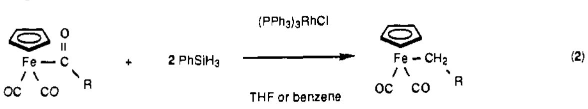
complexes **3b**, **5b**, and **8b**, which are contaminated only by small amounts of silane residues.[16]

Iron α-diethylsiloxyalkyl complexes **1b**–**8b**, all yellow-brown oils, also are stable as dichloromethane, benzene, or THF solutions. Their ^1H NMR spectra are especially diagnostic, with a Si–H quintet invariably appearing at δ (C_6D_6) 4.4–4.8. The α-methine hydrogen on straight-chain α-siloxyalkyls **2b** and **4b** and on **5b** (Table I) appears as a doublet of doublets due to vicinal coupling with diastereotopic β-methylene hydrogens. Other indications of the chiral centers on **1b**–**8b** include the presence of diastereotopic Si–ethyl groups (^1H and ^{13}C NMR spectroscopy) and diastereotopic carbonyls (^{13}C NMR).

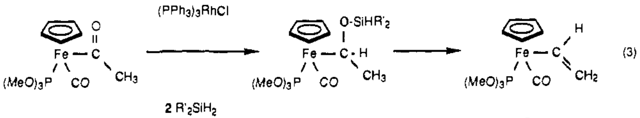


1a R = CH_3

8a R = Ph

Other hydrosilanes have been surveyed for their reactivity in the catalytic hydrosilation of iron acyls. Monohydrosilane Et_3SiH in the presence of $(PPh_3)_3RhCl$ (5 mol %) does not consume $FpCOCH_3$ (**1a**) (10 h, 22 °C) in benzene or THF solutions. Dihydrosilanes Ph_2SiH_2 and $PhMeSiH_2$, reacting analogous to Et_2SiH_2, quantitatively provide their stable α-siloxyethyl Fp complexes **9b** and **10b**, as determined by IR and ^1H NMR spectral monitoring.[18] The phenyl-containing dihydrosilanes proved less useful, however, as the isolated products **9b** and **10b** inevitably retained higher boiling disilanes and other silane residues.[16] Trihydrosilane $PhSiH_3$ reacting differently reduces Fp(acetyl) (**1a**) and Fp(benzoyl) (**8a**) in the presence of $(PPh_3)_3RhCl$ catalyst to their alkyl complexes (eq 2).[15c] Isolated yields after column chromatography of Fp(ethyl) (45%) and Fp(benzyl) (70%) are independent of the amount of $PhSiH_3$ used (2–4 mol equiv).

Hydrosilation of trimethyl phosphite substituted acetyl compounds **11a** (eq 3) is complicated by subsequent degradation of siloxyethyl **11b** to its vinyl complex **12**. ^1H NMR spectral monitoring of the diphenyl- and diethylsilane reactions with **11a** [1.7–5.0% $(PPh_3)_3RhCl$ and 1.0–2.0 equiv of silane in C_6D_6] clearly indicates that **11b** is the kinetic product. Workup of these reactions and removal of the catalyst (silica gel chromatography) affords product mixtures that range from 1:1 **11b** and **12** to exclusively vinyl complex **12**. In the absence of rhodium catalyst and dihydrosilane, **11b** does not transform to **12**.



11a 11b 12

Rh(I)-catalyzed hydrosilation of organoiron acyl complexes with dihydrosilanes occurs under mild conditions at the acyl ligand and produces stable α-siloxyalkyl complexes. Studies in progress are probing the role of Rh(III) hydrosilane adducts in converting iron α-siloxyalkyl complexes to their fully reduced alkyl or vinyl derivatives, surveying potential catalytic systems for hydrosilating a variety of acyl complexes, and extending these hydrosilation reactions to controlling the stereochemistry at the emerging chiral center.

Acknowledgment. We appreciate communication of unpublished results by M. Akita (ref 18). Support from the Department of Energy, Office of Basic Energy Science is gratefully acknowledged.

Supplementary Material Available: Table II containing ^1H and ^{13}C NMR and IR spectral assignments for **1b**–**11b** and **12** and microanalytical data (7 pages). Ordering information is given on any current masthead page.

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[16] In competing side reactions, $(PPh_3)_3RhCl$ efficiently catalyzes both silane redistribution and dehydrogenative coupling of dihydrosilanes to disilanes and oligomeric Si–Si bonded species.[17] Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

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[18] No reaction occurs between $FpCOCH_3$ in benzene or THF and the dihydrosilanes Ph_2SiH_2 and Et_2SiH_2 in the absence of $(PPh_3)_3RhCl$ catalyst. M. Akita and co-workers (Tokyo Institute of Technology) also have detected **9b** during $(PPh_3)_3RhCl$-catalyzed hydrosilation of FpC(O)CH_3 (**1a**), personal communication.

