Preparation and Photochemical Reactivity of Surfactant Ruthenium(II) Complexes in Monolayer Assemblies and at Water–Solid Interfaces[1,2]

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Abstract: The syntheses of several surfactant analogues of tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ is described together with a study of their photochemistry in spread films, monolayer assemblies, and at a monolayer assembly–water interface. It has been found that highly purified samples of the dioctadecyl ester of (4,4′-dicarboxy-2,2′-bipyridine)bis(2,2′-bipyridine)ruthenium(II)$^{2+}$ are inactive as catalysts for the photocleavage of water in monolayer assemblies. This is contrary to our previous findings, which employed a sample of the surfactant complex which has now been shown to contain several impurities, including other surfactant ruthenium(II) complexes. The properties of films and monolayer assemblies of these complexes are found to be quite sample sensitive even when different samples of high indicated purity are employed. The failure of the highly purified complex to serve as a catalyst appears partially due to a light-induced destruction of assemblies irradiated in contact with water, which is due at least in part to a photohydrolysis of the ester group.

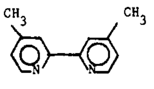
The photochemistry of the tris(2,2′-bipyridine)ruthenium(II) dication ($Ru(bpy)_3^{2+}$) and related metal complexes has been the subject of considerable recent investigation.[3-19] It has been found that the excited states of $Ru(bpy)_3^{2+}$ and other complexes having relatively long excited state lifetimes can be quenched by energy transfer, complex formation, and electron transfer processes. The latter have been observed both for cases where the excited state of $Ru(bpy)_3^{2+}$ serves as an electron donor[3-7] as well as for instances where it acts as an electron acceptor.[8-10] There has been intense interest in the possibility that light driven electron transfer reactions can serve as useful energy conversion and storage processes,[20-21] since the initial products of electron transfer are usually highly energetic, but stable, when isolated, molecules. In solution the high-energy products are rapidly degraded through reverse electron transfer with each other to form ground-state starting materials.[6,7] Recently, interest has developed in the possibility of inhibiting these back reactions by various techniques, including the initiation of competitive processes or the carrying out of the reactions in other media.[11,21]

In recent investigations, we have examined the photochemical reactivity of a number of chromophores in organized monolayer assemblies.[1,2,22-24] In several cases it has been found that the controlled and highly condensed environment provided by the assemblies can strongly modify photoreactivity and luminescence behavior from that observed in solution. Our interest in light driven electron transfer processes involving $Ru(bpy)_3^{2+}$ led us to prepare surfactant complexes of ruthenium(II) for incorporation into monolayer assemblies. In a recent communication[2] we reported that the strong luminescence of a surfactant ruthenium complex could be quenched by immersion of assemblies containing the complex into water. Concomitantly, the light-induced cleavage of water to yield hydrogen and oxygen was observed. The present paper reports details of the preparation of the surfactant ruthenium complex together with a more detailed study of the photochemistry and luminescence phenomena of the complexes in monolayer films and assemblies. The results of this study indicate that both the photochemical reactivity and the luminescence behavior of monolayer assemblies containing the ruthenium complex are strongly dependent on the sample employed and its purity. It has been found that highly purified samples of the surfactant ruthenium complex used in the original study are inactive toward catalytic light-induced cleavage of water under the same conditions used in the original study. In fact, films of the purified complex in contact with water are relatively rapidly degraded under irradiation in what appears to be at least partially an ester photohydrolysis. The results obtained in this study suggest that impurities in the original preparation, possibly other surfactant ruthenium complexes, may have been responsible for the observed photoinduced cleavage of water.

Experimental Section

General. Melting points were obtained on a Büchi apparatus and are uncorrected. Elemental analyses were performed by Integral Microlab, Raleigh, N.C. NMR spectra were obtained on a Jeolco 060 H 1 or Varian XL-100 spectrometer. Absorption spectra were recorded with a Cary 17 I spectrometer; for measurements on glass slides five coated slides were used with the reference beam passing through five slides, each coated with five layers of cadmium arachidate. Fluorescence excitation and emission spectra were recorded with a Hitachi-Perkin Elmer MPF-2A spectrophotometer containing a red sensitive Hamamatsu R-446 photomultiplier and were uncorrected for photomultiplier response. Comparison measurements were taken on the same day; spectroscopic reproducibility was generally within a few percent. Gas analyses were obtained on a VEECO GA 4 residual gas analyzer, on an MS-9 mass spectrometer, and on a Goll Mac gas chromatograph having a column filled with molesieves 4 Å, a thermoconductivity detector, and argon as a carrier gas. Blanks were run on wet air and standards containing hydrogen, oxygen, and wet air were also measured. Resolutions at room temperature for hydrogen, oxygen, and nitrogen were satisfactory. The lower detection limit for hydrogen was found to be 2–3 × 10^{-9} mol.

Preparation of 4,4′-Dimethyl-2,2′-bipyridine (1).[25] Freshly distilled 4-picoline (700 mL) and 28 g of palladium (10% on charcoal) were refluxed for 3 days. After addition of 250 mL of hot benzene reflux was continued for 0.5 h. The mixture was filtered from the catalyst when still hot. The filtrate was concentrated in vacuo to 300 mL. Almost colorless crystals precipitated. Recrystallization from ethyl acetate yielded 40 g of colorless crystals: mp 175–179 °C. Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.22; H, 6.56; N, 15.20. Found: C, 77.61; H, 6.47; N, 15.19. NMR spectrum (in $CDCl_3$): d at 8.54 (2), t at 8.24 (2), dq at 7.14 (2), and s at 2.42 ppm (6).



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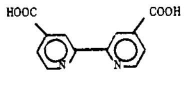

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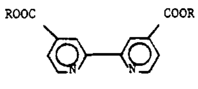


(3)

a R = $C_{18}H_{37}$

b R = $C_{27}H_{46}$

Preparation of 4,4′-Dicarboxy-2,2′-bipyridine (2). 1 (16 g) and 50 g of potassium permanganate were heated at reflux in 560 mL of water for 12 h. Removal of the brown precipitate by filtration gave a yellowish solution, which was extracted with ether to remove unreacted starting material. Addition of concentrated hydrochloric acid precipitated white crystals, which were washed well with water and were insoluble in all organic solvents. Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.30; N, 11.50. Found: C, 59.10; H, 3.66; N, 11.50.

