Table I. Hydroperoxidation of Linoleic Acid by Singlet Oxygen Generated by Photosensitization[a]

run	sensitizer	concn, μM		product distribution		ee,[b] %		yield,[c] %
		[1] or [2]	[3]	$\Delta^{12,13}$(4a/4b)	$\Delta^{9,10}$(4c/4d)	4a	4b	
1	2	10	1780	49 (40/9)	51 (11/40)			3
2	2	98	89	50 (40/10)	50 (10/40)			12
3	2 (in MeOH)	10	1780	51 (30/21)	49 (20/29)			17
4	2 (+ β-CD)[d]	98	89	50 (31/19)	50 (19/31)	∠2[e]	∠2[e]	6
5	1	10	1780	51 (32/19)	49 (17/32)	∠2[e]	∠2[e]	28
6	1	98	89	82 (51/31)	18 (11/7)	20	12	14

[a] The aqueous reaction mixture (1 mL) containing linoleic acid (3) and a sensitizer (1 or 2) was sonicated for 15 min and, bubbling with O_2 (100 mL/min), irradiated with a 500-W Xe lamp through a 380 nm cutoff filter at 0 °C for 1 h. The products were reduced by triphenylphosphine, methylated by a slight excess of diazomethane, and analyzed by a silica gel HPLC column (Wakosil 5Sil, 0.46 × 75 cm, hexane/*i*-PrOH = 99/1). The products corresponding to **4a** and **4d** were detected at 234 nm and those corresponding to **4b** and **4c** at 202 nm. [b] Enantiomeric excess (see footnote 6). [c] Total yields based on used 3. [d] The solution was saturated with β-cyclodextrin (6×10^{-3} M). [e] The values of ee are below the experimental error limit of HPLC integration.

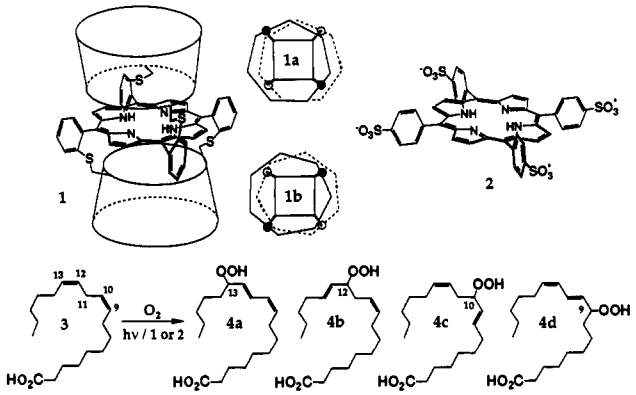

Figure 1. Porphyrin sensitizers and hydroperoxidation of linoleic acid by singlet oxygen.

singlet oxygen in the hydrophobic pocket of **1** during the reaction is essential for the present selective hydroperoxidation. This conclusion is further supported by the more interesting result that the main products obtained from the reaction using **1** (run 6) are significantly chiral, i.e., **4a** and **4b** have 20% (L-predominant) and 12% enantiomeric excess, respectively.[6] Since the reaction using **3** (45 μM) and an excess amount of **1** (196 μM) leads to the same chiral induction within the limit of error, the observed enantiomeric excess seems to reflect the chiral environment around the $\Delta^{12,13}$ double bond in the 1/1 complex of **3** and **1**. Thus, the hydrophobic cavity of **1** regulates not only the attacking position but also the attacking face of the alkene for singlet oxygen under the present conditions. To our knowledge, this is the first example of a chiral induction observed for the reaction of singlet oxygen.

In contrast with these observations, even when **1** is employed as a sensitizer, both regio- and stereospecificities are lost in the presence of a large excess of **3** (run 5) and the product distribution becomes practically the same as those of runs 3 and 4 where **2** is used as a sensitizer. This result may be due to the large contribution of the reaction of **3** with singlet oxygen outside of the cyclodextrin cavity of **1**. Since the lifetime of singlet oxygen in water is known to be ca. 2 μs, which corresponds to a ca. 100-nm diffusion distance,[7] such "outside" reaction is expected to be significant under the conditions of run 5. Finally, it should be noted that the "radical contribution" in the present photooxygenation which is evaluated from the product ratio of conjugated and nonconjugated diolefin products (**4a**/**4b** or **4c**/**4d**) seems to be more significantly suppressed in the system containing β-cyclodextrin or **1** than that in pure water (runs 1 and 2).[2d,8]

(6) The stereospecificity of **4a** was determined by comparison with standard samples are prepared enzymatically [soybean lipoxygenase (Sigma), **4a**/**4d** = 87/13, ee(L-**4a**) = 97%, cf. ref 3b] using a chiral HPLC column (Daicel Chiralcel OD, hexane/*i*-PrOH = 99/1), though the absolute configuration of **4b** obtained predominantly in this work was not known.

