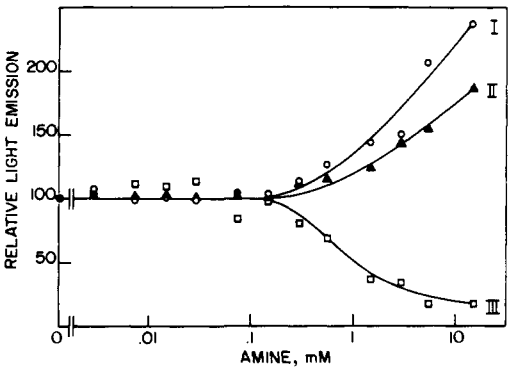

Figure 2. The effect of adding varying concentrations of the tertiary diamines, DABCO (I), II, or III, on the $^1O_2$ dimol emission produced by the $^1O_2$ generating system, peroxide/hypochlorite.

its acyclic analogue *N,N,N′,N′*-tetramethylethylenediamine (III).

As can be seen in Figure 2, at final concentrations above 1.5×10^{-4} M, both DABCO and II stimulated total light emission whereas the acyclic analogue III inhibited dimol emission. This light emission had the same relative amount of light passing the 634 and 703 nm interference filters, either in the presence or absence of the tertiary diamines. In all cases, the light emission at 670 nm was <1% of that observed at 634 nm. Therefore, even in the presence of tertiary diamines the light emission remains characteristic of $^1O_2$.[12] NaN_3 has also been reported to quench the chemical reactivity of $^1O_2$.[13,14] When added at a final concentration of 0.013 M, NaN_3 decreased $^1O_2$-specific light emission to <5% of a control sample. NaN_3 was also effective in inhibiting the light emission stimulated by DABCO. The final pH at the conclusion of each experiment ranged from 8.4 to 9.0 in the presence or absence of tertiary diamines. The amines, when added to either the H_2O_2 or the NaOCl alone, did not produce detectable light. Furthermore, when the reaction was allowed to go to completion by continuing the addition of NaOCl until all the peroxide was consumed, no difference was observed in the duration of light emission in the presence or absence of DABCO. This would indicate that the enhanced light emission in the presence of the tertiary amine was not due to an acceleration in the overall rate of the peroxide/hypochlorite reaction.

Thus, while DABCO reduces the extent of 634-nm gas-phase emission observed from radiofrequency discharge generated $^1O_2$[3,4] and quenches the chemical reactivity of $^1O_2$ in aqueous systems,[5-9] we have observed an enhancement of 634 and 703 nm emission from aqueous solutions in which $^1O_2$ has been formed chemically. This phenomenon is also seen with the monocyclic analogue II of DABCO but not with the acyclic analogue III of DABCO and may indicate that steric factors play a role in this reaction. The increased $^1O_2$ dimol emission observed in this system could be attributed to a change in either the localized concentration of $^1O_2$ in solution or in the rate or extent of nucleation of oxygen bubbles. The reaction of tertiary amines with $^1O_2$ has been proposed to be through a charge-transfer complex,[3] which might increase $^1O_2$ lifetime and actually facilitate dimol emission. Any possible effect on nucleation is unknown.

In either case, the $^1O_2$ would still be made unavailable for chemical reactions and thus the DABCO and II could simultaneously enhance dimol emission while still quenching the chemical reactivity of $^1O_2$.[15]

References and Notes

(1) T. Wilson and J. W. Hastings, *Photophysiology*, **5**, 49–95 (1970).
(2) D. R. Kearns, *Chem. Rev.*, **71**, 395–427 (1971).
(3) C. Ouannes and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527–6528 (1968).
(4) E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92**, 5034–5036 (1970).
(5) D. Bellus, H. Lind, and J. F. Wyatt, *J. Chem. Soc., Chem. Commun.*, 1199–1200 (1972).
(6) I. B. C. Matheson and J. Lee, *J. Am. Chem. Soc.*, **94**, 3310–3313 (1972).
(7) R. H. Young and R. L. Martin, *J. Am. Chem. Soc.*, **94**, 5183–5185 (1972).
(8) W. F. Smith, Jr., *J. Am. Chem. Soc.*, **94**, 186–190 (1972).
(9) R. H. Young, R. L. Martin, D. Feriozi, D. Brewer, and R. Kayser, *Photochem. Photobiol.*, **17**, 233–244 (1973).
(10) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **92**, 3293–3300 (1970).
(11) C. F. Deneke and N. I. Krinsky, Abstracts, 3rd Annual Meeting, American Society for Photobiology, Louisville, Ky., June 22–26, p 45 (1975).
(12) R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc., London*, 117 (1964).
(13) N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49–52 (1972).
(14) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, 45–48 (1972).
(15) Supported in part by NIH Grant AM 17745, NSF Grant BMS 74-18145, and by the Charlton Fund, Tufts University School of Medicine.

