The reactions were run in the following way. The appropriate olefin[1] (2-5 mmol) was added to a suspension of PdCl$_2$(CH$_3$CN)$_2$ (1.0 mmol) in 20 mL of THF and the resulting solution was cooled to -78 °C. Triethylamine (2.0 mmol) was added dropwise over 0.2 h, the mixture stirred for 0.25 h, and a solution of the nucleophile (2.0 mmol) in 10 mL of THF was added over 0.2 h. The reaction mixture was stirred for 1 h at -50 °C, then allowed to warm to room temperature (β-elimination), or exposed to an atmosphere of hydrogen (balloon) while warming (reduction). The resulting black suspension was filtered, the filtrate passed through a short silica gel column, and the solvent evaporated; the products were isolated by preparative GLC or silica gel column chromatography.

The procedure illustrates several interesting features of the reaction. Optimum results required the use of 2 equiv of triethylamine and 2 equiv of carbanion. With no added amine the yield of alkylation product was <1%, with 1 equiv it jumped to 30%, and with 2 equiv it was essentially quantitative. Triethylamine was the reagent of choice. Use of pyridine, diethylamine, trimethylamine, or ethyldiisopropylamine resulted in very low yields. Use of only 1 equiv of carbanion resulted in yields 10–20% lower than those obtained with 2 equiv. With dimethyl malonate anion, only 1 equiv of anion could be used when the β-elimination isolation was used, since excess anion led to 1,1-dialkylation of the olefin in ~80% yield. The probable course of the reaction is outlined in Scheme I and is similar to other palladium-assisted nucleophilic attack on olefins.[2-4]

Although stabilized carbanions have long been known to alkylate *chelate* diolefin palladium and platinum complexes,[5-7] prior to the work reported in this communication, alkylation of simple monoolefins complexed to palladium had not been achieved in usable yield.[8-10] Very recently dimethyl ethylmalonate was produced in 68% yield by the reaction of sodium dimethyl malonate with (ethylene)iron tetracarbonyl, followed by oxidation to remove the metal.[11] Similarly, stabilized carbanions alkylated the olefin in cationic (carbonyl)(olefin)cyclopentadienyliron complexes. Again oxidative removal of the metal was required.[12,13] In contrast, the method presented in this communication requires neither prior synthesis of the metal–olefin complex nor chemical removal of metal from the desired organic products. Rather, it is a direct, one-pot procedure resulting in the alkylation of olefins primarily at the 2 position, under very mild conditions. It is quite complementary to the recently reported *allylic* alkylations of olefins via their π-allylpalladium complexes,[14-25] which lead to alkylation at the 1 and/or 3 position of the potential allyl system.

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Photoinduced Redox Reactions of Hydrophobic Ruthenium(II) Complexes

Sir:

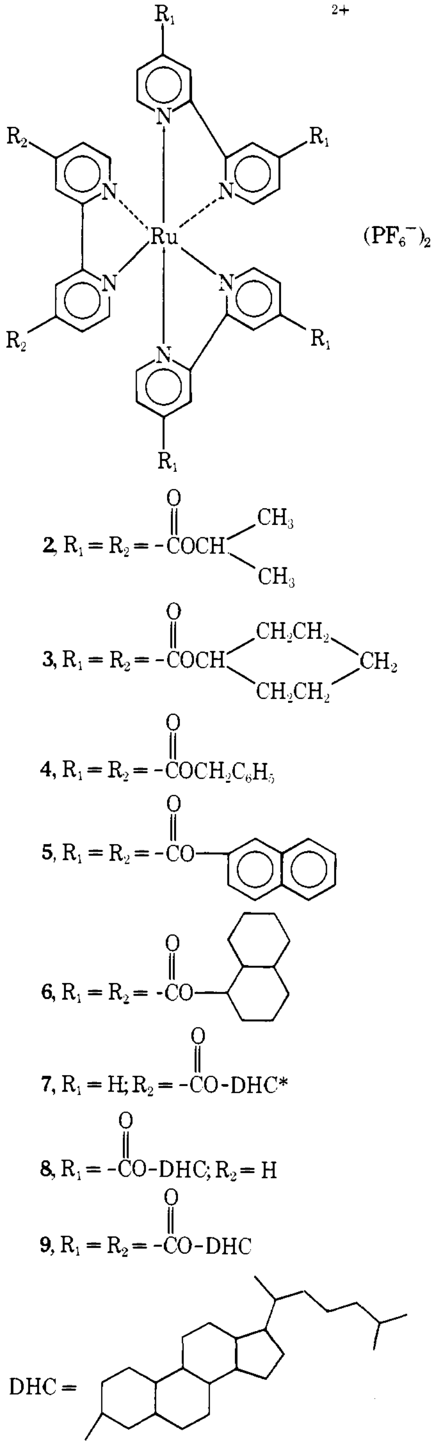
In several cases, it has been shown that light-induced electron-transfer reactions in solution can result in efficient energy conversion.[1-5] However, usually the practical utility of these reactions is limited by the subsequent occurrence of energy-wasting back-electron-transfer reactions which produce the ground states of the starting reagents.[2,4,5] Our studies involving photoreactions occurring in organized media have led to the synthesis of several surfactant molecules including a number of ruthenium(II) complexes which are surfactant analogues of the widely studied tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ (Ru(bipy)$_3{}^{2+}$, **1**).[6] We have recently synthesized a series of water-insoluble complexes **2–9** in which the polar, charged Ru(bipy)$_3{}^{2+}$ core is surrounded by aliphatic groups of varying size. These "hydrophobic" complexes appeared to be attractive candidates for solution studies of photoinduced electron-transfer reactions owing both to their high solubility in relatively nonpolar solvents where to date relatively few studies have been carried out and further to the possibility that the "shielding" of the reactive core by the hydrophobic sheath might impart a selectivity to electron-transfer reactions. In the present paper, we report results which suggest that such selectivity can indeed occur; more importantly, we find indications that substantial energy conversion and storage in the form of high energy redox products can be accomplished with these complexes.