(7) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1029.

(8) It had been reported that the radical reaction in the photooxygenation is more significant in water than in methanol; see: Terao, J.; Matsushita, S. *Agric. Biol. Chem.* **1977**, *41*, 2467.

Although it is evident that further investigation is necessary for the elucidation of the origin of the present regio- and stereospecificities, the system shown here provides a highly interesting example which suggests the relationships between molecular recognition and selectivity in the reaction of activated molecular oxygen.

Toward a Dinitrogen Electroreduction Catalyst: Characterization of a Bis-Ammine, a μ_2-Hydrazine, a μ_2-Diazene, and a Remarkably Stable μ_2-Dinitrogen Complex of a Ruthenium Cofacial Diporphyrin

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Received October 9, 1990

Since the discovery of μ_2-$N_2[Ru(NH_3)_5]_2[BF_4]_4$ in 1968,[3] bridging dinitrogen complexes have been pursued as model complexes in the context of both biological and chemical dinitrogen reduction.[4] Because of the successful application of bis-cobalt cofacial diporphyrins to the electrocatalytic reduction of dioxygen,[5] we are exploring analogous cofacial systems as possible dinitrogen reduction catalysts. If the two metals of a cofacial metallodiporphyrin can jointly bind and promote the protonation and reduction of dinitrogen, perhaps an electrode catalyst could be devised. Herein we report the synthesis and spectroscopic properties of (1) a remarkably stable, bridged dinitrogen complex of a cofacial metallodiporphyrin, μ_2-$N_2Ru_2(*L)_2DPB$ (Figure 1), and (2) the putative reduction intermediates of the dinitrogen complex: the μ_2-diazene, μ_2-hydrazine, and bis-ammine complexes (Figure 2).

Addition of 2 equiv of 1-*tert*-butyl-5-phenylimidazole, *L, to a benzene solution of the metal–metal-bonded bis-ruthenium cofacial diporphyrin, Ru_2DPB,[6] under a dinitrogen atmosphere

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(2) Abbreviations: OEP = octaethylporphyrinato dianion, DPB = biphenylenediporphyrinato tetraanion, TMP = *meso*-tetramesitylporphyrinato dianion, THF = tetrahydrofuran.

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(4) (a) Allen, A. D.; Harris, R. O.; Loescher, B. R.; Stevens, J. R.; Whiteley, R. N. *Chem. Rev.* **1973**, *73*, 11–20. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. (c) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197–292. (d) Leigh, G. J. *Transition Met. Chem. (London)* **1986**, *11*, 118–120.

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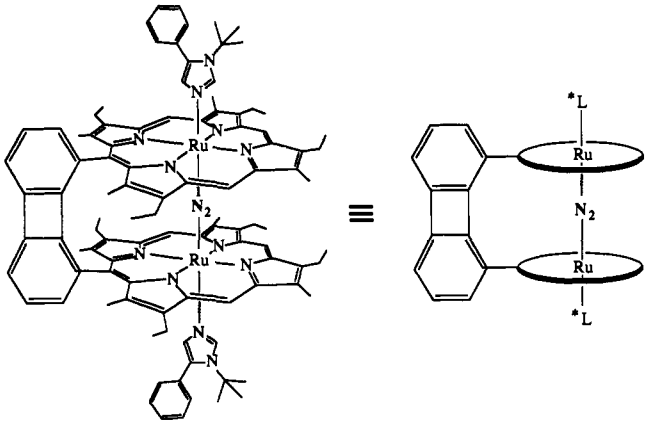
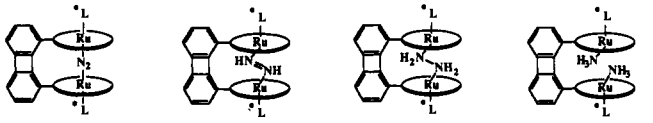


Figure 1. $Ru_2(N_2)$.