Esterification of 2. 2 (600 mg) and 6 mL of thionyl chloride were refluxed for 3 h. A yellow solution resulted. Excess thionyl chloride was evaporated under vacuum and the residue dried under vacuum for 2 h. Dry benzene (20 mL) was added and the solution treated with a slight excess of 1-octadecanol or dihydrocholesterol. The mixture was refluxed for 2 h more. Chloroform (40 mL) was added and the mixture treated with cold aqueous sodium bicarbonate. The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. Recrystallization from acetone/chloroform yielded colorless crystals. Octadecyl ester **3a:** mp 87 °C; NMR spectrum (in $CDCl_3$) d at 9.09 (2), t at 9.18, (2), dq at 8.12 (2), t at 4.62 (4), and m at 1.50 ppm (70). Dihydrocholesteryl ester **3b:** mp 280-285 °C dec. Anal. Calcd for $C_{66}H_{100}N_2O_4$; C, 80.48; H, 10.16; N, 2.84. Found: C, 78.37; H, 10.43; N, 2.56. NMR spectrum: d at 8.88 (2), t at 8.94 (2), dq at 7.92 (2), t at 5.00 (2),and 0.5-2.00 ppm, the typical dihydrocholesteryl pattern.

Preparation of *cis*-Dichlorobis(bipyridine)ruthenium (4). Commercial ruthenium trichloride (15.6 g) and 18.72 g of 2,2′-bipyridine were heated at reflux in 600 mL of *N,N*-dimethylformamide for 3 h. Most of the solvent was then distilled off. The remaining solution was then cooled to room temperature, treated with 500 mL of acetone, and kept at 0 °C overnight. The crystals formed were collected by suction filtration and washed with water. The crude product was suspended in 2500 mL of water-ethanol (1:1) and heated to reflux for 1 h, filtered from insoluble solid and treated carefully with 300 g of lithium chloride. Ethanol was distilled off and the resulting water solution was cooled in an ice bath. Dark crystals precipitated. They were dried in vacuo for 2 h. Absorption spectrum (in ethanol): 550 and 375 nm. Anal. Calcd for $C_{20}H_{20}N_4O_2Cl_2Ru$: C, 46.15; H, 3.84; N, 10.76; Cl, 13.65. Found: C, 44.65; H, 3.86; N, 10.70; Cl, 13.61.

Surfactant Derivatives of Tris(2,2′-bipyridine)ruthenium $(bpy)_2$-$Ru^{II}[bpy(COOC_{18}H_{37})_2]^{2+}$ (5). Sample 5a. 4 (250 mg) and 370 mg of **3a** were heated at reflux in 50 mL of degassed ethanol under nitrogen atmosphere for 4 h. Water and some sodium perchlorate were added to begin precipitation and the mixture was refrigerated overnight. The brown solid that formed was collected by filtration. In order to remove unreacted **3a** the complex was dissolved in acetone, in which **3a** is insoluble. This solid was then washed with water and pentane. Anal. Calcd for $C_{68}H_{96}N_6O_{12}Cl_2Ru$: C, 59.98; H, 7.12; N, 6.17. Found: C, 60.10; H, 7.07; N, 5.87. Absorption (in chloroform) 478 nm (ϵ_{max} 13 100); emission (in chloroform) 660 nm.

Samples 5b. Succeeding preparations were carried out following the same procedure. The obtained complex was purified by several recrystallizations from chloroform at −20 °C.

Sample 5c. In a similar preparation sodium perchlorate was replaced by ammonium hexafluorophosphate. No spectroscopic changes took place.

Sample 5d. A perchlorate sample prepared as **5b** by Dr. S. Valenty at the General Electric Laboratories.[31]

Sample 5e. 4 (520 mg), 300 mg of **2,** and 300 mg of sodium bicarbonate were heated in 15 mL of water and 10 mL of methanol for 2 h at reflux temperature. At the end of the reaction aqueous ammonium hexafluorophosphate was added and the solution refrigerated overnight. Red crystals of bis(bipyridine)-4,4′-dicarboxy-2,2′-bipyridineruthenium (**6**) precipitated. Anal. Calcd for $C_{32}H_{24}N_6O_4P_2F_{12}$: C, 39.73; H, 2.69; N, 8.78. Found: C, 40.46; H, 2.52; N, 8.85. Absorption (in water) 455 nm at pH 12.5 and 420 and 475 nm at pH 0.6.

The obtained diacid **6** was refluxed in a mixture of 20 mL of benzene and thionyl chloride (1:1) for 24 h. Evaporation of the solvents to dryness yielded a dark brown nonluminescing solid: absorption (in acetonitrile) 430 nm (shoulder at 475 nm). A dry benzene solution containing a slight excess of octadecanol was added and the mixture refluxed for 2 h. The solution was then carefully treated with cold aqueous sodium bicarbonate and evaporated to dryness. Recrystallization from chloroform at −20 °C yielded brown crystals of **5e,** which showed the same spectroscopic properties as the samples above.

$(bpy)_2Ru^{II}[bpy(COOC_{27}H_{46})_2]^{2+}$ (7). 7 was obtained by following essentially the same procedures: in the procedure for **5a, 3a** was replaced by **3b;** in the procedure for **5e,** octadecanol was replaced by dihydrocholesterol.

$[(bpy[COOC_{27}H_{46}]_2)_3Ru]^{2+}$ (8). (**A**) Ruthenium trichloride (87 mg) and 657 mg of **3b** were refluxed in 20 mL of *N,N*-dimethylformamide for 3 h. Most of the solvent was distilled off, acetone added, and the solution refrigerated overnight. Dark crystals of **9** precipitated. They were recrystallized from methylene chloride/acetonitrile. Anal. Calcd for $C_{132}H_{200}N_4O_8Cl_2Ru$: C, 72.79; H, 9.37; N, 2.57; Cl, 3.26. Found: C, 72.47; H, 9.13; N, 2.65; Cl, 4.14.

The tetraester **9** (550 mg) and 253 mg of **3b** were suspended in a little ethanol and heated in a sealed glass tube at 80-90 °C for 4 days. Ammonium hexafluorophosphate was added and the obtained solid recrystallized from acetone/dichloromethane. Anal. Calcd for $C_{198}H_{300}N_6O_{12}P_2F_6Ru$: C, 68.55; H, 9.03; N, 2.51. Found: C, 68.75; H, 9.03; N, 2.79.

(**B**) Ruthenium trichloride (260 mg) and 3.5 g of **3b** were suspended in ethanol and heated in a sealed glass tube at 140 °C for 4 days. Addition of some water precipitated dark crystals, which were not further investigated. The mother liquor was allowed to stand overnight at room temperature. Colorless crystals of **3b** precipitated. After filtration from these, half of the solvent was removed under vacuum. On addition of aqueous ammonium hexafluorophosphate brown crystals precipitated. They were collected and dried under vacuum: absorption (in chloroform) 460 nm; emission (in chloroform) 630 nm.