Ion Conductance along Lipid Monolayers

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Received April 3, 1989

We report here studies of ion conduction in lipid monolayers at water/air interfaces. Motivation for the work relates in part to the Nobel Prize-winning "chemiosmotic hypothesis" of Peter Mitchell:[1] Proton movement across a membrane creates a potential that drives ATP production. In 1983, Haines[2] proposed that this chemiosmotic flux is coupled to proton translocation *along* the membrane surface. More recently, Prats et al.[3] claimed, on the basis of fluorescent probe data, that protons do indeed diffuse rapidly among lipid headgroups. Gutman et al.,[4] however, strongly denied this assertion, citing evidence derived from a laser-excited proton emitter trapped near a membrane surface. Owing to the obvious importance of lateral ion movement along membranes and to the debate over its efficiency, we felt a direct measurement with electrodes (and requiring no incorporated probe) would be useful.

Lateral ion movement among lipids can in principle be investigated via their monomolecular films (assemblies that are structurally similar to membrane leaflets). Yet to our knowledge, only one published paper has appeared in which conductance of lipid films at various film pressures has been measured directly. Thus, Morgan et al.[5] reported enhanced conductance when a phospholipid monolayer was compressed above a critical packing density (Figure 1). In sharp contrast, we have observed a conductance *decrease* (Figure 2) upon compression of a distearoylphosphatidylcholine (DSPC) film. Details of this surprising result, possible sources of discrepancy with past work, and the mechanism of the interfacial conductance comprise the present communication.

It must be revealed forthwith that severe reproducibility problems were encountered when we (like Morgan et al.[5]) measured conductance with a dc electrical field. Thus, a dc voltage was applied to two bright Pt electrodes immersed in the subphase between the barriers of a film balance.[6] Ultimately we abandoned the dc approach because plots of conductance vs area were acceptably capricious despite a host of precautions and instrumental refinements: (a) A nitrogen atmosphere and Ascarite were used to protect the system from its extreme sensitivity to CO_2.[7] (b) An automatic dipping control was installed to achieve a repro-

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[6] Menger, F. M.; Wood, M. G., Jr.; Richardson, S.; Zhou, Q.; Elrington, A. R.; Sherrod, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6797. This article describes full experimental details on the precautions required in the use of a film balance (cleanliness, high water purity, etc.).

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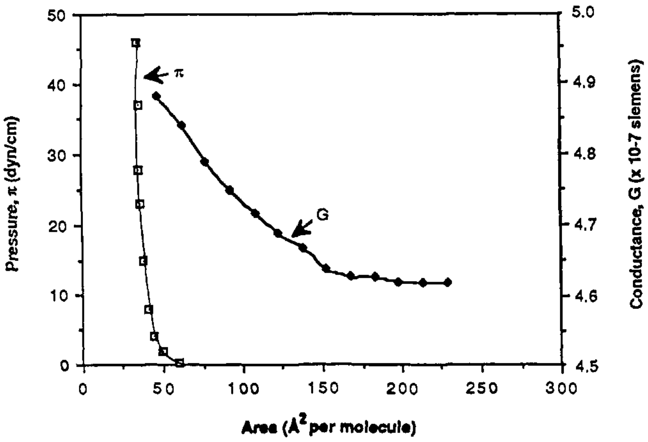

Figure 1. Plots of pressure (π) and conductance (G) vs film area for dipalmitoylphosphatidylethanolamine. Data are taken from Morgan et al.[5]

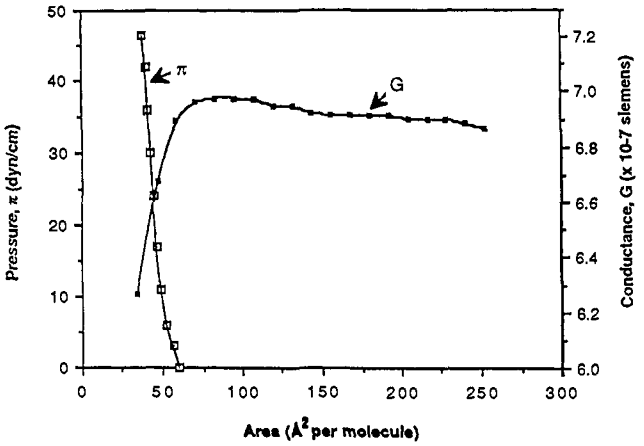

Figure 2. Plots of pressure (π) and conductance (G) vs film area for distearoylphosphatidylcholine at 23.5 °C. Plots were traced simultaneously using ac circuitry for the conductance measurements. Similar curves were obtained in deionized water and 0.5 μM NaCl as the subphase.