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Reduction of Molecular Nitrogen to Hydrazine. Structure of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II) and an ^{15}N Labeling Study of Its Reaction with Hydrogen Chloride

Sir:

We recently reported the synthesis and isolation of a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II), $[(C_5Me_5)_2ZrN_2]_2N_2$ (**1**), and noted further that on treatment with HCl one of the three N_2 ligands was reduced to hydrazine in 86% yield according to eq 1.[1]

$$[(C_5Me_5)_2ZrN_2]_2N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4 \quad (1)$$

The ready protonation and reduction of N_2 in **1** is of considerable interest in view of a general lack of such reactivity for other isolated dinitrogen complexes.[2] Accordingly we have investigated the structure of **1** and have carried out an ^{15}N labeling study to determine which dinitrogen ligand is reduced to hydrazine in the reaction with HCl.

The structure of **1** as recently determined by single-crystal x-ray diffraction methods is illustrated in Figure 1. The binuclear structure consists of two $(\eta^5\text{-}C_5Me_5)_2ZrN{\equiv}N$ moieties bridged by a third dinitrogen ligand. Terminal and bridging dinitrogen ligands are bound end-on with essentially linear Zr—N≡N and Zr—N≡N—Zr arrangements; NN distances are 1.116 (8), 1.114 (7), and 1.182 (5) Å, respectively.

The ^1H NMR spectrum of **1** at 5° (toluene-d_8) shows the expected two singlets attributable to the pairwise equivalent $(\eta^5\text{-}C_5Me_5)$ rings.[1] ^{15}N NMR data for $[(C_5Me_5)_2Zr(^{15}N_2)]_2(^{15}N_2)$ also support a solution structure for **1** identical with that in the crystalline state. Thus at −28° (toluene-d_8), the 18.25-MHz ^{15}N NMR spectrum for **1**-$(^{15}N_2)_3$ consists of two doublets attributable to the two ^{15}N nuclei of the two equivalent terminal dinitrogen ligands ($^1J_{^{15}N\text{-}^{15}N}$ = 6.2 Hz) centered 89.8 and 160.4 ppm upfield of a third singlet resonance due to the two ^{15}N nuclei of the μ-N_2. The ^{15}N NMR spectrum for **1**-$(^{15}N{\equiv}^{14}N)_3$ exhibits the same spectrum with the exception that the two upfield doublets now appear as the expected singlets. The results of a variable temperature ^1H and ^{15}N NMR study of **1** will be reported in a forthcoming full paper.[3]

We have also investigated the possibility that the terminal dinitrogen ligands are substitutionally more labile than the μ-N_2. Table I summarizes the results of our studies of the ex-

Table I. Results of N_2 Exchange of $[(C_5Me_5)_2Zr(^{15}N_2)]_2(^{15}N_2)$ (99.36% $^{15}N{\equiv}^{15}N$) with free natural N_2 (99.66% $^{14}N{\equiv}^{14}N$) in Toluene at −23° (estimated standard deviations).

$[(C_5Me_5)_2Zr)^{15}N_2)]_2(^{15}N_2)$ (mmol)	$^{14}N_2$ added (mmol)	$\bar{p}_{N_2}$ (atm)	Exposure time (min)	$X(^{14}N_2)$ calcd[a] / $X(^{15}N_2)$	$X(^{14}N_2)$ obsd / $X(^{15}N_2)$	mol N_2 exchanged per mol dimer
0.1255 (2)	2.106 (1)	1.0	15	0.887 / 0.106	0.886 (1) / 0.107 (1)	2.02 (2)
0.1906 (2)	2.164 (1)	1.0	30	0.844 / 0.149	0.841 (1) / 0.152 (1)	2.04 (2)
0.1091 (2)	2.338 (1)	1.0	60	0.908 / 0.0848	0.906 (1) / 0.0863 (10)	2.04 (2)
0.1217 (2)	2.154 (1)	1.0	5	0.892 / 0.101	0.921 (1) / 0.0728 (10)	1.44 (2)
0.1141 (2)	1.130 (1)	0.50	15	0.826 / 0.167	0.846 (1) / 0.147 (1)	1.77 (2)

[a] Mol fractions $^{14}N{\equiv}^{14}N$ and $^{15}N{\equiv}^{15}N$ expected in gas phase for complete exchange of terminal N_2 ligands only.