Preparation of a Surfactant Paraquat, 1,1′-Dioctadecyl-4,4′-bipyridine (10). 4,4′-Bipyridine (300 mg) and 3 g of $BrC_6H_4SO_3C_{18}H_{37}$ were refluxed in 70 mL of acetonitrile. On pouring the solution into 400 mL of anhydrous ether white crystals precipitated. They were recrystallized from acetonitrile. Anal. Calcd for $C_{58}H_{92}N_2Br_2S_2O_6$: C, 61.19; H, 8.15; N, 2.46; Br, 14.05; S, 5.64. Found: C, 59.82; H, 7.93; N, 2.35; Br, 13.29; S, 5.41.

Preparation of Octadecyltrimethylammonium Bromide (OT). 1-Bromooctadecane (266 g) and 12 g of trimethylamine were dissolved in 15 mL of ethanol and heated in a sealed glass tube at 90 °C overnight. Colorless crystals precipitated. They were recrystallized from ethanol, yield 25 g, mp 250 °C dec. Anal. Calcd for $C_{21}H_{46}NBr$: C, 64.28; H, 11.73; N, 3.57; Br, 20.40. Found: C, 63.93; H, 12.89; N, 3.42; Br, 19.96.

Preparation of (*p*-Methoxyphenyl)-8-phenyl-1,3,5,7-octatetraene (11). The method used for preparation of **11** has been previously reported.[22]

Micelles. The pure "spider-complex" **8** itself does not readily form micelles. Good micellization occurs in the presence of octadecyltrimethylammonium bromide (OT). In order to approximate the close packing order of monolayer assemblies, we attempted to incorporate as many complex molecules as possible into one micelle.

In a typical experiment 10 mg of **8** were stirred in 10 mL of a 10^{-5} M solution of OT in triply distilled water containing 1.288 g of sodium chloride per liter at room temperature for 6 weeks in the dark. The mixture was then allowed to settle for 3 days.

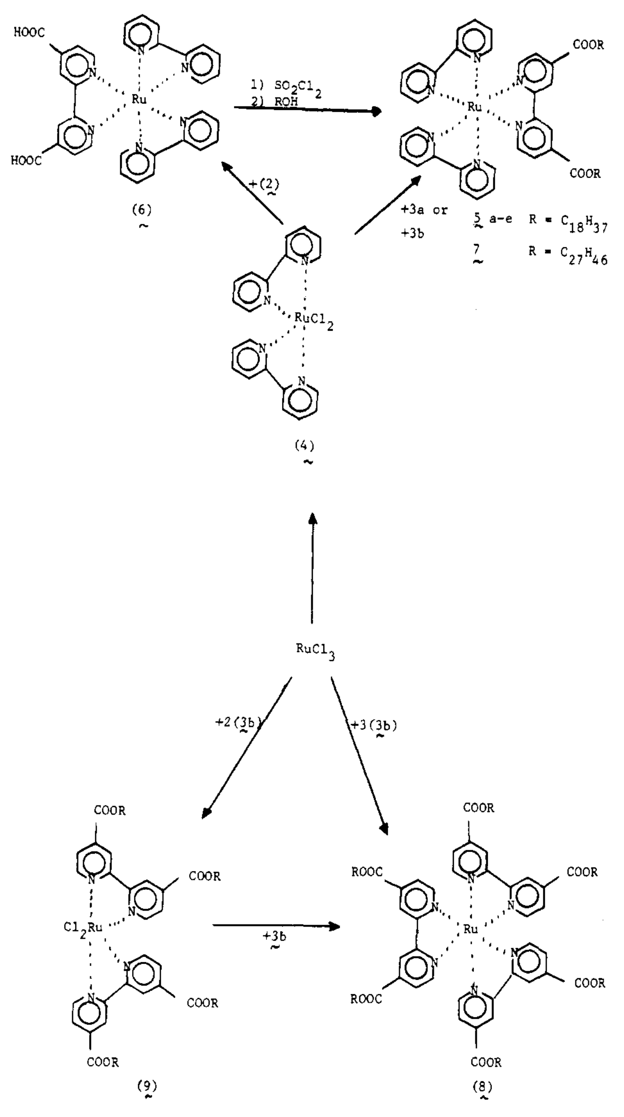
Micellar solutions exhibited an absorption maximum at 445 nm and a shoulder at 465 nm. They showed intense luminescence with a maximum at 655 nm. Based on absorbance measurements (ϵ 14.000) in the micelles and assuming complete statistical distribution the obtained micelles contain approximately seven molecules of **8** per molecule of OTAB. The aggregation number has not been determined. Chloroform easily extracted **8** from micelles. The solution showed an absorption maximum at 468 nm and emitted at 635 nm.

Preparation of Monolayers. Monolayer assemblies were prepared by spreading dilute (ca. 10^{-3} M) chloroform solutions of the surfactant molecules on a water surface in a trough[29] containing triple distilled water which was 0.5 × 10^{-4} M in sodium bicarbonate and 3 × 10^{-4} M in cadmium chloride.[29] The spread monolayers were transferred to glass slides by slowly (1 cm/min) passing the slides through the solution and the film at constant surface pressure (20 or 30 dyn/cm). The precise deposition ratio was not determined.

The glass slides were purchased from Gebrüder Rettberg, Göttingen, West Germany. They were cleaned prior to use in ultrasonic cleaners with a solution of Trokil 764 (a detergent purchased from J. A. Banckiser, Ludwigshafen, West Germany) and several successive rinses with doubly distilled water. Finally, they were dried by a heat gun.

Surface Pressure Area Diagrams. The isotherms were taken at 21.5 °C by spreading a known volume (usually 50-400 μL) of 10^{-3} M solutions at an initial surface pressure of 5 dyn/cm. The decrease of occupied area (measured by relative travel of the float) on adding

Scheme I



weights was observed until the monolayer collapsed; the measurement was made as soon as the float stopped its travel (within 5 s). The reproducibility was ±1 Å^2 at small areas (≤20 Å^2), ±5 Å^2 at larger areas (>40 Å^2). The curves obtained in this manner agreed well with those obtained for the same samples in other laboratories.[30]

Gas Generation Experiments. In typical experiments approximately 20-60 glass slides coated with six layers of arachidic acid and one layer of **5a** were placed into a teflon slide holder having slits of appropriate size. This device was placed into a beaker and covered with a glass dome (total volume 150-200 cm^3). The beaker and glass dome were filled with triple distilled water (by evacuating the air space with plastic tubing) and irradiated with (a) mercury flood lamp (100 W), (b) xenon lamp (1000 W), and (c) bright sunlight, collected by three mirrors. The slides were held ca. 1 mm apart and the light source was approximately 30 cm from the apparatus in the case of the mercury flood lamp. An estimated intensity of light reaching the sample through Pyrex in the initial experiments was 1-5 × 10^{-3} W cm^{-2}.