ducible electrode immersion depth of 3.0 mm. (c) Applied voltages were adjusted between 1.5 and 20 V to optimize response and stability. (d) A second pair of Pt electrodes was placed in the subphase but outside the film so as to subtract automatically any spurious effects. Yet even with these and other measures, the base lines (i.e., conductance vs area with no film) meandered and, in fact, often resembled the conductance data in Figure 1.

Since polarization effects, exacerbated by dc circuitry,[8] were a possible source of complications, we converted to an ac system (1000 Hz, 1.0 V rms) and thereby secured flat base lines and the data in Figure 2 on DSPC monolayers. Comparison of the pressure/area and conductance/area plots shows that DSPC has little affect on conduction, relative to the base line, until formation of a "condensed" film at high pressures causes the conduction to fall abruptly. Dioctadecyltrimethylammonium bromide monolayers display the same behavior as DSPC, proving that the "condensed film effect" is not specific to zwitterionic lipids. These observations are explainable by lateral ion movement that involves adventitious protons not the monolayer constituents. Protons move rapidly through structured water[9] believed to exist at the water/air interface.[10] This highly conducting water layer could be disrupted and proton transfer impeded, when film pressures of >3 dyn/cm create a close-packed film.

An alternative but reasonable rationale is consistent with Figure 2.[11] The ionic headgroups of a close-packed film might collect ions that normally swim freely in the subphase (similar to the way a micellar surface binds counterions).[12] Conductance would thereby decrease especially if the measurements reflect primarily the properties of the subphase. Although the molecular basis of Figure 2 is still uncertain, the data are noteworthy in showing no observable conductance along monolayers as argued for by Prats[3] and by Morgan[5] over the objections of Gutman.[4]

Several considerations mitigate against yet another explanation of Figure 2, namely that lipid is deposited on the Pt electrodes at high film pressures: (a) Deposition would have to be a highly cooperative phenomenon in order to generate an adsorption isotherm resembling the conductance/area curve in Figure 2. (b) No glitch was observed in the concurrently traced pressure/area plot as might be expected if lipid were being removed from the monolayer during compression. (c) Repeated dippings of clean electrodes through films at high pressure (20 dyn/cm) produced no detectable transfer of lipid. (d) Conductance/area curves are reversible; any binding to the electrodes would require fast desorption processes as the film re-expands.[13]

In summary, we have shown that lipid films at water/air interfaces lack any special propensity to conduct. The data are in conflict with previously published results,[3,5] but, more importantly, they imply that surfaces of biological membranes, in the absence of carriers, serve as poor conduits for ion movement.[14]

Acknowledgment. This work was supported by the Army Research Office and the National Science Foundation.

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(7) Morgan et al.[5] did not protect their system from CO_2 but, instead, allowed the subphase to equilibrate with atmospheric CO_2.

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(11) This was suggested by Professor Robert G. Bergman.

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(13) Professor Morgan has mentioned (private communication) that our results can be rationalized by a tiny decrease in the meniscus level at high film pressures. Such an effect cannot explain, of course, our flat nonconducting region from 75–250 Å²/molecule where Morgan et al.[5] claim the films conduct.

(14) Recent work has shown that rates of proton transfer in water *decrease* upon addition of 2 M NaCl. Politi, M. J.; Chaimovich, H. to appear in *J. Solution Chem.*

Diphenylbicyclo[2.1.0]pentane. A Persistent Hydrocarbon with a Very Weak C–C Bond

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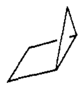
Received March 29, 1989

The bicyclo[2.1.0]pentane structure is unsurpassed among simple ring systems in the amount of strain energy (SE) released upon a single bond homolysis.[2,3] In the parent, **1**, C1–C4 bond cleavage to produce 1,3-cyclopentanediyl **2** relieves ca. 50 kcal/mol of SE.[3] This is manifest in the low barrier for the "bridge-flip" process (Figure 1), for which $\Delta H^{\ddagger} = 36.3$ kcal/mol and $\Delta S^{\ddagger} = 2.1$ eu.[4] As shown in Figure 1, 36 kcal/mol represents an upper limit to the bond dissociation energy (BDE) in **1**.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