Hydrophobic complexes **2–9** exhibit relatively intense absorption (Figure 1) and luminescence in the visible region in acetonitrile solution, similar but slightly red shifted compared to **1**. Lifetimes and $\lambda_{\max}$ for the luminescence in degassed acetonitrile are listed in Table I. Electrochemical oxidations and reductions of several of the complexes were also carried out in acetonitrile. As might be anticipated on the basis of substitution of the bipyridine ligand with electron-withdrawing carboxyl groups, the potentials for oxidation of hexacarboxy complexes **2–4** were shifted by ~0.3 V more anodic while the corresponding potentials for the reduction of the dication were shifted 0.4 V more anodic. Interestingly, it was found that acetonitrile solutions of **5**, **6**, **8**, and **9** were electrochemically

Table I. Properties and Excited-State Quenching Reactions of Hydrophobic Ruthenium(II) Complexes

Substrate	λ_{max}, emission	τ_0, s	$E_{1/2}$(oxidn)[b]	$E_{1/2}$(redn)[b]	K_q, M^{-1} s^{-1},[a] quenchers: Paraquat^{2+}	K_q, M^{-1} s^{-1},[a] quenchers: *N,N*-Dimethylaniline
1	610	0.85×10^{-6}	1.29	−1.32	2.8×10^9	7.1×10^7
2	629	2.39×10^{-6}	1.59	−0.9	1.2×10^8	3.7×10^9
3	630	2.21×10^{-6}	1.56	−0.91	1.7×10^8	4.5×10^9
4	636	1.93×10^{-6}	1.56	−0.95	N.D.[c]	4.7×10^9
5	631	2.19×10^{-6}	*d*	*d*	1.6×10^8	4.1×10^9
6	632	2.21×10^{-6}	*d*	*d*	N.D.[c]	4.3×10^9
7[e]	660	2.00×10^{-6}	1.35	−0.99	3.5×10^7	3.7×10^8
8[e]	644	2.10×10^{-6}	N.D.[c]	N.D.[c]	3.6×10^7	2.1×10^9
9[e]	638	2.14×10^{-6}	*d*	*d*	1.7×10^7	2.3×10^9

[a] Degassed solutions in acetonitrile (except where indicated) with substrate concentration 10^{-5} M. [b] Platinum electrode vs. SCE in acetonitrile with 0.1 M TBAH as supporting electrolyte. [c] Not determined. [d] Compound not electrochemically active. [e] 1:3 isobutyronitrile-acetonitrile.



inactive under conditions where the other complexes were easily oxidized and reduced. Presumably the large hydrophobic shield in these complexes inhibits approach of the electroactive portion of the complex to the platinum electrode surface.