Results and Discussion

Synthesis and Analysis of Surfactant Ruthenium(II) Complexes. As reported in detail in the Experimental Section and outlined in Scheme I, the surfactant ruthenium(II) complexes were generally prepared by complexing $RuCl_3$ or $(bpy)_2Ru^{II}Cl_2$ with the dioctadecyl or bis(dihydrocholesteryl) esters of 2,2′-bipyridyl-4,4′-dicarboxylic acid. In the initial preparation of the ruthenium complex with two octadecyl chains (**5a**) the material obtained from condensation of **3a** and **4** appeared completely converted to the trisbipyridine complex; this complex gave a satisfactory analysis and a reasonable ϵ_{max} 13 000 at 478 nm and was therefore used without further purification. This was the sample used in the photochemical experiments where sustained gas evolution occurred (vide infra). Subsequent analysis of this material by high-pressure liquid chromatography[31] revealed that this sample contained, in addition to the dioctadecyl ester, substantial amounts of two other ruthenium(II) complexes absorbing at 280 and 475 nm. Based on their retention times, these are tentatively identified as the monoethyl, monooctadecyl ester (**12**) and the dicarboxylic acid (**6**).[31] In subsequent preparations the initial product was purified by several recrystallizations from chloroform. Both perchlorate (**5b**) and hexafluorophosphate (**5c**) salts were obtained and purified through these procedures. Analyses by high-pressure liquid chromatography indicated small amounts of other ruthenium(II) complexes were present in each case. The perchlorate and hexafluorophosphate salts could also be obtained by preparing the dicarboxylic acid ruthenium(II) complex **6** and subsequently esterifying it via the acid chloride. The diester complex **5e** prepared in this manner probably has fewer impurities due to the lack of opportunity for transesterification or ester hydrolysis during the workup.

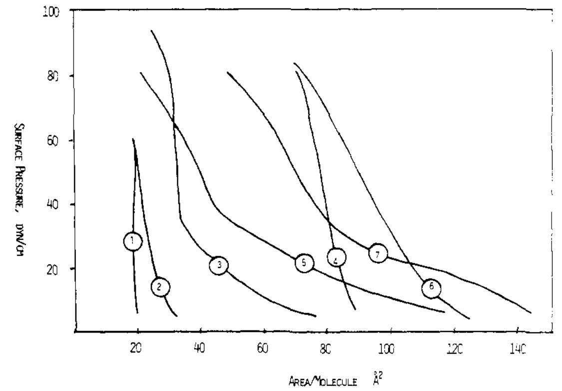


Figure 1. Surface pressure-area isotherms at 21.5 °C: curve 1, arachidic acid; curve 2, compound **3b**; curve 3, sample **5a**; curve 4, sample **5c**; curve 5, unpurified **5**; curve 6, compound **8**; curve 7, purified **5b**.

Monolayer Films of Surfactant Ruthenium(II) Complexes. Complexes **5a–e**, **7**, and **8** were insoluble in water and dropwise introduction of dilute (10^{-3} M) chloroform solutions onto a clean water surface led to the formation of monolayer films. The hexa(dihydrocholesteryl) ester complex (**8**) gave a reasonable surface pressure-area isotherm on water (21.5 °C) with an area per molecule of ca. 100 Å^2 at a surface pressure of 30 dyn/cm on a $Cd^{2+}/NaHCO_3$ subphase (Figure 1). The different samples of dioctadecyl ester (**5a–e**) gave rather different (but quite reproducible for each sample) isotherms, several of which are shown in Figure 1. The original preparation gave an isotherm which yielded a surprisingly low area of ca. 40 Å^2/molecule at 30 dyn/cm.[30] In contrast, the perchlorate purified by repeated recrystallization gave a somewhat similar isotherm which was displaced to higher areas/per molecule giving a value of 85 Å^2/molecule at 30 dyn/cm. The purified hexafluorophosphate salt gave a similar area per molecule at 30 dyn/cm, but its isotherm was much steeper, probably indicating a different packing in the film. A similar range of variations with different preparations has been noted by other investigators;[31,32] evidently, the packing in monolayer films is quite sensitive to surfactant impurities and to counterions present in the aqueous subphase.[32] In several cases it was found that film properties were time dependent; this could be noted both in the luminescence properties of transferred layers (vide infra) as well as by decreases in the area of the spread film on standing both in the dark and under irradiation. This was much more pronounced with certain samples (vide

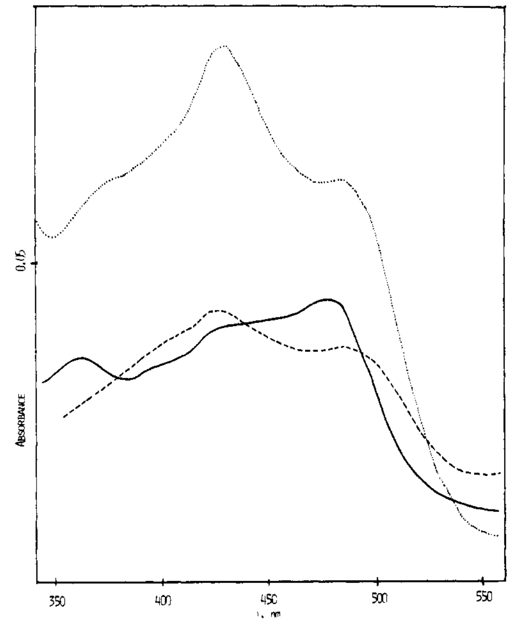


Figure 2. Absorption spectra of **5a** in chloroform solution (—) and in monolayer assemblies: (- - - -) single layer covering six layers of arachidate (5 slides); (· · ·) three layers of **5a** on glass (5 slides).