$Ru_2(N_2)$ $Ru_2(N_2H_2)$ $Ru_2(N_2H_4)$ $Ru_2(NH_3)_2$

Figure 2.

yields μ_2-$N_2Ru_2(*L)_2DPB$,[7] $Ru_2(N_2)$, quantitatively. The same reaction using ^{15}N-labeled dinitrogen yields $[^{15}N_2]Ru_2(N_2)$. Alternatively $Ru_2(N_2)$ is prepared by exposing a benzene solution of the dihydrogen complex, $Ru_2(*L)_2(H_2)DPB$,[8] to an atmosphere of dinitrogen. Recrystallization from dichloromethane/methanol yields analytically pure $Ru_2(N_2)$.[9]

The proton NMR spectrum of $Ru_2(N_2)$[10] shows that the two porphyrin rings are equivalent and that there are two equivalent axial imidazoles bound to the complex. The ratio of bound dinitrogen to each pair of ruthenium centers of the complex was determined to be 1:1 from the molecular ion in the mass spectrum.[10] The bridging nature of the dinitrogen ligand is confirmed by both the ^{15}N NMR[9] and Raman data.[10] The ^{15}N NMR spectrum of $[^{15}N_2]Ru(N_2)$ displays a singlet (at 108 ppm upfield of [^{15}N]nitrobenzene) indicating that dinitrogen is symmetrically bound between the two metals. Although a band corresponding to ν_{N-N} is not observed in the IR spectrum, the Raman spectrum of $Ru_2(N_2)$ shows a peak at 2112 cm^{-1}. This value for ν_{N-N} is in the normal range for linear ruthenium dinitrogen complexes (2060–2150 cm^{-1})[3,11] and suggests little if any decrease in bond order in the N–N bond.

Compared to terminal dinitrogen complexes of metalloporphyrins, $Ru_2(N_2)$ is unusually stable toward the loss of dinitrogen. Whereas terminal dinitrogen complexes of ruthenium porphyrins liberate dinitrogen readily upon degassing,[11] there is no measureable (as measured by ^1H NMR) loss of dinitrogen from $Ru_2(N_2)$ during five cycles of freeze–pump–thaw. Furthermore, $Ru_2(N_2)$ is air-stable indefinitely in the solid state and for several hours in solution. Although the dinitrogen ligand in $Ru_2(N_2)$ can be replaced by incoming ligands (e.g., pyridine, carbon monoxide) to form complexes containing two ligands in place of dinitrogen, this reaction is slow compared to the analogous replacement involving terminal dinitrogen complexes of ruthenium porphyrins.[11] The rate of replacement in the cofacial porphyrin is dependent on the nature and concentration of the incoming ligand. The stability of this bridged dinitrogen complex may derive from the fact that the two ruthenium centers are held in place by the rigid biphenylene linker[12] allowing the two metal centers to "chelate" dinitrogen. Studies are in progress to elucidate the mechanism of dinitrogen loss from $Ru_2(N_2)$.[13]

Because the bridging dinitrogen can be replaced by added axial ligands, $Ru_2(N_2)$ is a convenient precursor to other complexes where the ligands are bound between the two porphyrin rings. Treatment of a benzene solution of $Ru_2(N_2)$ with excess ammonia or hydrazine quantitatively yields $Ru_2(NH_3)_2$[14] and $Ru_2(N_2H_4)$,[15] respectively. In each case the proton NMR spectrum indicates that the symmetry of the parent complex is preserved in the products. In addition, each of these complexes displays a high-field singlet (−8.75 ppm for $Ru_2(NH_3)_2$[16] and −10.15 ppm for $Ru_2(N_2H_4)$[17]), which is assigned as the bound ammine or hydrazine resonances. These large upfield shifts are expected since the protons of the axial ligands are affected by the ring currents of both porphyrin rings. The upfield shifts of the hydrazine ligand in $Ru_2(N_2H_4)$ is similar to that found in the previously reported, analogous complex μ_2-$(N_2H_4)Ru_2(PPh_3)_2DPB$.

Bridged hydrazine complexes are easily oxidized to form bridged diazene complexes.[18] Treatment of $Ru_2(N_2H_4)$ with 1 equiv of *tert*-butyl hydroperoxide in toluene solution yields the bridged diazene complex, $Ru_2(N_2H_2)$.[19] The proton NMR spectrum[20]

(6) Collman, J. P.; Kim, K.; Leidner, C. R. *Inorg. Chem.* **1987**, *26*, 1152–1157.

