chemistry observed is the loss of H_2 and one dfepe ligand to give products formally derived from a 12-electron (dfepe)Ru fragment. Thus, the reaction of **1** with CO is complete after 72 h at 90 °C to give (dfepe)Ru(CO)$_3$ (**2**) (ν_{CO} = 2068, 2019 (sh), and 1996 cm^{-1}), with no evidence under these conditions of partial substitution products (dfepe)$_2$Ru(CO) or (dfepe)Ru(CO)$_2$(H)$_2$, or the expected product of complete substitution, $Ru_3(CO)_{12}$. The reaction of **1** with neat benzene or toluene similarly occurs at more elevated temperatures to give not the anticipated C–H addition product, (dfepe)$_2$Ru(H)(Ar), but instead the arene complexes (η^6-C_6H_5R)Ru(dfepe) (R = H, **3**; R = Me, **4**) as yellow sublimable solids in essentially quantitative yield.[19]

The thermal behavior of **1** in neat cycloalkane solvents is of special interest. While completely unreactive at temperatures up to 150 °C, warming **1** to 180 °C for 5 days in neat cyclohexane yields the benzene complex **3** as the major (>90%) observed product.[20] No product arene ring exchange with neat C_6D_6, production of free benzene, or deuterium incorporation into the arene C–H bonds of **3** by D_2 is seen after prolonged heating at 180 °C, indicating that the formation of **3** from **1** and cyclohexane is stoichiometric and irreversible. Monitoring this process by ^{19}F and ^{31}P NMR reveals that **3** and free dfepe are the sole products during the early stages of the reaction. After prolonged heating, several uncharacterized minor side products begin to appear due to secondary reactions of **1** with released dfepe. No difference in reaction rate was noted between samples heated in the presence and absence of light; the reaction rate was similarly unaffected by the addition of metallic mercury.[21]

The generality of this transformation has been confirmed by the reactions of **1** with neat methylcyclohexane and cyclopentane at 180 °C to give (η^6-C_6H_5Me)Ru(dfepe) (**4**) and (η^5-C_5H_5)-Ru(dfepe)H (**5**), respectively, as the major (>90%) products. Complex **5** may also be quantitatively prepared from the reaction of **1** with cyclopentene or cyclopentadiene at 130 °C. A qualitative comparison of arene substitution and dehydrogenation rates run to partial completion gives the reactivity ordering for this system of cyclopentene ≫ arene > cyclopentane ≈ C_6H_{12}.[22] The greater apparent reactivity of **1** toward arenes versus cyclohexane is confirmed by the thermolysis of **1** with cyclohexylbenzene, which gives (η^6-C_6H_5Cy)Ru(dfepe) (**6**) as the exclusive product at a rate comparable to that observed for the formation of **4**. Some preliminary mechanistic information is provided by a comparison of the thermolysis reactions of **1** in the presence and absence of ambient H_2 and D_2. An approximately 2-fold inhibition in the thermolysis rate for **1** in both neat benzene and cyclopentane under 500 Torr H_2 is observed, consistent with a mechanism involving H_2 loss and the generation of a reactive (dfepe)$_2$Ru intermediate. In addition, no incorporation of deuterium into either the hydride or ring positions of **5** during the thermolysis of **1** in cyclopentane under 500 Torr D_2 is detected, indicating that there is no reversible dissociation of hydrogen in the dehydrogenation steps subsequent to the initial addition of the hydrocarbon substrate.