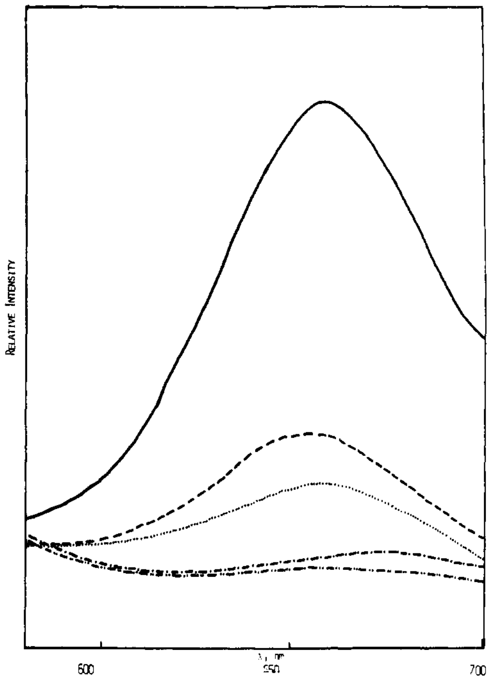


Figure 3. Luminescence spectra from monolayer assemblies of various samples of **5**: (—) **5a**; (· · ·) **5b**; (- - -) **5c**; (- · · · ·) "crude" **5b**; (- · · · · ·) **5d**.

infra) than with others. Evidently, the changes that occur when spread films of complex **5b** are allowed to stand on water do not involve a major decomposition of the ruthenium complex. In one set of experiments, films were spread and allowed to stand (a) in the dark for 30 min and (b) under irradiation with a 100-W mercury flood lamp for 30 min. In both cases the complex was recovered by aspiration of the film; analysis by absorption, eission, and excitation spectra revealed no detectable difference in either case.

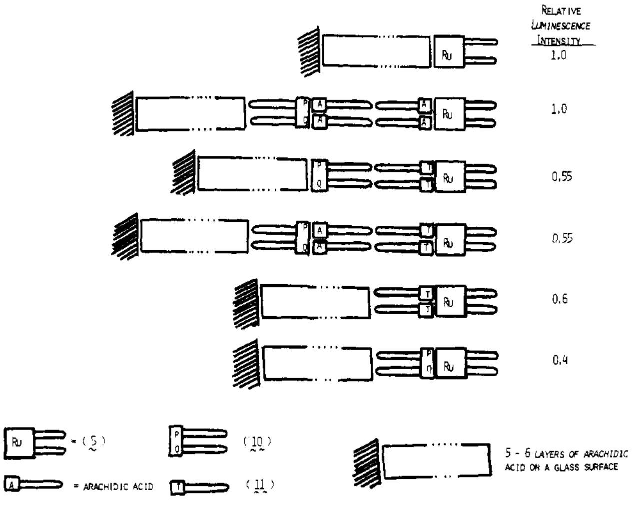
Monolayer Assemblies of Surfactant Ruthenium(II) Complexes. Although the various samples of complex **5** readily form monolayer films either alone or in mixtures with fatty acids such as arachidic acid, we have found it difficult to build monolayer assemblies containing more than a single transferred layer of pure **5** or **5**-arachidic acid mixtures with a ratio **5**/arachidic acid greater than 1:5. Furthermore, we have found it difficult to coat slides having an outermost layer of **5** with films containing other surfactant molecules. In some cases we have obtained assemblies containing three layers of **5** by direct deposition on glass slides; however, in most cases, we have employed assemblies where a single layer of pure **5** is the last layer deposited onto a hydrophilic surface of the assembly. The formation of good assemblies only on hydrophilic surfaces seems to be a property of all surfactant ruthenium complexes examined, including **5**, **7**, **8**, and others containing two and four surfactant groups whose properties and preparation are not reported here. Attempts were made to improve the coating properties by forming less viscous triple mixtures[33] containing various amounts of arachidic acid (4.5–47.6%), methyl stearate (33.3–82%), and ruthenium complex (1.6–33.3%). In no case were the coating properties noticeably improved.

For absorption and luminescence studies, we have generally employed glass slides coated with six layers of cadmium arachidate and an outermost layer of pure **5**. The absorption spectrum of one of these assemblies is shown in Figure 2; although there are some small variations in intensity, all samples of **5** give essentially the same absorption spectra in the assemblies. The absorption spectrum in the assemblies of **5** is altered from that in chloroform solution; the solution absorption maximum of 468 nm is replaced by a maximum 425 nm in the assemblies with a shoulder at 480 nm. Multiply coated (three layers) slides gave essentially the same spectra with the anticipated increase in absorbance.

Although the solution absorption and emission spectra of all samples of **5** included in this study were identical, the emission spectra obtained for different samples for monolayer assemblies prepared under comparable conditions show dramatic differences as illustrated in Figure 3. Strong variations were observed in both the intensity of the emission and the location of the maxima; however, good reproducibility for each sample was observed demonstrating that the effect is sample dependent, not measurement dependent. For example, the emission intensity of **5a** is nearly 200 times that of **5d**; the emission maxima varied from 645 to 670 nm. Although transfer ratios were not measured, the absorbance produced by slides containing different samples of **5** was the same within experimental error, indicating that the relative emission intensities should be an indication of relative luminescent efficiencies. Samples **5a** and **5c** showed no dependence on the time the spread monolayer film was allowed to remain on the water surface before deposition; however, some preparations of **5b** and **5d** showed rather striking dependence with a decrease in the emission intensity and a shift in the emission maxima to longer wavelength for the films allowed to remain standing before deposition.

Luminescence Quenching. Since it has been shown in numerous investigations that the strong luminescence of nonsurfactant ruthenium(II) complexes such as $(bpy)_3Ru^{II\,2+}$ can be quenched in solution through electron transfer and energy transfer processes, it was of interest to determine whether the same processes can occur in monolayer assemblies. Assemblies were constructed in which complex **5** was positioned in layers adjacent to layers containing the surfactant electron acceptor (**10**) and the potential triplet quencher (**11**). In each case the presence of **10** or **11** in adjacent layers or in the same layer led to significant quenching of the luminescence from **5** (Table I). Separation of layers containing **10** from those containing **5** by two or more layers of cadmium arachidate generally resulted in no quenching of the luminescence as expected for an electron transfer process which requires near contact of the electron donor and acceptor. Although both **10** and **11** produced sig-

Table I. Quenching of the Luminescence of Surfactant Complex **5** by Potential Electron Acceptors and Energy Acceptors within Monolayer Assemblies



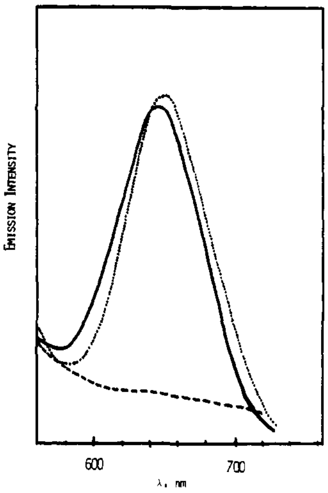


Figure 4. Quenching and regeneration of the luminescence of **5a** in monolayer assemblies: (···) freshly coated slide; (- - -) after immersion in water; (—) after gentle heating in vacuum.