(7) Under a dinitrogen atmosphere, 2 equiv of 1-*tert*-butyl-5-phenylimidazole (284 μL of a 61.4 mM benzene stock solution) was added to a solution of 11.4 mg (8.73 μmol) of Ru_2DPB in two mL of dry, deaerated benzene. After 30 min of stirring, the solvent was removed under reduced pressure to yield $Ru_2(N_2)$ quantitatively.

(8) Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S.; Lewis, N. S.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1990**, *112*, 8206–8208.

(9) Analysis calculated for $C_{102}H_{108}N_{14}Ru_2$: C, 70.73; H, 6.28; N, 11.32. Found: C, 70.47; H, 6.20; N, 11.31.

(10) ^1H NMR ($Ru_2(N_2)$, C_6D_6, ppm): porphyrinic resonances, H_{meso} 9.02 (s, 4 H), 8.80 (s, 2 H), biphenylene 7.20–7.10 (4 H, obscured by residual solvent peak), 6.90 (t, 2 H), CH_2CH_3 4.15 (m, 4 H), 3.92 (m, 4 H), 3.42 (m, 8 H), CH_3 3.48 (s, 12 H), 3.02 (s, 12 H), CH_2CH_3 1.67 (t, 12 H), 1.58 (t, 12 H); imidazole resonances, para phenyl 6.26 (t, 2 H), meta phenyl 6.04 (t, 4 H), ortho phenyl 5.04 (d, 4 H), $H_{imidazole}$ 0.48 (s, 2 H), 0.39 (s, 2 H), *tert*-butyl −0.70 (s, 18 H). MS: LSIMS, m/e = 1733 ($[M + H]^+$). Raman (benzene, 413.13-nm excitation): ν_{N-N} of $[^{14}N_2]Ru_2(N_2)$ = 2112 cm^{-1}, ν_{N-N} of $[^{15}N_2]Ru_2(N_2)$ = 2042 cm^{-1}.

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(12) (a) The metal–metal distance in metallo-DPB complexes is 3.73 Å[12b] to 3.81 Å[12c] when both of the metals are in the plane of the porphyrin and lengthens to 4.37 Å[12d] when one of the metals is distorted out of the porphyrin plane. (b) Collman, J. P.; Hutchison, J. E.; Ibers, J. A.; Seok, W. K., manuscript in preparation. (c) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417–424. (d) Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Collman, J. P., manuscript in preparation.

(13) Collman, J. P.; Hutchison, J. E.; Wagenknecht, P. S.; Lopez, M. A.; Guilard, R., work in progress.

(14) The dinitrogen complex, $Ru_2(N_2)$ (1.2 mg in 1 mL of benzene), was stirred under 39 psig of ammonia for 19 h. Removal of the solvent under reduced pressure gave the bis-ammine complex, $Ru_2(NH_3)_2$, in quantitative yield.

(15) The dinitrogen complex, $Ru_2(N_2)$ (2.5 mg in 1.5 mL of toluene), was stirred with 0.5 mL of anhydrous hydrazine under a dinitrogen atmosphere for 24 h. The solvent was removed under reduced pressure to give the bridged hydrazine complex, $Ru_2(N_2H_4)$, in quantitative yield.

(16) ^1H NMR ($Ru_2(NH_3)_2$, C_6D_6, ppm): porphyrinic resonances, H_{meso} 8.79 (s, 2 H), 8.38 (s, 4 H), biphenylene 7.01 (d, 2 H), 6.92 (t, 2 H), 6.79 (t, 2 H), CH_2CH_3 3.36 (m, 16 H); CH_3 3.29 (s, 12 H), 2.71 (s, 12 H), CH_2CH_3 1.55 (t, 12 H), 1.36 (t, 12 H); imidazole resonances, para phenyl 6.36 (t, 2 H), meta phenyl 6.15 (t, 4 H), ortho phenyl 5.31 (d, 4 H), $H_{imidazole}$ 1.65 (s, 2 H), 1.51 (s, 2 H), *tert*-butyl −0.49 (s, 18 H), NH_3 −8.75 (s, 6 H).