Table II. Results of N_2 Labeling Experiments for the Reaction: $[(C_5Me_5)_2ZrN_2]N_2 + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + 2N_2 + N_2H_4$ (estimated standard deviations)

$X(^{15}N_2)$ in two positions of $[(C_5Me_5)_2ZrN_2]_2N_2$		$X(^{15}N_2)$ in N_2 evolved on HCl addition		$X(^{15}N_2H_4)$ in hydrazine obtained on HCl addition	
Terminal	Bridge	Calcd[a]	Obsd[b]	Calcd[a]	Obsd[b]
0.107 (5)	0.9936 (1)	0.328 (4)	0.368 (1)	0.550 (3)	0.528 (1)
0.152 (5)	0.9936 (1)	0.362 (4)	0.388 (1)	0.573 (3)	0.547 (1)
0.086 (5)	0.9936 (1)	0.313 (4)	0.329 (1)	0.540 (3)	0.488 (1)
0.350 (5)	0.9936 (1)	0.510 (4)	0.580 (1)	0.671 (3)	0.665 (1)
0.270 (5)	0.9936 (1)	0.446 (4)	0.525 (1)	0.629 (3)	0.634 (1)
0.394 (5)	0.9936 (1)	0.539 (4)	0.619 (1)	0.691 (3)	0.682 (1)
0.079 (5)[c]	0.9936 (1)[c]	0.308 (4)[c]	0.335 (1)[c]	0.536 (3)[c]	0.522 (1)[c]

[a] Calculated for reaction proceeding 100% according to eq 2. [b] No $^{15}N{\equiv}^{14}N$ was formed in reaction. [c] DCl substituted for HCl.

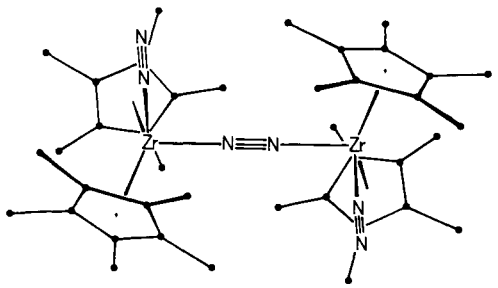

Figure 1. The molecular structure of **1**.

change of free $^{14}N_2$ with **1**-$(^{15}N_2)_3$. In a typical experiment ca. 0.1 mmol of **1** was dissolved in 8.0 ml of toluene in vacuo over a 15-min period at 0°. This solution was then cooled to −23°, natural $^{14}N_2$ admitted, and the system quickly closed off. After a period of stirring at −23° the exchange was quenched by rapid cooling to liquid nitrogen temperature. The gas phase was then transferred to a sample bulb by means of a Toepler pump and analyzed by mass spectrometry for $^{14}N{\equiv}^{14}N$, $^{14}N{\equiv}^{15}N$, $^{15}N{\equiv}^{15}N$.

The first three entries in Table I demonstrate that after 15 min exposure to free $^{14}N_2$, the composition of the gas phase above the solution is in close agreement with that predicted for complete exchange of two of the three dinitrogen ligands of **1**. This observation requires that under these conditions exchange occurs between free N_2 and only the two equivalent terminal dinitrogen ligands. Incomplete exchange is observed after 5 min, permitting an estimate of the terminal N_2 exchange half-life of 2.6 (1) min ($\bar{p}_{N_2}$ = 1 atm). On the basis of the experiment conducted at reduced pressure the exchange rate appears proportional to free N_2 concentration ($t_{1/2}$ = 5.0 (3) min, $\bar{p}_{N_2}$ = 0.50 atm).

The results of these exchange experiments allow an accurate assessment of the extent of ^{15}N labeling in both terminal and bridge positions for **1**, and thus should allow a determination of which of the three dinitrogen ligands of **1** is reduced to hydrazine in the reaction with HCl. Following exchange of free $^{14}N_2$ with the terminal positions of **1**-$(^{15}N_2)_3$, a 20 M excess of HCl was condensed onto the frozen toluene solution of the resulting complex. This mixture was warmed slowly to −80° whereupon an immediate reaction accompanied melting (<10 s to completion) as evidenced by a color change from intense red to pale yellow. After warming slowly to room temperature, N_2 was collected (1.93 (6) mol of N_2/mol of **1**), a small amount of H_2 (0.13 (2) mol of H_2/mol of **1**) removed by passage through CuO at 320°, and a sample analyzed by mass spectrometry for $^{14}N{\equiv}^{14}N$, $^{14}N{\equiv}^{15}N$, and $^{15}N{\equiv}^{15}N$. Hydrazine was extracted from the residue with 0.1 M HCl and oxidized with 0.1 M KIO_3 to N_2, which was collected via a Toepler pump and also analyzed for $^{14}N{\equiv}^{14}N$, $^{15}N{\equiv}^{14}N$, and $^{15}N{\equiv}^{15}N$.[4]