The luminescence of complexes **2–9** is quenched by a wide range of electron donors and acceptors in acetonitrile solution. For neutral acceptors—tetracyanoethylene, *o*-dinitrobenzene, and *p*-dinitrobenzene—there is relatively little variation in the quenching rates in the series **2–9** for each quencher. As was observed for quenching of excited **1** by the same quenchers,[2] there are no transients detectable by microsecond flash photolysis occurring as a consequence of the quenching and no permanent photobleaching. Apparently, electron-transfer quenching in these cases produces a very short-lived ion pair which rapidly decays back to starting materials. In contrast to the neutral acceptors, the dication paraquat^{2+} (*N,N'*-dimethyl-4,4'-bipyridine) quenches the hydrophobic complexes **2–9** at reduced rates compared to **1** and with rate constants that are strongly substituent dependent. For **7**, **8**, and **9**, where the hydrophobic groups are extremely large, the rate constants are reduced by more than two orders of magnitude even though electron-transfer quenching of the excited state by paraquat^{2+} should be energetically favored.[7]

The marked difference between the behavior of neutral acceptors such as tetracyanoethylene and the positively charged paraquat with the hydrophobic ruthenium(II) complexes suggested that similar effects could be observed in back-electron-transfer reaction rates, particularly in cases where electron-transfer quenching of an excited state produced products having like charges. A particularly appealing system for investigating this appeared to be reductive quenching of the hydrophobic complexes by neutral amines. Here the quenching step should be relatively unaffected while the back-reaction between two cations might be substantially retarded. Quenching of **1*** by *N,N'*-dimethylaniline (DMA) has been previously investigated; the quenching is slower than diffusion controlled because of an energy barrier while the reverse reaction in acetonitrile has a rate constant of 4.1×10^9 M^{-1} s^{-1}.[8] It was found that DMA quenches excited states of complexes **2–9** with rates only slightly below diffusion controlled. The more rapid rates are consistent with the more favorable free-energy charges arising because of the enhanced oxidizing strength of the excited states. However, attempts to observe the back-reactions with several of the complexes were unsuccessful since only a permanent bleaching could be observed when these solutions were irradiated by flash or steady-state illumination. This is in marked contrast to **1** where simple back-electron transfer is observed.[8] Since the photochemical changes with DMA and the hydrophobic complexes appeared to be complicated, the complexes were irradiated in the presence of the somewhat better behaved triethylamine. Here again efficient quenching of the luminescence of com-

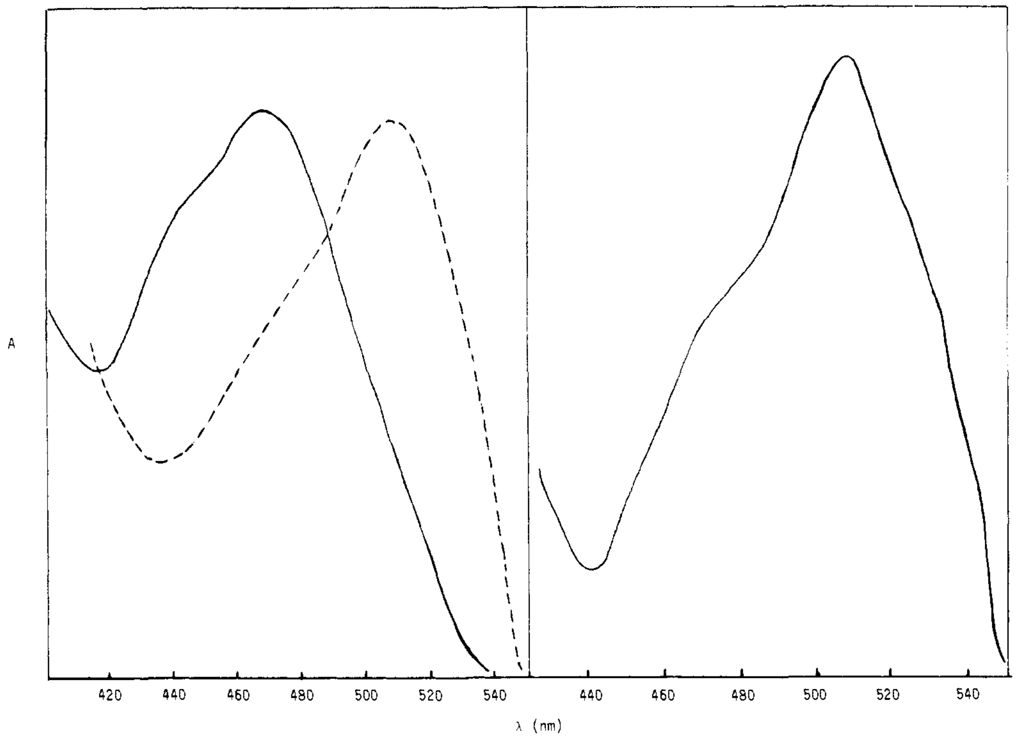


Figure 1. Left trace: spectrum of **2** before (solid line) and after (dashed line) photolysis in triethylamine-acetonitrile. Right trace: spectrum of the one-electron reduction product of **2** in acetonitrile.

