *J. Am. Chem. Soc.* **1978**, *100*, 3015.

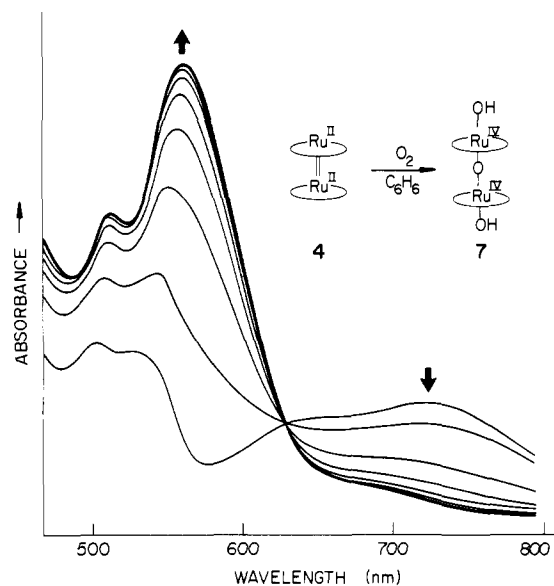


Figure 2. UV/VIS spectral monitoring of **4** reacting with oxygen in benzene at 24.3 °C. Porphyrin concentration was ~0.1 mM. Time between scans: 101 s. The initial spectrum (of **4**) has absorption maxima at 376 (Soret, not shown), 503, 528, 650 (shoulder), 724 nm. The final spectrum (of **7**) has maxima at 375 (Soret), 512, and 561 nm.

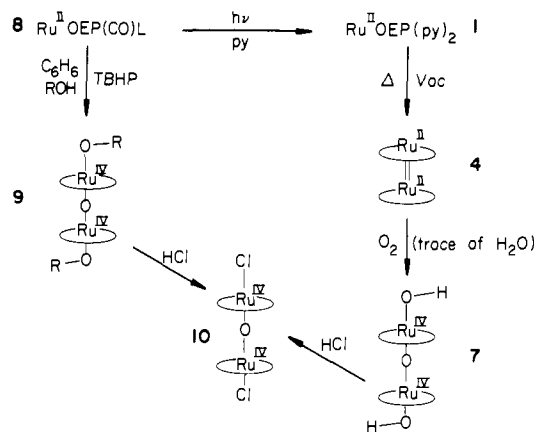
4 and **5** quantitatively affords the diamagnetic starting complexes **1** and **2**.¹⁶ The oxidation state of the metal thus remains unchanged in the pyrolysis.

In order to characterize the magnetic properties of **4** and **5**, the temperature dependence of the isotropic proton shifts was measured. With the exception of the β -pyrrolic protons of **5**, all shifts exhibit excellent linear dependencies with inverse temperature. Such behavior is consistent with the Curie law, indicating a single spin state is populated throughout the observed temperature range (from -90 to +90 °C).¹⁷ Determination of the solution magnetic moment¹⁸ for **4** yielded $\mu_{\text{eff}} = 2.8 \mu_{\text{B}}$, corresponding to two unpaired spins, $S = 1$.

Two structural possibilities are consistent with the NMR and analysis data: (a) a monomer (RuP), with the metal significantly out of the porphyrin plane, as in the case of Pb(II) porphyrins¹⁹ and (b) a dimer (RuP)₂, held together by some type of metal-metal bonding and/or porphyrin π - π interactions.²⁰ In order to establish the dimeric nature of **4** and **5**, mixed porphyrin dimers were prepared by pyrolyzing homogeneous mixtures¹³ of **1** and **3**. Selecting porphyrins with opposite substitution patterns leads to the simple expectation that if a mixed porphyrin dimer, e.g., (OEPRuRuTTP), **11**, is formed, a doubling of all proton resonances for **4** and (RuTTP)₂, **6**, should be observed. This is indeed found to be the case. The proton NMR spectrum of the pyrolysis mixture exhibits two β -pyrrolic singlets, +12.7 and +14.1 ppm (upfield from Me₄Si), two meso proton singlets, -10.2 and -9.9 ppm, two *p*-tolyl methyl singlets, -3.45 and -3.50 ppm, and a doubling of all other ethyl and phenyl proton signals.