The results (Table II) clearly indicate that the dinitrogen ligand which is reduced to hydrazine is *not exclusively* the μ-N_2 as might be anticipated. Rather the composition of both evolved N_2 and hydrazine is in close agreement with that expected for the reaction proceeding according to eq 2.[5,6]

$$[(C_5Me_5)_2Zr(N_2{}^t)]_2(N_2{}^b) + 4HCl \rightarrow 2(C_5Me_5)_2ZrCl_2 + \tfrac{3}{2}N_2{}^t + \tfrac{1}{2}N_2{}^b + \tfrac{1}{2}N_2{}^tH_4 + \tfrac{1}{2}N_2{}^bH_4 \quad (2)$$

Furthermore, we have also observed that treatment of $[(\eta^5\text{-}C_5Me_5)_2Zr(CO)]_2N_2$[7] (**2**) with HCl under identical conditions yields $(C_5Me_5)_2ZrCl_2$, CO (1.29 mol/mol of **2**), H_2 (1.19 mol/mol of **2**), and N_2 (1.02 mol/mol of **2**).[8] Thus no reduction

of the μ-N_2 of **2** is observed, an indication that the terminal dinitrogen ligands are playing roles beyond that of mere spectators in the reaction of **1** with HCl.

The data require a reaction sequence mediated by a symmetric species in which one terminal N_2 and the μ-N_2 have become equivalent.[9] While a number of mechanisms satisfying this requirement could be formulated, we favor one involving protonation of a terminal dinitrogen of **1**, loss of the other terminal N_2, and generation of the symmetric reaction intermediate $(C_5Me_5)_2Zr(N_2H)_2$ (**3**).[10] Consistent with the labeling experiments, **3** would then lead to 1 mol each of N_2 and N_2H_4 (eq 3).

$$(C_5Me_5)_2Zr(N_2H)_2 + 2HCl \rightarrow (C_5Me_5)_2ZrCl_2 + N_2 + N_2H_4 \quad (3)$$

Generation of the neutral, monomeric species **3** from **1** would require a formal two-electron transfer to the N_2-bearing Zr accompanied by release of the other zirconium in the fully oxidized state, i.e., as $(C_5Me_5)_2ZrCl_2$. Strong electronic coupling of the two Zr(II) centers through the μ-N_2 of **1** as suggested by its structural features, ir, and visible spectra should facilitate such a Zr-to-Zr charge transfer.

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References and Notes

(1) J. M. Manriquez and J. E. Bercaw, *J. Am. Chem. Soc.*, **96**, 6229 (1974).
(2) Notable exceptions are complexes of the type $ML_4(N_2)_2$ (M = Mo, W; L = PMe_2Ph, $PMePh_2$), which have recently been shown to liberate up to 1.8 mol of ammonia in acid methanol: J. Chatt, A. J. Pearman, and R. L. Richards, *Nature (London)*, **253**, 39 (1975); J. Chatt, *J. Organomet. Chem.*, **100**, 17 (1975).
(3) J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chan, and J. E. Bercaw, manuscript in preparation.
(4) Colorimetric determinations of ammonia (indophenol; J. A. Russell, *J. Biol. Chem.*, **156**, 457 (1944)), and hydrazine (*p*-dimethylaminobenzaldehyde; I. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", Vol. IIA, D. Van Nostrand, New York, N.Y., 1959, p 707), indicate that the reduced N_2 consists of 0.86 mol of N_2H_4 and 0.24 mol of NH_3 per mol of 1. Treatment of **1** with anhydrous N_2H_4 in toluene at −80° (instantaneously) yields N_2 (3 mol) and NH_3 (2 mol), thus indicating that ammonia could arise from interference of this reaction during the latter stages of the reaction with HCl.
(5) A small correction for residual N_2 trapped in the frozen toluene (0.0185 mmol as determined by a blank) was made in calculating the expected fraction of $^{15}N_2$ evolved in the addition of HCl.
(6) Since (1) the reaction proceeds only 86% according to eq 2 (footnote 4), and (2) iodate oxidizes N_2H_4 but not NH_3 to N_2, hydrazine labeling should be somewhat more reliable.
(7) **2** is prepared by treatment of **1** with CO at −23° and isolated as metallic green crystals. On the basis of analytical data, ir (ν(CO) 1902 (ms), 1860 (s); ν(NN) 1682 (ms)), and NMR ((toluene-d_8) s, δ 1.80 (30 H); s, 1.82 (30 H)), the structure of **2** is believed to be identical with **1** with carbonyl substituted for the terminal dinitrogen ligands.
(8) Apparently some carbon monoxide is reduced when **2** is treated with HCl. The identity of the reduction product(s) is presently under investigation.
(9) This intermediate need only be symmetric on the reaction time scale, so that a monoprotiated species such as $[(C_5Me_5)_2Zr(N_2)(N_2H)]^-$ is a possibility, providing proton transfer between dinitrogen ligands is sufficiently rapid. No significant variation in $X(^{15}N_2)$ was observed with DCl (Table II), so that if this is the case such a proton transfer cannot be so slow as to be comparable to the rate of subsequent reaction steps.
(10) Our data do not exclude the possibility that this symmetric intermediate could, in fact, be dimeric (e.g., $[(C_5Me_5)_2Zr(\mu\text{-}N_2H)_2Zr(C_5Me_5)_2]^{2+}$, $[(C_5Me_5)_2Zr(\mu\text{-}N_2H_2)_2Zr(C_5Me_5)_2]^{4+}$); however, in view of the high charges necessarily associated with such dimers, we favor the neutral monomer **3**.

