materials confirmed the production of 1 equiv of acetone in this reaction.

Methylidene complex **2** is air-sensitive and thermally stable only below −40 °C. Attempts to isolate it have proven unsuccessful; removal of solvent, even at low temperature, results in decomposition to an uncharacterized brown oil. Although we have been unable to isolate **2**, its stability in solution has allowed us to begin an exploration of its chemistry; our results are summarized in Scheme I. The material shows ubiquitous reactivity toward organic acids. For example, treatment of a toluene solution of **2** with 1 equiv of anilinium chloride results in the instantaneous formation of the known chloro(methyl) complex $Cp^*(PMe_3)Ir(CH_3)Cl$ (**3**) in 70% isolated yield. Compound **2** also undergoes reaction with phenols. Addition of α,α,α-trifluoro-*p*-cresol gives the methyl phenoxide complex **4** in 85% isolated yield. Likewise, complex **2** reacts with succinimide to give the methyl succinimate **5** as a yellow powder in 78% isolated yield. Compounds **3**–**5** were synthesized independently by treatment of $Cp^*(PMe_3)Ir(CH_3)_2$ with the appropriate organic acids at elevated temperature. Comparison of the ^1H NMR spectra of these compounds confirms the identity of the products obtained on reaction of these acids with **2**.

Acids of much higher pK_a also react readily with **2**, and this provides access to complexes that are difficult to make in other ways. For example, treatment of the methylidene complex with *tert*-butylthiol proceeds slowly at −40 °C, giving the methyl *tert*-butylthiolate complex **6** in quantitative yield (NMR). This material shows a characteristic Ir–Me resonance at δ 0.84 ppm (doublet, $J_{P-H} = 7$ Hz) in the ^1H NMR spectrum; to our knowledge this is the first cyclopentadienyl(alkyl)(thioalkyl)iridium complex that has been prepared. Primary alcohols also react (some surprisingly rapidly) with the methylidene complex. These reactions lead uniformly to the hydrido(methyl) complex $Cp^*(PMe_3)Ir(CH_3)H$ (**8**) (observed earlier in our methane C–H activation studies[7]), rather than to methyl(alkoxy)iridium complexes, even at low temperature. For example, methanol induces this reaction immediately at −60 °C, presumably giving formaldehyde polymer (not detected) as coproduct; benzyl alcohol reacts with **2** over 10 h at −40 °C, leading to **8** and benzaldehyde (95% yield by NMR). Presumably, this reaction proceeds via ion pair **7a** and/or the methyl alkoxide **7b** (both illustrated in Scheme I) which then undergoes hydride transfer to give the observed products. No trace of **7b**, however, is observed when the reaction is monitored by ^1H NMR spectroscopy. Thus far, we have been unable to independently synthesize **7b** in order to test its stability to the reaction conditions.

Warming **2** in the presence of alkenes or alkynes does not lead to detectable amounts of addition products before spontaneous decomposition of the methylidene complex sets in. However, the complex does exhibit reactivity toward other nonprotic reagents. For example, methyl hydride **8** is also the product of reaction of **2** with dihydrogen. This reaction is quite slow, taking several weeks to reach completion at −40 °C. Most interestingly, carbon dioxide reacts slowly with **2** to give the addition product **9** as yellow crystals in 45% isolated yield.[8] The methylene protons shift dramatically upfield in the ^1H NMR spectrum (1.96 and 1.56 ppm), and a C–O stretching band is noted in the IR spectrum at 1662 cm^{-1}. Degradation of **9** with an excess of dry HCl in toluene gives the known $Cp^*(PMe_3)IrCl_2$ and 1 equiv of acetic acid (as determined by ^1H NMR and GC analysis of the volatile materials).

Traditionally, electrophilic reactivity at the alkylidene carbon has been attributed to late transition-metal carbene complexes and nucleophilic reactivity to their early transition-metal analogues. However, the complexes on which these comparisons have been based often differ greatly in either the molecular charge or the substituents on the carbene carbon.[9] The results reported here affirm that the nucleo- or electrophilicity of a methylidene ligand is more dependent upon the ligands on the carbene and the metal center than upon the position of the metal in the periodic table. They also suggest that other unsaturated monomeric $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir{=}X$ complexes (e.g., X = O, NR) may be more easily accessible than had previously been believed.[10]

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Supplementary Material Available: Spectroscopic and analytical data for complexes **2**, **4**, **5**, **6**, and **9** (2 pages). Ordering information is given on any current masthead page.

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Photochemical Switching in Conductive Langmuir–Blodgett Films

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Conductive Langmuir–Blodgett (LB) films have recently attracted much interest from the viewpoint of ultrathin film conductors at the molecular level.[1-11] We have reported that the structure of the TCNQ (7,7,8,8-tetracyanoquinodimethane) column in the LB film of *N*-docosylpyridinium 7,7,8,8-tetracyanoquinodimethane is changed by the variation of the subphase temperature.[2] In addition, a partial charge transfer state of *N*-docosylpyridinium bis(7,7,8,8-tetracyanoquinodimethane) is stable at the air–water interface and the as-deposited LB film is highly conductive without doping or any other treatments.[3] It will open up a wide scope of applications if the functions of the LB films can be controlled by external stimuli such as light, heat, or chemical treatments.[12] One of the most promising candidates for this purpose is to introduce a switching unit into an amphiphilic molecule. Figure 1 shows a schematic representation of an organic switching device of this type. When "the switching unit" is

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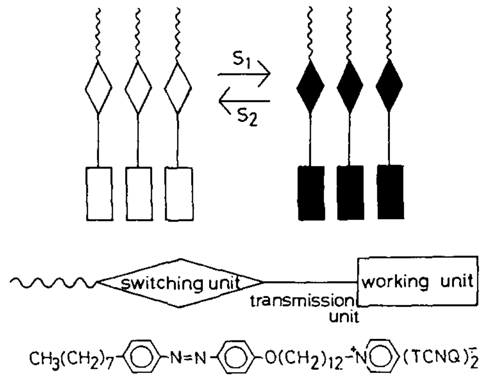

Figure 1. Schematic representation of an organic switching device using the LB technique and a structural formula of the molecule used in this study.