(17) ^1H NMR ($Ru_2(N_2H_4)$, C_6D_6, ppm): porphyrinic resonances, H_{meso} 8.53 (s, 6 H), biphenylene 7.03 (d, 2 H), 6.97 (d, 2 H), 6.82 (t, 2 H), CH_2CH_3 3.80 (m, 4 H), 3.63 (m, 4 H), 3.50 (m, 8 H), CH_3 3.23 (s, 12 H), 3.00 (s, 12 H), CH_2CH_3 1.68 (t, 12 H), 1.62 (t, 12 H); imidazole resonances, para phenyl 6.30 (t, 2 H), meta phenyl 6.08 (t, 4 H), ortho phenyl 5.15 (d, 4 H), $H_{imidazole}$ 1.40 (s, 2 H), other $H_{imidazole}$ peak obscured by CH_2CH_3 resonances, *tert*-butyl −0.57 (s, 18 H), N_2H_4 −10.75 (s, 4 H).

(18) Back, R. A. *Rev. Chem. Intermed.* **1984**, *5*, 293–323.

(19) A toluene solution of *tert*-butyl hydroperoxide (2.1 mL of a 345 μM solution) was added dropwise to a solution of the hydrazine complex, $Ru_2(N_2H_4)$ (1.2 mg in 2 mL of toluene). The solvent was removed under vacuum to give the product, $Ru_2(N_2H_2)$, contaminated by a small amount of $Ru_2(N_2)$.

indicates that the complex is diamagnetic and that both porphyrin rings are equivalent; however, the resonance for the bound diazene protons could not be unambiguously assigned. Because the protons of diazene complexes are normally shifted substantially downfield,[21] this shift may counteract the porphyrin ring current effect, causing the peak to occur in the range of and be obscured by porphyrinic signals. In support of this formulation, oxidation of the diazene complex, $Ru_2(N_2H_2)$, by an additional equivalent of *tert*-butyl hydroperoxide (under argon) yields the stable dinitrogen complex, $Ru_2(N_2)$.

Oxidation of $Ru_2(NH_3)_2$ with slightly more than 1 equiv of *tert*-butyl hydroperoxide yields a mixture of $Ru_2(N_2H_4)$, $Ru_2(N_2H_2)$, and $Ru_2(N_2)$, as well as unreacted $Ru_2(NH_3)_2$. Thus the four complexes are interconvertible via successive two-electron oxidations. We are exploring chemical and electrochemical means for their interconversion, as well as studying the detailed steps involved in these oxidations. In addition, attempts to interconvert the complexes via reductions, and attempts at electrocatalytic dinitrogen reduction using cofacial diporphyrins are currently in progress.

Acknowledgment. J.E.H. acknowledges support from the Franklin Veatch Memorial Fellowship Fund, 1987-1989. R.A.R. is the recipient of NIH individual service award GM 12197. Support from the National Science Foundation and the National Institutes of Health is acknowledged. We thank the Mass Spectrometry Facility, University of California, San Francisco, supported by the NIH Division of Research Resources, Grant RR01614. We thank Dr. Thomas G. Spiro for the use of the Raman Laboratory at Princeton University, which is supported by funds from the U.S. Department of Energy and the National Institutes of Health. We also thank Dr. Philip Hampton, Paul Wagenknecht, and Dr. D. Scott Bohle for helpful discussions.

(20) ^{1}H NMR ($Ru_2(N_2H_2)$, C_6D_6, ppm): porphyrinic resonances, H_{meso} 8.75 (s, 4 H), 8.66 (s, 2 H), biphenylene 7.15-6.65 (m, 6 H), CH_2CH_3 3.92 (m, 4 H), 3.71 (m, 4 H), 3.51 (m, 8 H), CH_3 3.28 (s, 12 H), 3.03 (s, 12 H), CH_2CH_3 1.70-1.60 (m, 24 H); imidazole resonances, para phenyl 6.29 (t, 2 H), meta phenyl 6.08 (t, 4 H), ortho phenyl 5.13 (d, 4 H), $H_{imidazole}$ 1.14 (s, 2 H), 1.04 (s, 2 H), *tert*-butyl -0.61 (s, 18 H).

(21) (a) Sellmann, D.; Brandl, A.; Endell, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1019-1020. (b) Sellmann, D.; Jödden, K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 464-465. (c) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 4066-4068.