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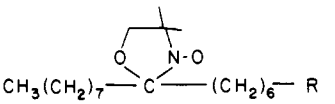
A New Measurement of Surface Charge in Model and Biological Lipid Membranes

Sir:

We report that the distribution of charged, amphiphilic spin labels,[1] **1** and **2**, between lipid membranes and buffered salt solutions is related quantitatively to the surface charge density of the membrane. Previous measurements of conductance across model bilayer membranes[2] and of surface potentials of lipid monolayers[3] demonstrated that the relation between surface charge density and binding of electrolytes at the lipid–water interface is described to a first approximation by the Gouy–Chapman double layer analysis.[4,5] The principal aims of the study reported here are to develop a technique whereby changes in surface potential may be measured under similar conditions in both model and biological membranes and at the same time to detect changes in lipid fluidity. This approach should also be useful in assessing the bilayer free energy in a lipid phase separation.[6]



$R = -CH_2\overset{+}{N}(CH_3)_3$ (1)

$= -COO^-$ (2)

Two overlapping paramagnetic resonance signals are evident in Figure 1. A sharp, three-line spectrum (indicated by arrows) arises from label **1** tumbling rapidly in aqueous solution. The portion of label bound to membranes contributes the broad signal. The relative intensities of the two signals are a function of lipid surface charge density, total lipid concentration, and lipid fluidity.

In typical measurements, samples initially containing 10^{-4} M label and 10^{-2} M multilayered lipid liposomes[7] in buffer (0.1 M NaCl, 0.05 M Tris, pH 8.0) are diluted with buffer and allowed to equilibrate overnight. Quantitative determination of sharp signal intensity is made by comparison of lipid samples with a standard containing only label and buffer. Figure 2 shows that the distribution of label **1** between lipid and aqueous solution is linear over a 20-fold lipid concentration range, and increases as the fraction of lipid bearing a net negative charge increases.

At low ratios of label to lipid, the relation between binding of label and membrane surface potential, Ψ, is

$$\text{label bound/label free} = k \exp(\pm F\Psi/RT) \quad (1)$$

Assuming that the lipid suspensions contain large particles (~1000 Å diameter[7]) so they may be treated as flat diffusely charged layers, the Gouy–Chapman analysis may be applied:

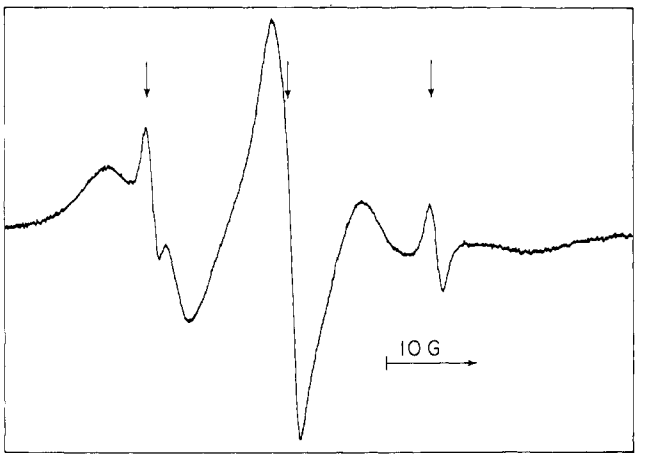


Figure 1. Typical EPR signal of label **1** in 1% (w/w) aqueous, lipid dispersion.