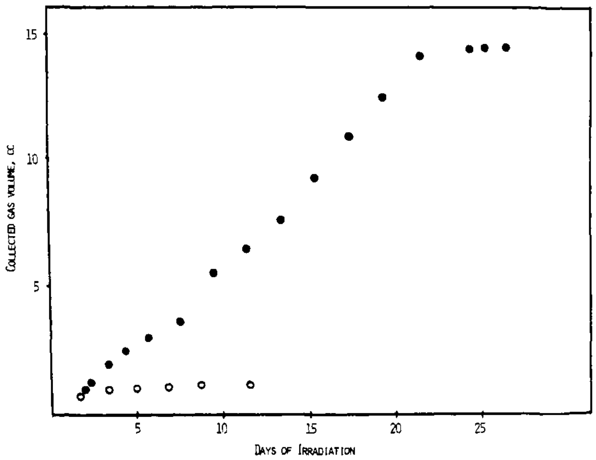


Figure 5. Gas generation experiment with monolayer assemblies of **5a** irradiated in contact with water (light source 1000-W xenon lamp): open circles, "blank" experiment; closed circles, gas generated from irradiation of 20 slides.

nificant quenching of the luminescence of **5** no permanent bleaching was observed, at least on short-term irradiation. This suggests that electron transfer quenching of excited **5** by **10** is followed by rapid return to the ground states of the starting materials as is usually observed in solution.

Although the luminescence of **5** is not quenched by addition of water, aqueous acid, or aqueous base to tetrahydrofuran or dioxane solutions, the emission of **5** in monolayer assemblies is strongly quenched when these assemblies are immersed in water. In the case of assemblies containing **5a**, the emission is nearly 100% quenched (Figure 4). The other samples of **5** were quenched to a slightly lesser extent; however, in no case was the quenching <80%. No significant changes in the absorption spectrum of **5a** in the assemblies were observed concurrent with the quenching. The luminescence remained quenched when the slides were removed from the water. Luminescence from the assemblies of **5** could be regenerated by gentle heating in vacuo (3 mmHg, 70 °C for 10 h); in the case of **5a** (Figure 4) the regeneration was ~100% while with other samples the regeneration was 60–80%. Renewed immersion of the luminescent slides resulted again in quenching. For slides containing three layers of **5b** the initial luminescence was ca. three times as intense as that observed for slides with only a single layer; luminescence quenching for these slides was nearly complete, indicating that the quenching activity of water extends beyond the outermost layer. Slides containing monolayers of the hexa(dihydrocholesteryl) complex **8** also exhibited strong luminescence that was quenched by water; the reproducibility of the quenching with these slides was relatively low and the observed quenching ranged from a few percent in some cases to nearly complete in others.

Photochemistry of Surfactant Ruthenium(II) Complexes at a Solid–Water Interface. The observation that water quenched the luminescence of monolayer assembly-bound **5** suggested that a photoreaction involving **5** and water could be occurring. In order to test this possibility assemblies containing six inner layers of cadmium arachidate and an outer layer of pure **5a** were irradiated under water as described in the Experimental Section. As blanks assemblies consisting of (a) slides coated only with five layers of cadmium arachidate, (b) uncoated glass slides, and (c) teflon slide holder only were irradiated in parallel. Upon irradiation of the assemblies containing slides of **5a** a steady generation of gas began which generally ended after 2–3 weeks. Figure 5 shows results of a typical experiment with a xenon lamp through Pyrex; other light sources which produced similar results included a mercury lamp and sunlight (Table II). In contrast, irradiation of the "blank" assemblies led to an initial evolution of some gas bubbles (maximum 1–2 mL) which ceased after several hours. At the time **5a** was investigated assemblies consisting of several surfactant porphyrins and metalloporphyrins over cadmium arachidate with absorbance comparable to those of **5a** were also irradiated under the same conditions;[34] these experiments gave results identical with those of the "blank" assemblies. Analysis of the collected gas by a gas analyzer or by mass spectrometry indicated it contained hydrogen, nitrogen, and oxygen as major components. Although it was not possible to determine precise ratios with the gas analyzer, the intensity of hydrogen was comparable to that of nitrogen (which probably appears as a result of outgassing of air contained in the nondegassed water). The oxygen/nitrogen ratio from assemblies of **5a**, as determined by gas chromatography, was several times that observed for air. The gas from irradiation of "blank" samples contained no hydrogen and only oxygen and nitrogen in the ratio found for air.

Although slides containing monolayers of **5a** repeatedly gave sustained gas evolution upon irradiation, irradiation of assemblies formed from subsequent preparations of **5** under identical conditions has not produced comparable results. In each case we have found only an initial production of gas

Table II. Photolysis of Ruthenium Complex (**5a**) Monolayers at a Water-Solid Interface

Run	Light source	Dome volume, cm^3	No. of slides	Solution	Volume gas collected, cm^3	No. days irradiated
1	*a*	~150	20	water, pH 6.2[d]	13	30
2	*a*	~150	20		14	30
3[e]	*a*	~150	20[e]		<1	5
4	*a*	~150	20	water, pH 4.7	13	30
5	*a*	~150	57	water, pH 6.2	7.5	18
6	*a*	~150	*f*		<1	5
7	*a*	~30	5[g]		<1	8
8	*b*	~200	58		7	8
9	*c*	150	20		18	30
10	*c*	150	20	water, pH 9	15	30

[a] 100-W mercury flood lamp. [b] Sunlight. [c] 1000-W xenon lamp. [d] Triply distilled water. [e] Slides coated with five layers cadmium arachidate. [f] Slide holder, dome, and water only. [g] Solid suspension (4 mg) of **5a.**

bubbles similar to that observed in the "blank" experiments described above. In each case, analysis of the small amount of gas produced with the subsequent preparations reveals only oxygen and nitrogen in the "normal" ratio obtained for air and no hydrogen. This has been the case with all "purified" samples of **5** that we have examined. Recovery of the slides from these experiments and subsequent rinsing of them with chloroform (soaking for 2-3 h with stirring) indicates that no detectable ruthenium complex remains on the slides following even short-term irradiation. Thus, in addition to not observing production of hydrogen from these preparations, we are observing a rapid removal of the ruthenium complex from the assemblies.