Thus, the NMR, analytical, and chemical data above are only consistent with a dimeric structural model for **4** and **5**. A plausible ground-state electronic configuration for the ruthenium d electrons is $\sigma^2\pi^4\eta^4\pi^*2$.²¹ The triplet spin system observed for these com-

Scheme I



plexes apparently arises from two singly occupied, degenerate π^* orbitals. The net bond order between the metals, accordingly, is 2.

Exposure of a benzene solution of **4** to O₂ results in a rapid, irreversible reaction with clean isosbestic behavior (Figure 2). The product, **7**, is a diamagnetic dimer, and its NMR and UV/VIS spectra are virtually identical with those originally reported by Whitten et al.,⁵ with the exception of an additional sharp singlet in the NMR spectrum at +9.4 ppm (upfield from Me₄Si).²² This signal integrates as two protons, is broadened by H₂O, and is lost by exchange with D₂O. From these observations we conclude that **7** is, in fact, a neutral, oxo-bridged porphyrin dimer possessing two axial hydroxo ligands. The structural characterization of **7** arose from our investigations of the reaction between *tert*-butyl hydroperoxide (TBHP) and carbonylruthenium(II) porphyrins, Ru^{II}P(CO)L.²³ In the case of **8** (Scheme I), reaction with TBHP in C₆H₆/ROH solvent mixtures at room temperature quantitatively produces the dialkoxo- μ -oxido dimer **9**.⁶ The UV/VIS and NMR spectra of **9** are similar to those of **7**. Treatment of a solution of either **9** or **7** in MeOH with aqueous HCl affords the same product **10**, identified from its spectral and analytical properties as [Ru^{IV}(OEP)Cl]₂O.²⁴ The structures of **10**^{25a} and an analogous example from the tetraphenylporphyrin system [Ru^{IV}TTP(OC₆H₄-*p*-CH₃)₂O]₂^{25b} (the structure of **12** were determined by single-crystal X-ray structure studies. The dichloride complex **10** exhibits a crystallographically imposed linear oxo bridge, while the Ru-O-Ru angle for the di-*p*-cresol anion complex **12** is 177°. Both complexes exhibit a Ru-O bridge distance of 1.79 Å and, in the case of **10**, a RuCl distance of 2.32 Å.²⁶ These results are in complete agreement with the structure of [RuOEP(OH)]₂O recently reported by Masuda et al.^{3d}

Scheme I summarizes the new chemistry of ruthenium porphyrins presented here. We have shown the following: (1) The pyrolysis of bis(pyridine)ruthenium(II) porphyrins yields the first well-characterized binuclear ruthenium porphyrins possessing a direct metal-metal double bond. (2) These highly unsaturated, binuclear complexes react with added ligands to produce the six-coordinate, ruthenium(II) di-L-porphyrin complexes and also with molecular oxygen to form stable ruthenium(IV) μ -oxo dimers. These high-valent dimers are identified as those originally studied

(16) All titrations were performed anaerobically. Both UV/VIS and NMR spectra were used to monitor the transformation of **4** into **1**.

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(20) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869. Wayland, B.; Newman, A. *J. Am. Chem. Soc.* **1979**, *101*, 6472.

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(22) We believe that trace amounts of water contained by the solvent are the source of this proton.

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(24) (RuOEPCl)₂O = Ru₇₂H₈₈N₈OCl₂. Anal. Calcd: C, 63.84; H, 6.55; N, 8.27. Found: C, 64.10; H, 6.42; N, 8.12. UV/VIS (CHCl₃) 383 (Soret) 494, 554, 604, 684 nm; NMR (C₆D₆) δ 9.42 (s, 1 H), 4.31 (m, 2 H), 4.00 (m, 2 H), 1.92 (t, 6 H).

(25) (a) Space group *P4/nnc*. Unit cell dimensions: *a* = 13.91, *c* = 17.70 Å; 2 molecules per unit cell. (b) Space group *P1*. Unit cell dimensions: *a* = 16.91, *b* = 19.80, *c* = 12.98 Å; α = 99.96, β = 104.31, γ = 77.53°; 2 molecules per unit cell. Full details of the structures of **10** and **12** will be reported shortly.⁵

(26) Matheson, A. M.; Mellor, D. P.; Stephenson, N. C. *Acta Crystallogr.* **1952**, *5*, 185.

by Whitten.⁵ (3) We have independently synthesized these high-valent dimers by the oxidation of ruthenium(II) carbonyl porphyrins with *tert*-butyl hydroperoxide. We are currently investigating the structural and chemical properties of the metal-metal bond in 4. The conversion of ruthenium(II) porphyrins to stable ruthenium(IV)-porphyrin complexes via O₂ is without precedent in iron porphyrin chemistry.⁴ This encourages us in our own attempts to prepare ruthenium analogues of the high-valent iron porphyrin intermediates involved in the catalytic cycle of cytochrome P-450.

