Hepes buffer (0.3 M, containing 0.1 M sucrose, pH 7.5). After 3 min, DTT (0.5 M, 0.100 mL) and TET (0.5 M, 0.85 mL) were added and the solution was mixed thoroughly and poured onto 50 mL of glass beads (B. Braun Melsungen Apparatebau) (1.00 mm). The beads were mechanically stirred for ca. 6 min to provide a uniform coating with the PAN solution as well as to prevent their clumping as the solution gelled. After 1 h, the invertase/PAN coated glass beads were suspended in Hepes buffer (0.1 M, pH 7.5, containing 50 mM ammonium sulfate), and gentle stirring was continued for 20 min. A jacketed column (Pharmacia, 1.5 × 30 cm) was filled with ca. 85% of these beads. The column was thermostated at 45 °C and a 0.5 M solution of sucrose, pH 4.8, containing 25 mM acetate, was pumped continuously through the column for a period of 350 h at a flow rate of ca. 2.4 L per day. The initial column activity was ca. 960 U at 45 °C and pH 4.8. At the end of the experiment, the column activity dropped to ca. 700 U.

Magnetically Responsive Invertase/PAN Gel. Invertase (20 mg, 12,000 U) was mixed with 3.0 g of PAN-500 in 12.0 mL of Hepes buffer (0.3 M, containing 0.1 M sucrose, pH 7.5). After 3 min, DTT (0.5 M, 0.100 mL), TET (0.5 M, 1.275 mL), and aqueous ferrofluid (Ferrofludics Corp., Burlington, Mass., magnetic saturation of 200 G, 0.5 mL) were added, and the solution was mixed until it had gelled. The brown-colored gel particles, obtained following the standard work-up procedures, contained 4500 U (37%) of the invertase activity.

Column Operation: Invertase/Magnetically Responsive PAN Gel. A jacketed column (Pharmacia, 3 × 43 cm) was placed between the poles of an electromagnet (Varian, V-4004, 2 A, ~10 kG). A 10-cm plug of stainless steel wool (International Steel Wool Corp., fine grade) was placed in the magnetic field zone and a suspension of the magnetically responsive invertase/PAN-500 gel particles (ca. 0.5 g of PAN-500) was filtered through the plug. The particles immediately adhered to the plug. The column was thermostated at 45 °C and a 0.5 M solution of sucrose, pH 4.8, containing 25 mM acetate, was pumped continuously through the column for a period of 20 days at a rate of ca. 1.8 L/day. The initial column activity of ca. 215 U at 45 °C and pH 4.8 dropped to ca. 90 U.

Treatment of Gel- and Glass-Immobilized Hexokinase with Soluble Proteases. The experimental protocols used in these experiments were unexceptional extensions of those already described. Exact analysis of the rate of loss of hexokinase activity is unprofitable, since autoproteolysis also significantly lowered the activity of the proteases during the course of the experiments. Separation of the gel particles from the reaction mixtures and analysis of the solution established that most of the protease activity was present in the solution, rather than associated with the gel.

Coimmobilization of Hexokinase and Trypsin. Hexokinase (2.0 mg, 510 U) and trypsin (2.0 mg, 780 U (*p*-tosyl-L-arginine hydrochloride as substrate)) were coimmobilized in PAN-500 (0.200 g) dissolved in 0.3 M Hepes buffer (pH 7.5, containing 15 mM $MgCl_2$, 10 mM ADP, 25 mM glucose, and 5 mM benzamidine hydrochloride) following the small-scale immobilization procedure for hexokinase. After the standard washing procedure (three washes), an assay of 200 U (39%) of hexokinase activity and 351 U (45%) of trypsin activity was determined in the gel particles. To decrease the concentration of the benzamidine, a potent trypsin inhibitor ($k_i = 1.84 \times 10^{-5}$ M),[48] the gel particles were washed five more times with 0.05 M Mops buffer, pH 7.0 (gel particles volume to total volume ratio ca. 5) at 0 °C.