The removal of complex **5** from assemblies immersed in water is evidently light induced. In an experiment with **5b** it was found that the material from five slides coated as described above and irradiated with a mercury flood lamp for 12 h was 60% removed; in contrast, the removal of material from five identical slides treated in the same manner but unirradiated was negligible. The removal of complex **5** from slides irradiated under water has been observed by other workers;[32] however, in at least one case it has been reported that the stability of assemblies containing highly purified **5** is much greater than observed in these studies.[32] In the initial investigation of assemblies containing **5a,** it was found that "exhausted" slides contained no detectable ruthenium complex; however, the still-functioning slides were not examined by interrupting the irradiation. However, as mentioned above in connection with the luminescence quenching, brief irradiation does not bleach or cause removal of **5a** from the assemblies.

In experiments conducted to determine the fate of complex **5b** on irradiation in assemblies in contact with water, we irradiated 75 glass slides coated with a single layer of **5b** and immersed in a small volume (150 mL) of purified water for 24 h with a mercury flood lamp (100 W). Both the water and slides were examined following the irradiation. The slides were treated with methylene chloride and the resulting methylene chloride solution was examined spectrally. The absorption and emission spectra of the methylene chloride solution were essentially identical with that of unirradiated **5b;** quantitative analysis by absorption indicated that after irradiation 11% of the starting material remained on the slides as a tris(2,2′-bipyridine)ruthenium(II) complex. The aqueous solution contained some material having the characteristic tris(2,2′-bipyridine)ruthenium(II) absorption and emission; however, quantitative analysis by absorption spectroscopy was not possible due to the presence of other light-absorbing materials in the water and the small amount of material present. After concentration of the aqueous solution under reduced pressure to a small volume (ca. 30 mL) an absorption at 550 nm (onset) with a broad shoulder at 420-480 nm was observed; the emission occurred at 630 nm with an excitation maximum at 463 nm, characteristic of other ruthenium(II) complexes. Addition of NaOH to the concentrated aqueous solution produced no change in the emission spectrum or its intensity; however, addition of HCl shifted the emission maximum from 630 to 670 nm and strongly reduced the emission intensity.

These results indicate that some ester hydrolysis has taken place, since the shifts observed in the emission spectrum are characteristic of those we and others have observed for the dicarboxylic acid **6.**[31,35] Since only a small amount of material was obtained in this experiment, it is not possible to determine whether the product formed in the photoreaction is actually **6,** monoester monocarboxylic acid, or a mixture of **6** and the monoester. As mentioned above, light-absorbing impurities present in the aqueous phase make it impossible to quantitatively estimate the amount of ruthenium complex present by absorption spectroscopy; however, quantitative measurements of the emission intensity enable a crude estimate of ca. 17% of the starting material from the slides present as soluble or finely suspended material in the aqueous phase. Since the major amount of complex **5b** has not been accounted for, it appears likely that some true photobleaching has occurred and that some insoluble ruthenium(II) complex (perhaps **6** or half ester) has escaped detection by the techniques used. It is significant that no bis(2,2′-bipyridine)ruthenium(II) complexes have been detected (these would have been easily seen by their characteristic shifted absorption); thus the major photobleaching evidently does not involve ligand substitution or ejection processes. Although some hydrolysis might have occurred during concentration of the aqueous solution, it appears likely that this would be minimal with the mild conditions used. Thus the hydrolysis most likely arises through photolysis of the monolayer bound **5b** at the water-monolayer interface. Although photohydrolysis reactions of other esters of carboxylic acids have been observed,[36-40] the present phenomenon is apparently the first case of a transition metal complex undergoing such a process. It is also unusual in that shorter wavelength irradiation is usually required in most photohydrolysis reactions and the excited states involved are generally ester π,π^* states.

The observations that irradiation of monolayer bound **5a** in water led to production of hydrogen and oxygen suggested that **5** and similar ruthenium complexes might provide a useful system for solar energy conversion. The obvious difficulties associated with the preparation and utilization of monolayer assemblies on a large scale and the extremely low light absorption by single layers of pure **5** suggested that other surface-solution interfaces might provide more practical systems. It was found that the solid-state luminescence of **5a** was unquenched by water and irradiation of a suspension of **5a** in water led to no production of gas. Similarly, coating of alumina with **5a** produced a strongly luminescent powder whose luminescence was also unquenched by water. Although we have not examined **5a** or other preparations of **5** in micelles, it was found that the hexa(dihydrocholesteryl) complex **8** forms good mixed micelles with OT which contain a high concentration of **8.** The micelles containing **8** showed strong luminescence and did not yield any gaseous products on prolonged irradiation. Some spectral changes (Figure 6) were observed on prolonged irradiation of the micelles containing **8**, but relatively little "bleaching" was observed.

As mentioned above, our initial observation of sustained evolution of gas, consisting of hydrogen and oxygen, on irradiation of assemblies containing **5a** in the presence of water suggested that **5** and related ruthenium complexes might serve as the basis for relatively simple and useful catalytic systems for solar energy conversion. The finding that these experiments are not reproducible with subsequent and more highly purified preparations of **5** is clearly a discouraging result. From our results as well as those obtained in other laboratories,[31,32] both with regard to the photochemical experiments and to the luminescence behavior and film properties, it is clear that the monolayer chemistry of **5** and other surfactant ruthenium complexes is much more complicated than our initial experiments with **5a** suggested. It seems fairly certain at this time that highly purified **5** is not by itself a sufficient catalyst to bring about the light induced cleavage of water. Whether the failure of purified **5b** to act as a photocatalyst for the cleavage of water is due to its inactivity in the process or to its rapid destruction by photohydrolysis and related photobleaching processes remains undetermined, since the generation of stoichiometric amounts of hydrogen and oxygen would be impossible to detect using the small amounts of material contained in the monolayer assemblies. The initial success with **5a** on a catalytic scale indicates either that an impurity in the initial sample is the active compound or that an impurity present acting in conjunction with **5** produces the observed cleavage of water. It is, of course, not at all unreasonable that in a highly condensed system such as the monolayers produced from undetected ruthenium complex impurities or "trap sites" can play a major role in controlling net excited-state reactivity and luminescence behavior. In previous investigations with other surfactant chromophores we have demonstrated the occurrence of such phenomena. The wide variance of luminescence behavior for the different analytical samples of **5** having comparable solution properties indicates the ruthenium complex monolayers are strongly affected by subtle factors involving the "molecular architecture" of the assemblies that are not understood at the present time. The fact that **5a** has been found to contain significant amounts of other ruthenium(II) complexes suggests, but by no means establishes, that these compounds, possibly in conjunction with **5**, may form reactive sites in the condensed assemblies. We are presently attempting to isolate **12** and other impurities formed in preparation of **5** to determine their reactivity in assemblies constructed from pure **12** or mixtures with **5.**