Acknowledgment. We are grateful to Dr. B. D. Santariero for the X-ray photographic analyses and space group determination of 10. Financial support for this work was provided by the National Institutes of Health, Grants GM17880 (to J.P.C.) and HL13157 (to J.A.I.) and the National Science Foundation, Grant CHE78-09443 (to J.P.C.). NMR experiments were performed on instruments supported by the NIH Grant RR00701 and NSF Grants 23633 (Stanford Magnetic Resonance Laboratory, 360 MHz), GP28142, and CHE77-08810 (Stanford University).

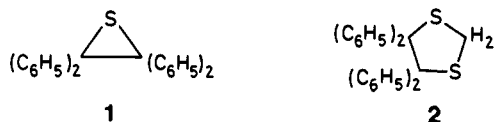
Diazomethane and Thiobenzophenone: Mechanistic Elucidation of the Schönberg Reaction

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Two reaction modes of diazoalkanes with aromatic thioketones have been described: the formation of thiiranes, e.g., 1 + N₂ from diphenyldiazomethane and thiobenzophenone,¹ and 1,3-dithiolanes, e.g., 2 + N₂ from diazomethane and 2 mol of thiobenzophenone.^{2,3} Schönberg et al.⁴ have studied reactions of 18 diazoalkanes with 32 thiocarbonyl compounds over the range of 40 years,⁵ in no case have 1:1 and 1:2 products of type 1 and 2 been isolated side by side.



We added an excess of ethereal diazomethane to thiobenzophenone⁶ in ether at 20 °C, and after a vigorous reaction with N₂ evolution had taken place, we isolated 4,4,5,5-tetraphenyl-1,3-dithiolane (2)⁷ in 95% yield. Obviously, the second molecule of thiobenzophenone is consumed faster by an intermediate than the first one by diazomethane. On introducing diazomethane in THF into the blue solution of thiobenzophenone at -78 °C, a surprisingly rapid decolorization made a titration feasible; now the stoichiometry was 1:1, and no N₂ was eliminated. Evaporation

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(2) Bergmann, E.; Magat, M.; Wagenberg, D. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 2576-2584.

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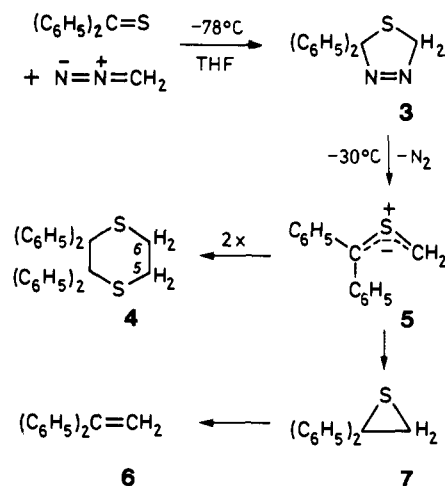
(4) Schönberg, A.; König, B.; Singer, E. *Chem. Ber.* **1967**, *100*, 767-777. The authors review ~100 products from diazoalkanes and thiocarbonyl compounds in tables and state "Leider waren alle Versuche, dem Chemismus der Reaktionen durch Isolierung von Zwischenprodukten oder auf andere Weise näher zu kommen, bisher erfolglos".

(5) Last paper: Schönberg, A.; Knöfel, W.; Frese, E.; Praefcke, K. *Chem. Ber.* **1970**, *103*, 938-948.

(6) N₂ atmosphere for all experiments to protect thiobenzophenone from autoxidation.

(7) Mp 207-209 °C dec (blue melt); 166-167 °C,² 199-200 °C;³ ¹H NMR (CDCl₃) δ 3.73 (s, CH₂).

of the solvent at -78 °C left 2,2-diphenyl-1,3,4-thiadiazoline (3) in colorless crystals which went "pfft" around -20 °C.