The Endocyclic Restriction Test: Experimental Evaluation of Transition-Structure Geometry for a Nucleophilic Displacement at Neutral Nitrogen

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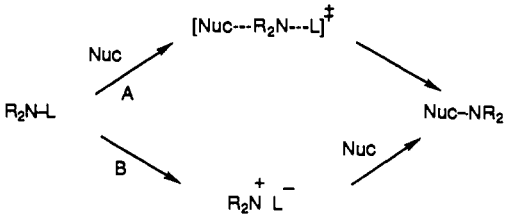
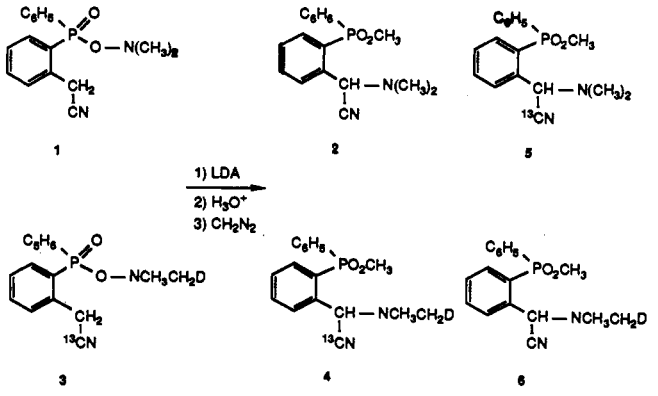
Received November 13, 1990

The mechanism of nucleophilic substitution at a formally neutral nitrogen atom is a matter of chemical and biochemical interest.[1-3] The limiting possibilities are shown in the first drawing as A a concerted reaction in which the transition structure has entering and leaving groups associated with nitrogen and B an ionization process involving the formation of an ion pair which is subsequently attacked by a nucleophile. Both reaction pathways are precedented in the literature.[2,3] In order to distinguish between these alternatives, we have evaluated the geometry of a nucleophilic substitution at a nitrogen bearing two methyl groups and addressed the possibility of reversible formation of an ion pair. The results, which provide the first experimental evidence for the geometry of a transition structure in a nucleophilic displacement at neutral nitrogen, are consistent with a concerted S_N2 mechanism.[3]



Suggestions of geometries for transition structures in substitutions at nonstereogenic atoms generally are made by analogy to formally similar processes at stereogenic atoms. The endocyclic restriction test, however, offers an experimental approach for evaluation of transition-structure geometries that is independent of the stereogenicity of the reaction center.[4,5] The work of Boche et al. which establishes that nucleophilic substitution occurs at the nitrogen of *N,N*-dimethyl-*O*-(diarylphosphinyl) derivatives allows application of this approach to a formally neutral nitrogen.[6] We have investigated the conversion of **1** to **2** which occurs in 11% yield on treatment of **1** with lithium diisopropylamide (LDA) in tetrahydrofuran followed by reaction with water, acidification, and treatment with diazomethane. If there is a geometrical requirement such that reaction cannot occur endocyclically within the confines of a six-membered ring, e.g., an S_N2 reaction, the reaction would occur intermolecularly. If reaction could occur within the confines of a formal six-membered ring, e.g., via an ion pair, the reaction could be intramolecular. A double labeling experiment was carried out with a mixture of **1** and **3** to distinguish the intermolecular and intramolecular pathways. For an intermolecular reaction the products would be **2**, **4**, **5**, and **6**, while an intramolecular reaction would give only **2** and **4**. The expectations for each possibility and the experimentally observed results of label scrambling which show that transfer of the dimethylamino group in the conversion of **1** to **2** is an intermolecular reaction are shown in Table I.[7] Recovered reactants were unscrambled, and a control experiment established that scrambling of the label in the products does not occur under these conditions.



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(2) For discussion of aromatic nitrenium ions, see: Panda, M.; Novak, M.; Magonski, J. *J. Am. Chem. Soc.* **1989**, *111*, 4524. Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498 and references cited therein.

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(5) Beak, P.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc.* **1986**, *108*, 6016. That work addresses the question of the geometry of displacement at a formally negative nitrogen of a lithium alkoxyamide by an organolithium reagent, and we have suggested that lithium bridging is a critical feature which brings the reactive components together for an S_N2 transition structure.[3] The present results in which the displacement occurs at a formally neutral nitrogen may be considered more general in revealing the favored geometry of nucleophilic substitution at a nitrogen.

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