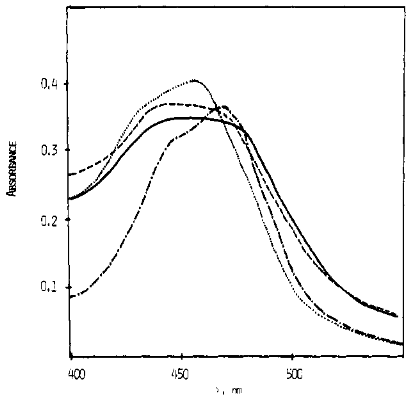


Figure 6. Spectral changes in absorption spectra occurring on irradiation of **8** in OT micelles: (···) chloroform solution of **8**; (—) monolayer assembly of **8**; (- - -) micellar solution of **8**-OT in water before irradiation; (-····) micellar solution of **8**-OT after irradiation.

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Studies in Nuclear Resonance Spectroscopy. 14. Characterization and Structures of Lithioisobutyrophenone Aggregates in Ether Solvents[1]

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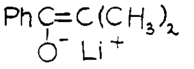
Abstract: Proton, ^{13}C, and ^{7}Li magnetic resonance spectroscopy, including studies of spin-lattice relaxation times, have been used to investigate the nature of ion pair aggregates of lithioisobutyrophenone (**1**) in several ether solvents. As previously observed for dioxolane solutions, **1** in tetrahydrofuran-d_8 and dioxane exists as two rapidly exchanging species, the relative concentrations of which are strongly temperature dependent. Two species also exist in dimethoxyethane but the equilibrium is much less temperature sensitive and the exchange is slow on the NMR time scale at −50 °C. The complex between **1** and LiCl in dioxolane has been shown to be $Li_4Cl(C_{10}H_{11}O)_3$. Carbon-13 chemical shifts indicate that in all species, except the major species in dimethoxyethane, the enolate ions have the same electron distribution. T_1 measurements for ^{13}C nuclei indicate that all species are tetramers except the major species in dimethoxyethane which appear to be a dimer. Quadrupole splitting constants for lithium-7 and the ^{13}C chemical shifts show trends expected for tetramer and dimer models. T_1 measurements for ^{13}C nuclei of solvent dimethoxyethane show that the dimer has one solvent molecule per lithium atom. Similar measurements for the other solvents indicate considerable internal rotation of solvent molecules bound to the aggregates. The above results are interpreted in terms of a cubic array of Li and O atoms in the tetramer and a planar square array for the dimer.

In part 11,[2] we reported proton NMR studies of solutions of lithioisobutyrophenone (**1**) in several ether solvents. Measurements of the chemical shifts of the two methyl groups in dioxolane at various temperatures revealed the occurrence of two species, one existing exclusively below −50 °C, the other exclusively above 50 °C. In the intermediate temperature range the two species coexist but are involved in a chemical exchange which is rapid on the NMR time scale. The position of equilibrium was shown to be independent of the concentration of lithium enolate and the thermodynamic parameters ($\Delta H = -10.3$ kcal mol^{-1}; $\Delta S = -38.7$ cal mol^{-1} deg^{-1}) are consistent with the two species being differently solvated ion pairs or ion pair aggregates.[3] It was also observed that the addition of lithium chloride or bromide to solutions of the enolate in dioxolane gives a new species which, at appropriate temperatures and concentration ratios, coexists with the two species referred to above. Exchange of the enolate ion between this new species and the other two is comparable with the proton NMR time scale. The empirical formula for the halide complex was found to be $Li_{4-5}X(\text{enolate})_{3-4}$. The higher values appeared to fit better the data for the chloride complex although the lower value was more consistent with that for the bromide system. We have now considerably refined our techniques for sample preparation and analysis and it is clear (see below) that the formula of the chloride complex is $Li_4Cl(\text{enolate})_3$.



$$\underset{O^- \; Li^+}{PhC}{=}C(CH_3)_2$$

1

In this paper we report more extensive NMR studies, including ^{13}C and ^{7}Li resonances as well as measurements of spin-lattice relaxation times, which further delineate the various species existing in different ether solvents and in the presence of lithium chloride, and which permit the tentative formulation of the structure of these species as various ion pair aggregates.

Experimental Section

Materials. All compounds and solvents were prepared as previously described.[2]

Preparation of Lithium Isobutyrophenone Solutions. The vacuum line technique described earlier was modified to eliminate as many stopcocks as possible and is illustrated in Figure 1. *n*-Butyllithium was obtained by distillation of its solution (1.6 M) in *n*-hexane (Alfa) either directly into the reaction flask, A, through a short side arm heated (130 °C) by heating tape or into a break-seal storage bulb, B, which was subsequently attached to the neck of the reaction flask as illustrated. Diethyl ether stored over lithium aluminum hydride in the storage bulb, C, was degassed by several cycles of freezing, pumping, and thawing and then transferred to the reaction flask containing *n*-butyllithium (if the *n*-butyllithium was contained in the storage vial, the seal was broken at this stage and the contents were transferred to the flask by repeatedly condensing ether in the opened vial). The vial, D, containing degassed isobutyrophenone trimethylsilyl enol ether was opened, and the contents were vacuum transferred to the reaction flask. The mixture was then stirred at room temperature for 12 h. The diethyl ether was removed and replaced by degassed solvent stored over lithium aluminum hydride in the storage bulb E. This solvent was removed and the entire system was pumped down until the vacuum gauge F registered less than 2 μm. The storage bulb G was opened and the solvent was degassed and transferred to the reaction flask. If required, tetramethylsilane was introduced from a storage vial, H, at this stage. The reaction flask was then sealed and removed from the manifold. The contents of the reaction flask were drained through a medium porosity sintered glass septum J (Figure 2) into the flask of the "spider" K. Appropriate quantities were then transferred to the various attachments of the spider. Depending on the particular experiment, these consisted of 5 and 10 mm NMR tubes (the latter