plexes such as **2**, **3**, and **9** was observed but no back-reaction could be detected and a permanent change occurred on irradiation of dry acetonitrile solutions. The most detailed results have been obtained with **2** and appear to be typical. Irradiation of 5×10^{-4} M **2** in dry acetonitrile containing 0.3 M triethylamine leads to the spectral changes shown in Figure 1. The product spectrum is easily identifiable as the one-electron reduction product of **2** which can also be produced by electrochemical reduction (Figure 1). Similar spectra have been obtained for transients formed by reductive quenching of other ruthenium(II) complexes.[8,9] The product is stable over a period of days in *dry* acetonitrile but rapidly reverts to the starting material when air or water are introduced. The quantum yield for the reduction as measured by disappearance of **2** is >0.35 with irradiating light of λ 470 nm.[10,11] The reaction is noteworthy in that the back-reaction in this case is almost entirely avoided and a very high energy and reactive product—the $Ru(II)^{+1}$ species—can be isolated. Evidently with the hydrophobic complexes, the energy-wasting back-reaction has been retarded sufficiently to allow other reactions of one of the products to ensue.[10] In this case, two possible paths involving the triethylamine radical cation can be proposed (eq 1 and 2

$$\cdot\overset{+}{N}Et_3 + CH_3CN \longrightarrow H\overset{+}{N}Et_3 + \cdot CH_2CN \qquad (1)$$

$$2CH_2CN \longrightarrow \begin{array}{c} CH_2CN \\ | \\ CH_2CN \end{array} \qquad (2)$$

$$\cdot\overset{+}{N}Et_3 + :NEt_3 \longrightarrow Et_2\ddot{N}\dot{C}HCH_3 + H\overset{+}{N}Et_3 \qquad (3)$$

$$Et_2\ddot{N}\dot{C}HCH_3 \xrightarrow{-e^-} Et_2\overset{+}{N}{=}CHCH_3 \qquad (4)$$

and eq 3 and 4). Both sequences have been proposed in related cases.[12,13] Reactions 3–4 have good analogy in the photooxidations of amines by other oxidants;[10,14,15] an intriguing possibility is that occurrence of step 4 is coupled with a second reduction of the ruthenium(II) complex, thus giving a net two-electron reduction as a consequence of one photon absorbed. Radicals such as that shown in step 4 are known to be powerful reducing agents and may be capable of reducing ruthenium(II).[14,16] In either case thermochemical calculations indicate a substantial fraction of the excitation is stored in the form of the high energy $ruthenium(II)^{+1}$ species.

To determine the course of the reaction we have irradiated **2** in moist acetonitrile containing triethylamine. Under these conditions, no permanent conversion of **2** to the reduced form occurs, thus permitting sustained irradiation at 470 nm. The major organic product detectable by VPC is acetaldehyde which increases monotonically with irradiation time; presumably it arises through hydrolysis of the imine formed in eq 4. A trace of product having a retention time identical with that of succinonitrile is also detected, but it appears that reaction of the triethylamine radical cation to acetaldehyde via reactions 3 and 4 is the major path.

Clearly the most interesting aspect of this work is the finding that the high-energy $ruthenium(II)^{+1}$ can be formed in good yield as shown spectroscopically in these systems. The net reaction involves the use of visible light with relatively efficient conversion and storage of energy. The $ruthenium(II)^{+1}$ species, while stable under the photolysis conditions, is highly reactive toward a wide variety of reagents including oxygen and water. The formulation of a practical system for prolonged energy storage in this case will require use of an efficient secondary electron acceptor to facilitate regeneration of the photoactive $ruthenium(II)^{2+}$ complex.

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Direct Reaction of Dibromoborane–Methyl Sulfide, $HBBr_2·S(CH_3)_2$, with Alkenes. The Remarkable Reactivity of $HBBr_2·S(CH_3)_2$ as a Hydroborating Agent as Compared with Related Dichloroborane Derivatives

Sir:

In contrast to dichloroborane-ethyl ether and dichloroborane–methyl sulfide, which require the presence of a Lewis acid, usually boron trichloride, for the satisfactory hydroboration of alkenes, the new reagent, dibromoborane–methyl sulfide, readily hydroborates representative alkenes directly. This development makes readily available for the first time such alkyldibromoboranes and the numerous derivatives into which they can be transformed. At the same time, a fascinating theoretical question is raised. Why should $HBBr_2·SMe_2$, which theory predicts and experiment confirms to be a stabler addition compound than $HBCl_2·SMe_2$, be a more reactive hydroborating agent?