Acknowledgment. Dr. Orn Adalsteinsson carried out initial experiments in this project. Measurements of gel particle sizes used microscopes in the M.I.T. Materials Research Laboratory. A number of individuals in the group—especially Mr. Victor Rios-Mercadillo, Ms. Sharon Haynie, Dr. Hans-Jürgen Leuchs, Dr. Shimona Geresh, and Dr. Yen-Shiang Shih—have used this immobilization method in their work, and their experience has contributed to its development. We thank our colleague, Professor Mary Roberts, for her collaboration in the immobilization of several phospholipases.

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Communications to the Editor

Free-Radical Dynamics in Organized Lipid Bilayers

Sir:

Organized lipid bilayers are the principal structural units of most cell membranes and a major site for enzymes important in cellular metabolism. Destruction of membrane lipids and other cell components by adventitious free-radical oxidants is believed to constitute one component of the aging process in higher organisms, including man. The presence of vitamin E, a powerful antioxidant, in most cell membranes is cited as evidence of the damaging effects of free-radical oxidants on biological systems.[1-3] Quantitative studies of radical oxidants in lipid bilayers are virtually unknown although a qualitative literature exists.[4-8]

This report describes kinetic experiments with a lipophilic peroxy radical source, azobis[(2-*n*-butylcarboxy)propane],[9] $[Me_2C(CO_2Bu)]_2N_2$ (ABCP), and a phenolic antioxidant, 2,6-di-*tert*-butyl-4-methylphenol (BHT), both in model cell membranes and homogeneous solution. From these data, we are able to deduce some quantitative effects of lipid bilayers on free-radical dynamics.

Table I. Effect of Solvent on Decomposition of ABCP at 50.0 °C

solvent	10^2-$[ABCP]_o$, M	$10^6 k_d$, s^{-1}	$t_{1/2}$, h[a]
dodecane	3.0	1.38 ± 0.08	140
Nujol	3.0	1.56 ± 0.08	123
methyl laurate	2.0	1.82 ± 0.02	106
1-butanol	3.0	3.02 ± 0.02	64
CH_3CN/H_2O, 1:1	3.0	3.7 ± 0.5	53
DLPC bilayer	2.0[b]	2.2 ± 0.3	89
DSPC bilayer	2.0[b]	1.7 ± 0.05	111

[a] Half-life for decomposition. [b] Concentration in lipid phase of a 1% w/v suspension, pH 7.

In several solvents, ABCP (10^{-2} M) decomposes with clean first-order kinetics with a half-life of 53-140 h at 50.0 °C, depending on solvent polarity, but not viscosity. As shown in Table I, decomposition is faster in more polar media, increasing by a factor of three upon going from dodecane to CH_3CN/H_2O. Increased solvent viscosity, however, is not expected to retard the decomposition of ABCP because symmetrical azoalkanes decompose by concerted two-bond cleavage.[10,11] We find a slight increase in k_d upon going from dodecane (0.92 cP) to Nujol (37 cP), indicating that viscosity is not a controlling factor.

In synthetic bilayer suspensions of L-α-dilauroylphosphatidylcholine (DLPC) or L-α-distearoylphosphatidylcholine

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(9) ABCP was synthesized by HCl-catalyzed butanolysis of azobis(2-cyanopropane) (AIBN) by using the procedure of Mortimer, G. *J. Org. Chem.* **1965**, *30*, 1632. The viscous liquid product was purified by recrystallization from pentane at −50 °C. NMR and UV spectral data confirmed the structure, and high-pressure liquid chromatography (high-pressure LC) showed less than 5% contamination by AIBN. We thank C. Gould for the synthesis.