The thermal dehydrogenation reactions of **1** uniquely differ from most previously reported dehydrogenation systems[7,23] in that no hydrogen acceptor (*tert*-butylethylene) or photochemical conditions are required to drive the process. This difference in reactivity is presumably due to unusually strong Ru–(arene) binding in the systems examined compared to Rh and Ir analogues,[10b,24] as well as the thermal accessibility and surprising stability of reactive, highly unsaturated monochelate intermediates under the harsh conditions employed. It is particularly significant that no P–C cleavage products such as C_2F_5H have been detected in our system.[25] Furthermore, although activation of sp^2 and sp^3 C–H bonds by known thermal or photogenerated 16-electron $(\widehat{P\,P})_2M$ ($\widehat{P\,P}$ = dmpe, depe, dppe; M = Fe, Ru) intermediates is complicated by the competitive formation of inter- or intramolecular orthometalation products such as (dppe)Fe($C_6H_4PPh_2$)(H),[26] analogous "tuck-in" products derived from C–F bond addition from dfepe ligands have thus far not been identified in the reactions of **1**. In light of these observations, we believe that (fluoroalkyl)phosphine complexes offer considerable promise in the design of practical hydrocarbon activation systems. Currently our efforts are directed toward detailed mechanistic studies of the above dehydrogenation reactions and the extension of this work to more labile, potentially catalytic group VIII and IX systems.

Acknowledgment. This work has been supported by grants from the National Science Foundation (CHE-8912697) and the NSF EPSCoR program (RII-8610680).

Supplementary Material Available: Spectroscopic and analytical data for complexes **1–6** and crystallographic data for complexes **1** and **3**, including ORTEP figures, collection and refinement parameters, and tables of positional parameters and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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(19) With the exception of **2**, which was obtained as an oil contaminated with ≈10% dfepe, all reported compounds were isolated in 69–81% yield as analytically pure crystalline solids; see supplementary material for full characterization data. Selected data for **3**: ^{1}H NMR (C_6D_6) δ 5.10 (s, 6 H, C_6H_6), 1.75 (m, 4 H, PCH_2); ^{13}C NMR ($(CD_3)_2CO$) δ 88.49 (d, $^1J_{CH}$ = 175 Hz, C_6H_6). For **5**: ^{1}H NMR (C_6D_6) δ 4.83 (s, 5 H, C_5H_5), 1.76 (m, 4 H, PCH_2), −13.58 (t, $^2J_{PH}$ = 35 Hz, 1 H, RuH); ^{13}C NMR (C_6D_6) δ 83.25 (dt, $^1J_{CH}$ = 179 Hz, $^2J_{CP}$ = 7 Hz, C_5H_5). The crystal structure of **3** has also been determined; details are included in the supplementary material.

(20) The production of H_2 in the conversion of **1** to **3** was qualitatively verified by GC.

(21) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

(22) Preliminary kinetic experiments were run on 1.30 × 10^{-3} M solutions of **1** (0.5 mL) in sealed 5-mm NMR tubes and followed by ^{19}F NMR. The following approximate half-lives were obtained: C_5H_8 (164 °C, $t_{1/2}$ = 45 min), C_6H_6 (164 °C, $t_{1/2}$ = 12 h), C_5H_{10} (195 °C, $t_{1/2}$ = 35 h), C_6H_{12} (195 °C, $t_{1/2}$ = 60 h). At these concentrations, no inhibition by released H_2 was observed.

(23) Rhodium-catalyzed homogeneous dehydrogenation of cyclooctane under H_2 purge conditions has recently been reported: Fujii, T.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 757.

(24) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217.

(25) This observation is consistent with Hoffmann's prediction that electron-withdrawing phosphorous substituents should be less prone to P–C cleavage: Ortiz, J. V.; Havlas, J.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

(26) Azizian, H.; Morris, R. H. *Inorg. Chem.* **1983**, *22*, 6.