Monochloroborane-ethyl ether,[1] $H_2BCl·OEt_2$, and monochloroborane-methyl sulfide,[2] $H_2BCl·SMe_2$, readily hydroborate alkenes (eq 1).

$$RCH{=}CH_2 + H_2BCl·SMe_2 \xrightarrow[25\ °C]{pentane} (RCH_2CH_2)_2BCl·SMe_2 \quad (1)$$

However, the dichloroborane derivatives are much less reactive hydroborating agents.[2,3] They require the presence of a Lewis acid, generally BCl_3, to achieve simple hydroboration, without redistribution (eq 2).

$$RCH{=}CH_2 + HBCl_2·SMe_2 + BCl_3 \xrightarrow[25\ °C]{pentane} RCH_2CH_2BCl_2 + Cl_3B·SMe_2\downarrow \quad (2)$$

The lower reactivity of the dichloroborane derivatives was attributed to the stronger Lewis acidity of $HBCl_2$, reducing the dissociation of the addition compounds, $HBCl_2·OEt_2$ and $HBCl_2·SMe_2$, over that of the monochloroborane derivatives.[2,3]

Boron tribromide is a stronger Lewis acid than boron trichloride.[4,5] Consequently, we had anticipated that $HBBr_2·SMe_2$, would be even less reactive than the dichloroborane derivatives. Accordingly, our early experiments with this new hydroborating agent utilized BBr_3 as a coreagent. However, a fortunate blank experiment revealed the error of our theoretical extrapolation. This experiment revealed that $HBBr_2·SMe_2$ was capable of reacting directly with representative alkenes without added BBr_3. Consequently, we undertook to explore this unexpected development.

Table I. Directive Effect in the Hydroboration of Olefins with Dibromoborane–Methyl Sulfide in Refluxing Methylene Chloride.

		Rel yields of products, %	
Olefin	Product	$HBBr_2·SMe_2$[a]	$H_2BBr·SMe_2$[b]
1-Hexene	1-Hexanol	99.6	99.6
	2-Hexanol	0.4	0.4
Styrene	2-Phenylethanol	96	96
	1-Phenylethanol	4	4
2-Methyl-1-pentene	2-Methyl-1-pentanol	98	98
	2-Methyl-2-pentanol	2	2
cis-2-Pentene	2-Pentanol	67	63
	3-Pentanol	33	37
2-Methyl-2-butene	3-Methyl-2-butanol	93	97
	2-Methyl-2-butanol	7	3
1-Methylcyclopentene	*trans*-2-Methylcyclopentanol	98	97.5
	1-Methylcyclopentanol	2	2.5

[a] Total yields were 95 ± 5%. [b] At 25 °C in CH_2Cl_2.[6]

The more reactive olefins react at a satisfactory rate at 25 °C. However, the reaction times for less reactive species are undesirably long at this temperature. Fortunately, essentially all reactions go to completion in 3 to 6 h in refluxing methylene chloride, 1 M in each reactant. Accordingly, we adopted this as our standard reaction condition (eq 3).

$$RCH{=}CH_2 + HBBr_2·SMe_2 \xrightarrow[40\ °C]{CH_2Cl_2} RCH_2CH_2BBr_2·SMe_2 \quad (3)$$

The directive effect in the hydroboration stage was determined by oxidizing the intermediate with alkaline hydrogen peroxide and examining the product by GC. The results are summarized in Table I.

Perhaps the only unexpected feature is the formation of 7% of the tertiary derivative in 2-methyl-2-butene, enhancing the 3% previously observed for $H_2BBr·SMe_2$.[6] These values are considerably greater than those observed for $H_2BCl·OEt_2$,[1] $H_2BCl·SMe_2$,[2] and even $H_3B·O(CH_2)_4$.[7]

The reaction appears to be quite general (Table II). The products are formed as the $RBBr_2·SMe_2$ addition compounds, and can be isolated as such by vacuum distillation.

The alkyldibromoborane can be freed from dimethyl sulfide by distillation in the presence of 1 mol equiv of boron tribormide (eq 4).

$$RBBr_2·SMe_2 + BBr_3 \rightarrow RBBr_2 + Br_3B·SMe_2\downarrow \quad (4)$$

The product, $RBBr_2·SMe_2$, is readily converted into the corresponding boronate by treatment with $NaOCH_3$ in methanol (eq 5).

$$RBBr_2·SMe_2 + 2NaOCH_3 \xrightarrow[CH_3OH]{CH_2Cl_2} RB(OCH_3)_2 + SMe_2 + 2NaBr\downarrow \quad (5)$$

The following experimental procedures are representative.