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Table II. Cage Escape Fraction (a) of Radicals from ABCP at 50.0 °C in Selected Media

solvent (viscosity, cP)	scavenger[a]	a
n-hexane	I_2	0.57 ± 0.02
(0.24)[b]	BHT	0.58 ± 0.02
n-dodecane	I_2	0.43 ± 0.01
(0.92)[b]	BHT	0.45 ± 0.02
n-tetradecane	I_2	0.46 ± 0.02
(1.3)[b]	BHT	0.43 ± 0.02
methyl laurate	I_2	0.39 ± 0.02
(2.0)[c]	BHT	0.34 ± 0.02
methyl myristate	BHT	0.29 ± 0.01
(2.7)[c]		
Nujol[d]	I_2	0.12 ± 0.01
(37 cp)[10]		
DLPC bilayers[e]	BHT	0.21 ± 0.03
DMPC bilayers[e]	BHT	0.25 ± 0.04
DSPC bilayers[e]	BHT	0.2 – 0.5

[a] Starting concentrations of BHT and I_2 ranged from 0.5–1.5 mM in homogeneous solvents. In lipid bilayers, the initial BHT concentration was 2.5 or 7 mM. [b] Karapet'yants, M. Kh.; Kuosen, Y. *Zh. Fiz. Khim.* **1958**, *37*, 1106. [c] Gouw, T. H.; Vlugter, J. C.; Roelands, C. J. A. *J. Am. Oil Chem. Soc.* **1966**, *43*, 433. [d] McKesson heavy liquid petrolatum (USP) used as received. [e] Air or oxygen was used in these experiments. For experimental details, see ref 20 and 21.

(DSPC), 1% w/v in pH 7 buffer,[12] ABCP has a half-life of 89 or 111 h, respectively, bracketing its half-life in methyl laurate but much longer than in CH_3CN/H_2O or butanol. The half-life also is much shorter than that in dodecane. These results coupled with partition measurements[13] indicate that the time-average position of ABCP is in the liposomal bilayer, in a region of moderate-to-low polarity.

Activated azoalkanes such as ABCP decompose to give pairs of carbon radicals, only a fraction of which (a) escape from the solvent cage (eq 1–4).[14] In the presence of sufficient oxygen,

$$R_2N_2 \rightarrow (2R\cdot)_{cage} + N_2 \quad (1)$$

$$(2R\cdot)_{cage} \xrightarrow{a} 2R\cdot \quad (2)$$

$$(2R\cdot)_{cage} \xrightarrow{1-a} R\text{–}R \quad (3)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \quad (4)$$

escaping carbon radicals will be converted to peroxy radicals.[15] The magnitude of a is dependent on solvent viscosity and is close to 0.5 at 40–70 °C for azobis(isobutyronitrile) in nonviscous hydrocarbon solvents.[14] Fluorescence and ESR probe measurements at 50 °C in cholesterol-free lecithin bilayers indicate very high microviscosities (20–1000 cP) compared to viscosities in light hydrocarbon solvents.[16–19] These results predict that free-radical production from azoalkanes or other homolytic initiators would be dramatically inhibited in bilayers.

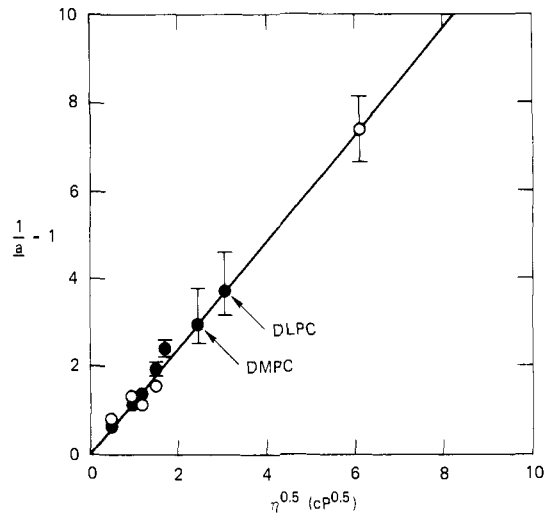

Figure 1. Plot of $1/a - 1$ vs. $\eta^{0.5}$ by using the data contained in Table II. (○) I_2 scavenger. (●) BHT scavenger. Data calculated for DLPC and DMPC bilayers fall on the abscissa to give an equivalent viscosity of about 8 cP at 50 °C.