Nitrogen was liberated from the THF solution of 3 at -30 °C, and 2,2,3,3-tetraphenyl-1,4-dithiane (4)^{8,9} was formed in 95% yield; the mother liquor contained 1% 1,1-diphenylethylene (6). The ¹H NMR signals of the ring protons of 4 (AA'BB') at 35 °C, A₄ at 102 °C) reveal hindered inversion; in the ¹³C NMR spectrum C5 and C6 are equivalent whereas the phenyls are pairwise different. A two-step head-head dimerization of the *thiocarbonyl ylide* 5 with the first bond being formed between the CH₂ groups is conceivable.

Rate measurements for 3 → 5 at -45 °C indicate first order with half-lives of 34 min in CDCl₃, 55 min in THF, 58 min in ethyl acetate, and 65 min in methanol. The data do not exclude a fast subsequent reaction 5 + 3 → 4 + N₂ which is regarded less likely.¹⁰

When the THF solution of 3, kept at -78 °C, was added portionwise to stirred ether at 20 °C, the yield of dimer 4 dropped to 41%, and 38% (6 + 7) was observed; t_{1/2} ~ 16 h at 20 °C was estimated for the sulfur extrusion, 7 → 6, on the basis of ¹H NMR spectra.¹¹ Due to the lower concentration of 5 and the higher temperature coefficient of the cyclization 5 → 7 (compared with dimerization), this electrocyclic ring closure of 5 to the thiirane 7 becomes competitive. Kellogg et al.¹² established the conrotatory course of thiocarbonyl ylide cyclization.

Loss of N₂ from 3 in the presence of dipolarophiles allowed an interception of the thiocarbonyl ylide 5. After generating 3 in THF at -78 °C, 1 equiv dipolarophile was added and the solution warmed to -30 °C. When the N₂ evolution had ceased, the cycloadducts 2 and 8-14 were isolated in the yields stated.^{9,13} Thiobenzophenone as dipolarophile provided the dithiolane 2 in 96% yield, thus clarifying the mechanism of the Schönberg re-

(8) 4: mp 166-169 °C dec; the colorless crystals turn violet on exposure to sun light. ¹H NMR (C₆H₅Br) δ 2.66-3.43 (AA'BB', 4 H, 4-H₂ and 5-H₂) at 35 °C, 2.90 (s, A₄) at 102 °C, coalescence at 74 °C. ¹³C NMR (CDCl₃) δ 64.5 (C1 and C2), 31.4 (C4 and C5), 144.7 and 146.3 (quaternary, aromatic C).

(9) Satisfactory CH and S analyses were obtained for all new compounds except 3.

(10) The disappearance of the ¹H NMR singlet for CH₂ of 3 at δ 3.73 was measured against δ 6.47 of trichloroethylene as internal standard, 48 values over 3 half-lives. In addition, volumetric analysis of the N₂ evolution from the magnetically stirred solution was carried out.

(11) 7 was not obtained pure. Its decrease in the mixture with 6 was diagnosed from the CH₂ singlet integrals at δ 2.98 for 7 and 5.38 for 6.

(12) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045-4060.

(13) Selected ¹H NMR signals (CDCl₃, δ): 8, mp 165-167 °C, 4.08 (s, CH₂); 9, mp 140-142 °C, 3.47, 3.71 (2s, 2OCH₃), 4.01 (s, CH₂); 10, mp 126-128 °C, 2.64 (dd, J_{5A,5B} = 12.5 Hz, J_{4,5B} = 7.5 Hz, 5-H_B), 3.23 (d, J_{5A,5B} = 12.5 Hz, 5-H_A), 3.78 (t, J_{3,4} = J_{4,5B} = 7.5 Hz, 4-H), 4.33 (d, J_{3,4} = 7.5 Hz, 3-H); 11, mp 174-176 °C, 2.70 (dd, J_{5A,5B} = 12.8 Hz, J_{4,5B} = 7.6 Hz, 5-H_B), 3.29 (dd, J_{5A,5B} = 12.8 Hz, J_{4,5A} = 1.0 Hz, 5-H_A), 3.62 (dt, J_{3,4} = J_{4,5B} = 7.6 Hz, J_{4,5A} = 1.0 Hz, 4-H), 4.12 (d, J_{3,4} = 7.6 Hz, 3-H), 2.84 (s, NCH₃); 12, m 208-209 °C, 13, mp 177-178.5 °C, 4.43 (s, CH₂); 14, mp 98-100 °C, 3.28, 3.46 (2s, 2OCH₃), 4.63 and 5.13 (AB, J = 9.8 Hz, CH₂).