Gemini Surfactants: Synthesis and Properties

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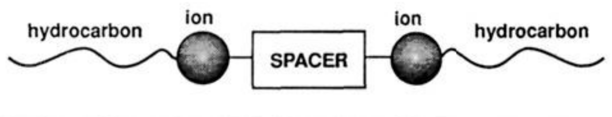
Single-chained amphiphiles (e.g., sodium dodecyl sulfate) form, in aqueous solution, spherical aggregates called micelles. Ionic head-groups of micelles lie near the water, whereas the hydrocarbon tails project inwardly.[1] Double-chained amphiphiles (e.g., didodecyldimethylammonium bromide) form bilayer sheets. These aggregates are also organized such that the ionic groups reside on the outside while the hydrocarbon tails extend into the bilayer away from the water.[2] We have synthesized and studied a new type of amphiphile, called gemini surfactants, which are intriguing because (unlike conventional surfactants) there is no way for them to aggregate without exposing hydrocarbon moieties to the water. The molecules possess, in sequence, a long hydrocarbon chain, an ionic group, a rigid spacer, a second ionic group, and another hydrocarbon tail. Initial concern that the compounds might not



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(1) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982. Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978. Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

(2) Ostro, M. J. *Liposomes*; Marcel Dekker: New York, 1983.

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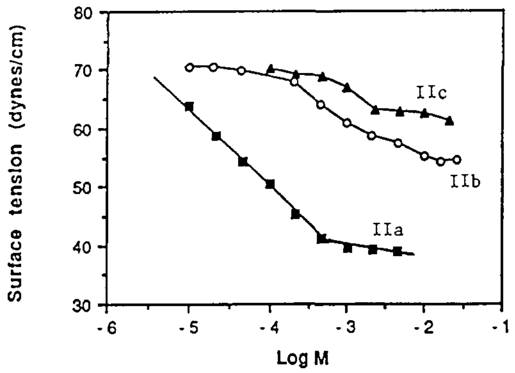
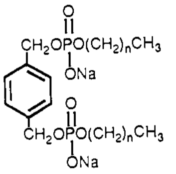
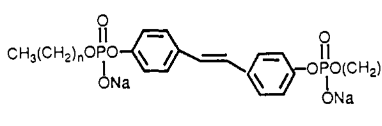


Figure 1. Plots of surface tension at 23 °C vs log concentration of IIa, IIb, and IIc. IIa (but not IIb or IIc) shows a break attributable to micelle formation. Only small differences were noted with surfaces aged 24 h.

even dissolve in water turned out to be unfounded, so we prepared two series of them (I and II) and report on their highly unusual properties below.



I
a, n = 7
b, n = 11
c, n = 15



II
a, n = 11
b, n = 15
c, n = 19

Compounds Ia and Ib were obtained by reacting α,α'-dibromo-*p*-xylene with a dianionic long-chain alkyl phosphate (yields: Ia, 50%; Ib, 84%).[3,4] Series II and Ic were obtained by phosphorylating the diol of the appropriate spacer with $POCl_3$ and then reacting the product with a long-chain alcohol to form the mixed dialkyl phosphate ester (yields: IIa, 38%; IIb, 73%; IIc, 80%; Ic, 40%).[5] Compounds were (a) purified as the free acid by recrystallization and/or trituration; (b) characterized by elemental analysis, NMR, and FAB-MS; and (c) converted into the sodium salts.

Critical micelle concentrations (cmc's) were determined at 23 and 50 °C by means of surface tension (ST) measurements.[6] Plots of ST vs log concentration for Ia and Ib at 23 °C gave sharp breaks corresponding to cmc's of 5.5 and 0.17 mM, respectively. The two surfactants at their cmc's lowered the ST of water by 28 dyn/cm. In contrast, Ic showed no cmc and lowered the ST of water by only 11 dyn/cm at 5 mM. At 50 °C, all three compounds were surface active, but Ic (with two C_{16} chains) had a cmc of 2.0 mM, which was much higher than the cmc of 0.11 mM for Ib (with two C_{12} chains). A higher cmc (i.e., a lower propensity to aggregate) for a longer chain analogue runs counter to all previously reported trends in surfactant chemistry.[1]

We next examined series II in which the ionic head-groups are forced apart even further by a stilbene spacer. Full "side-by-side" contact between two chains of the same molecule (as in phospholipid bilayers) was thereby precluded. Figure 1 shows that at 23 °C IIa (but not IIb or IIc) displays a cmc. Figure 2 shows that at 50 °C all three are surface active, but IIa with C_{12} chains has a cmc 23 times *lower* than that of IIc with C_{20} chains!