We have measured a at 50 °C for ABCP in homogeneous solvents of different viscosities and in DLPC, L-α-dimyristoylphosphatidylcholine (DMPC), and DSPC multilamellar bilayers to assess the effect of phase organization on a.[20] In deoxygenated solvents, iodine was used to scavenge all escaping carbon radicals.[14,21] In oxygenated solutions and in lipid bilayers, BHT was used to scavenge peroxy radicals.[14] At sufficiently high scavenger concentrations, all radicals will react to deplete scavengers. To calculate a, we compared the loss of scavenger to initiator destruction over a timed interval, under conditions where each scavenger reacts with two radicals and $a = \Delta$ scavenger$/\Delta R_2N_2$.[21]

Results are summarized in Table II. In hydrocarbon and ester solvents, a values obtained by both scavenging methods agree, as expected.[14] We observe a monotonic decrease in a with increasing viscosity in the model solvents. Liposomal suspensions produced escape efficiencies significantly smaller than corresponding model solvents of the same chain length. In DLPC bilayers, the initial concentrations of both BHT and O_2 were varied over 3- and 5-fold, respectively, with no effect on a, indicating that all carbon radicals reacted with O_2 and then with BHT.

Reactions in annealed DSPC bilayers were hard to reproduce because we found difficulty in quantitatively sequestering reagents into DSPC bilayers, coupled with the subsequent concentration measurement of ABCP, which was interfered with by BHT.[20] This scatter may also be related to the high gel–liquid crystalline phase

(12) ABCP decomposition in homogeneous solution was monitored at 363 nm. First-order rate constants were obtained by fitting to the regression equation $\ln (A_\infty/A_t) = k_d t$. Solutions of ABCP were three times freeze-pump thawed at 0.03 torr in degassable UV cuvettes and, after sealing off, were thermolyzed in a water bath at 50.0 ± 0.1 °C. In liposomal suspensions, ABCP loss was measured by high-pressure LC, monitoring at 230 nm. To prevent oxidative damage to liposomes, 2,6-di-*tert*-butylphenol was added on a one-to-one basis with ABCP (BHT was found to coelute with ABCP).

(13) Centrifugation of these suspensions demonstrated quantitative association of ABCP with the liposomal pellet; less than 1% ABCP was found in the aqueous supernatant; 4% BHT was found in the supernatant by this method.

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(20) Multilamellar liposome suspensions were prepared by codissolving 0.16 μmol of ABCP, 0.05 or 0.017 μmol of BHT, and 16 μmol of synthetic lipid in 100 μL of MeOH. The solution was dried to a thin film, and 1.00 mL (pH 7, 10 mM) of imidazole buffer was added. The mixture was shaken until suspension occurred. The resultant mixture gave concentrations of 0.02 M and 0.0070 or 0.0023 M ABCP and BHT, respectively, in the lipid phase. BHT loss at 50.0 °C in bilayers was followed by high-pressure LC, monitoring at 280 nm. ABCP coelutes with BHT but did not interfere because of its negligible absorbance at 280 nm.

(21) With sufficient scavenger ($\sim 10^{-4}$ M), all radicals are captured by the scavenger, and all radical propagation and termination steps become negligible. In the case of BHT, the stoichiometry becomes $2aO_2 + R_2N_2 + a$BHT = inactive products + N_2. Under normal kinetic conditions, each BHT scavenges two peroxy radicals,[23,24] leading to the above equation. At low $RO_2\cdot$/BHT ratios, phenoxy radical disproportionation will change the number of radicals scavenged by each BHT to one, but the equation is preserved because BHT is thereby regenerated.[25] We find 40% of the peroxycyclohexadienone expected in the absence of phenoxy radical disproportionation,[23] indicating that this reaction pathway is probably occurring in the bilayer experiments. We calculated the loss of ABCP from the reaction Δ ABCP = $[\text{ABCP}]_0(1 - e^{-k_d t})$ where k_d is the appropriate value from Table I. Loss of BHT was followed by high-pressure LC and loss of I_2 by diminuation of the visible absorption band at 520 nm in hydrocarbon solvents and 480 nm in ester solvents.

transition temperature (54.9 °C)[22] of DSPC, which is in excess of our reaction temperature.

Using model solvent data in Table II, we find a linear relationship between the quantity $(1/a - 1)$ and η, where η is bulk solvent viscosity[26] (Figure 1). The a data for DLPC and DMPC fall on the abscissa to give a bilayer microviscosity equivalent to about 8 cP at 50 °C.

We conclude that free-radical cage escape is depressed in the bilayer system compared with bulk-phase hydrocarbon solvents of the same chain length. Escape is more efficient, however, than predicted by microviscosities measured by probe studies.[16-19] Ester solvents match in polarity but are less viscous than the membrane environment probed by ABCP and BHT. Studies of the effect of bilayer structure on a and on antioxidant reactivities are continuing.

Acknowledgment. This work was supported by NIH-NIA Grant AG-486-05.

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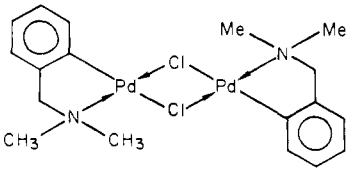
Synthesis of New Heteropolymetallic Compounds with Carbonylmetallate Anions as Bridges between Two Palladium Atoms: X-ray Crystal Structures of $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\text{-}\{Co(CO)_4\}\mu Cl]$ and $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\text{-}\{Mo(CO)_3(\eta\text{-}C_5H_5)\}\mu Cl]$

Sir:

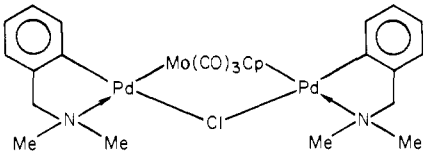
Since our discovery of the first stable dimetallic species containing a Pd-Co or a Pd-Mo bond by the reaction of carbonylmetallate anions with monomeric cyclopalladated compounds,[1] we have explored the reaction of these anions with dimeric cyclopalladated species. A related reaction has been used previously[2] to transfer orthometallated azobenzenes on cobalt, manganese, or rhenium carbonyls. Herein we report that by using different cyclopalladated dimers a completely different reaction occurs since this time trimetallic compounds are obtained.

sym-Di-μ-chloro-bis[2-[(dimethylamino)methyl]phenyl]dipalladium **1** suspended in THF reacts quasi-instantaneously at room temperature with $NaMo(CO)_3(\eta\text{-}C_5H_5)$ (2×10^{-2} M solution in THF) in a 1:1 ratio. A deep red solution is obtained



1

from which black crystals are precipitated 1 day after the addition of hexane at -20 °C (70% yield). Microanalytical and spectroscopic data indicate the general formula as $[\{\overline{Pd(NMe_2CH_2C_6H_4)}\}_2\mu\text{-}\{Mo(CO)_3(\eta\text{-}C_5H_5)\}\mu Cl]$[3] **2**. In order to establish the geometry of this new type of compound on a firm basis, a single-crystal X-ray-diffraction study was carried out on **2**. Suitable crystals for X-ray study were obtained by slow diffusion of hexane into a dichloromethane solution of **2** at -20 °C. Crystal data[4] for **2** ($Pd_2MoClO_3N_2C_{26}H_{29}$) are the following: $M_r = 761$; monoclinic; space group $P2_1/n$; $a = 20.501(9)$, $b = 15.625(6)$, $c = 8.403(4)$ Å; $\beta = 99.83(5)°$; $V = 2652$ Å^3; $Z = 4$; $d_{obsd} = 1.88$ g/cm^3, $d_{calcd} = 1.90$ g/cm^3, $\mu(MoK\alpha) = 19.0$ cm^{-1}. Final $R = 0.040$ ($R' = 0.054$) for 2330 absorption-corrected intensities [293 K, $1.1° < 2\theta < 55°$] with $I > 3\sigma(I)$.