In view of these remarkable results, it seemed prudent to examine aggregation by an independent method. A spectrophotometric study using a dye, pinacyanol chloride, was therefore initiated.

Pinacyanol chloride (5×10^{-6} M) is pink below the cmc of anionic surfactants and bright blue above it.[7] Dye in solutions

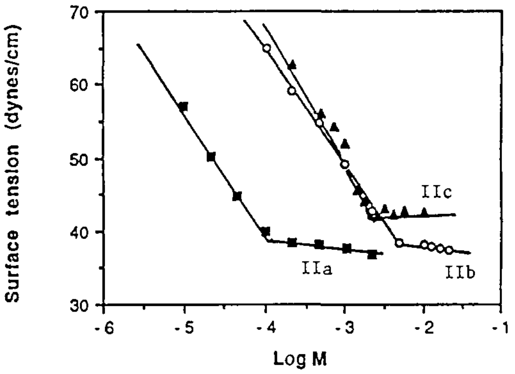
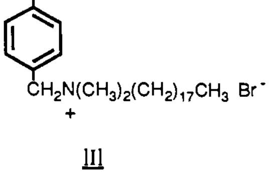


Figure 2. Plots of surface tension at 50 °C vs log concentration of IIa, IIb, and IIc. Note that the break in the plot (corresponding to the cmc) is lowest for the shortest chain surfactant, IIa.

of IIa gave a color change at about 1×10^{-4} M (23 °C), corresponding to a cmc somewhat lower than that obtained by the ST method. More interestingly, IIb and IIc produced characteristic micellar spectra (i.e., a blue color with absorbance at 610 nm) at all surfactant concentrations examined ($\geq 1 \times 10^{-5}$ M) and at both 23 and 50 °C. Even *below* the cmc's evident in Figure 2, IIb and IIc manifested micelle-type spectral effects. This cannot be due to some sort of 1:1 charge-transfer complex because, as indicated above, mixtures of dye and the analogous IIa are an "uncomplexed" pink below the cmc of the latter. The simplest explanation is that IIb and IIc form small ST-undetectable aggregates[8] at very low concentrations. Only above 10^{-3} M at 50 °C is there any evidence of cooperative aggregation (Figure 2). Thus, the cmc of IIc at 50 °C represents the aggregation of small clusters into larger ones; it occurs at a 23-fold-higher concentration than does the monomer-to-micelle conversion with the short-chained IIa.[9] In summary, IIc has a high cmc, despite its two 20-carbon chains, because the compound is substantially preassembled well below the cmc.

Quaternary ammonium gemini surfactants tended to be much less water soluble than the phosphate derivatives. In fact, III was sufficiently water insoluble to permit monolayer studies on a film balance.[9] Pressure–area isotherms at 23 °C revealed an abnormally large lift-off area[10] of 246 Å^2/molecule (compared to only 60 Å^2/molecule for distearoylphosphatidylcholine). Molecular mechanics gave a calculated area for fully extended III of about 236 Å^2/molecule. This shows that III has a singular preference for lying absolutely flat on the water surface at the onset of intermolecular contact. Nonhorizontal orientations, which would force an unbent chain into the aqueous subphase, are clearly disfavored.



III

Characterization of the gemini surfactants by quasi-elastic light scattering, NMR, and other methods is continuing.

Acknowledgment. This work was supported by the National Institutes of Health and the National Science Foundation. We thank Dr. Susan Richardson for carrying out the film balance measurements.

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(5) Eibl, H. *Methods Enzymol.* **1983**, *98*, 623.

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(8) A few cases are known in which surfactant molecules cannot align at the air/water interface even though they aggregate in water. See: Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1980**, *102*, 549.

(9) Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.

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