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The molecular structure (Figure 1) reveals that the two palladium atoms are bridged by a chlorine atom and the Mo-$(CO)_3(\eta\text{-}C_5H_5)$ moiety. Two of the carbonyl groups are semibridging to the palladium atoms[5] whereas the third one is triply bridging on the Pd_2Mo triangle. The arrangement of the Mo-$(CO)_3(\eta\text{-}C_5H_5)$ moiety between the palladium atoms is in fact reminiscent of that found in the heterotetrametallic $Pd_2Mo_2(\eta\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PEt_3)_2$ cluster[6] in which two Mo-$(CO)_3(\eta\text{-}C_5H_5)$ groups are bridged between two palladium atoms. In this latter case, however, there was a Pd-Pd bond [Pd-Pd = 2.582 (1) Å] whereas in compound **2** the Pd1-Pd2 distance is 3.241 (1) Å, which excludes, therefore, a metal-metal interaction. The geometry of the metalated ligand is close to what has been found for related compounds.[7] There is no plane of symmetry in the molecule because the two cyclometallated ligands behave

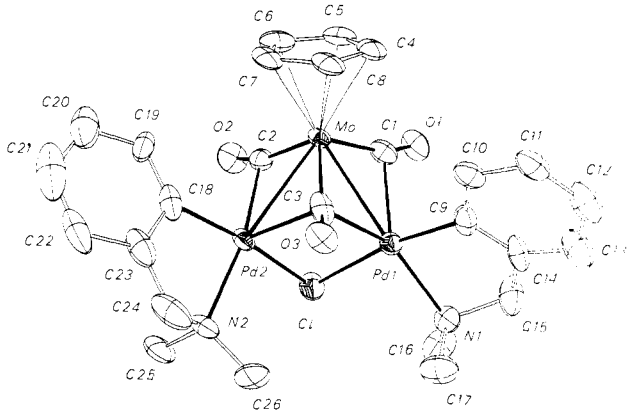

Figure 1. The molecular geometry of $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\{Mo(CO)_3\eta\text{-}C_5H_5\}\mu Cl]$, including the atomic-numbering scheme. Bond lengths: Pd1-Mo 2.832 (1), Pd2-Mo 2.788 (1), Pd1-Cl 2.470 (3), Pd2-Cl 2.454 (3), Pd1-C1 2.28 (1), Pd1-C3 2.39 (1), Pd2-C2 2.20 (1), Pd2-C3 2.37 (1), Mo-C1 1.98 (1), Mo-C2 1.98 (1), and Mo-C3 2.05 (1) Å. Angles: Pd1-Mo-Pd2 70.43 (3), Pd1-Cl-Pd2 82.32 (9), Mo-C1-O1 1.62 (1), Mo-C2-O2 163 (1), and Mo-C3-O3 161 (1)°.

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(3) Compound **2**: IR ν_{CO} (KBr pellet) 1844 (s), 1770 (vbr s); ν_{PdCl} (polyethylene pellet) 197 cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) 7.03-6.81 (m, 4 H, C_6H_4), 5.30 (s, 5 H, C_5H_5), 4.21, 4.03 (AB pattern, 2 H, CH_2, J_{HH} = 13.3 Hz), 2.87 (s, 3 H, CH_3), 2.68 ppm (s, 3 H, CH_3).
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