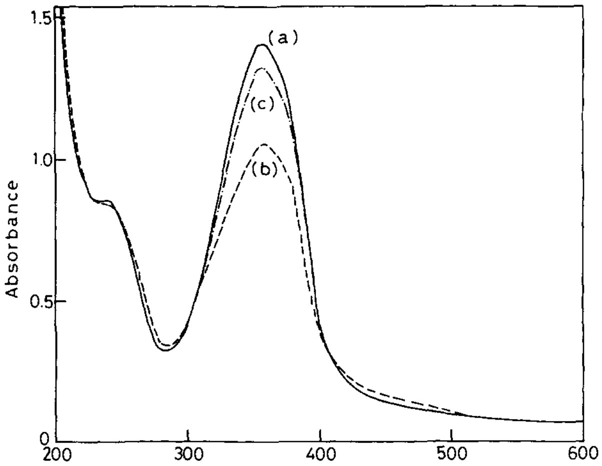

Figure 2. Absorption spectra of the LB film at the incident angle of 0°: (a) before irradiation; (b) after irradiation with 365 nm (λ_1) light for 5 min; (c) after irradiation with 436 nm (λ_2) light for 3 min.

triggered by an external stimulus, the signal is conveyed through "the transmission unit" to "the working unit" and induces a change in the structure and functions of "the working unit".

In this paper, we use the azobenzene as "the switching unit", the alkyl chain as "the transmission unit", and the charge-transfer complex of TCNQ as "the working unit". In this arrangement, the photoisomerization of the azobenzene induces the reversible change in the lateral conductivity of the LB film.

The donor part of the amphiphilic charge-transfer complex *N*-[*p*-(*p*-octylphenylazo)phenyloxy]dodecylpyridinium bis(7,7,8,8-tetracyanoquinodimethane) was synthesized according to Shimomura et al. with slight modifications.[13] The charge-transfer complex was prepared as previously described[2] and gave satisfactory UV-visible and IR spectra. The monolayer of the trans isomer was stable up to 40 mN $\mathrm{m^{-1}}$ and was transferred as an X-type film with use of the horizontal lifting (Fukuda-Nakahara) method[14] at 25 mN $\mathrm{m^{-1}}$ onto hydrophobized quartz plates. All the experiments were done at room ambient.

The absorption spectra of a 60-layered LB film at the incident angle of 0° [15] are shown in Figure 2. The monochromatic light at 365 and 436 nm from a 500-W high-pressure Hg lamp was used for photoisomerization. Intense monomeric absorption of *trans*-azobenzene at 356 nm[13] decreased on irradiation at 365 nm (λ_1) while absorption at 450 nm due to *cis*-azobenzene increased, corresponding to the trans-to-cis photoisomerization ((a) → (b)). Conversion to the cis isomer in the photostationary state was estimated to be ca. 25% from a calculation based on the difference spectra.[16] By the irradiation at 436 nm (λ_2) the *trans*-azobenzene was regenerated ((b) → (c)).[17] The spectra were reproducible for the further irradiation cycles ((b) $\rightleftarrows$ (c)), although spectrum (c) was slightly different from the initial one (a). The decrease in absorbance was ca. 1% in ten cycles ((b) $\rightleftarrows$ (c)). The half-life of thermal cis-to-trans isomerization in the LB film was 3 h at room temperature.

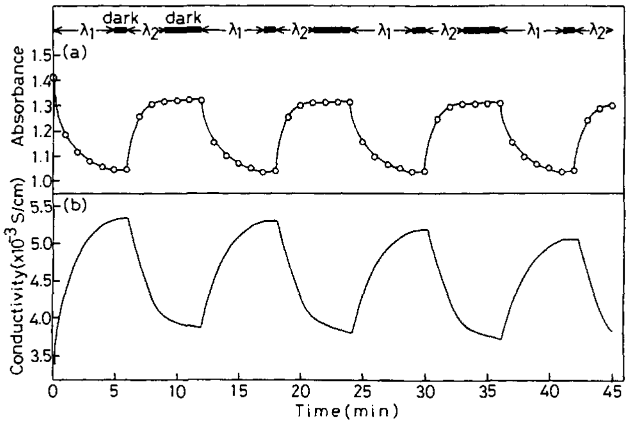

Figure 3. Changes of (a) absorbance at 356 nm and (b) conductivity of the LB film on alternate irradiation with ultraviolet (λ_1 = 365 nm) and visible (λ_2 = 436 nm) light.

Figure 3 shows the changes in the absorbance and the lateral conductivity of the LB film upon alternate irradiation with ultraviolet and visible light. The conductivity was determined by the d.c. two-probe method using silver paste as electrodes. The conductivity increases by ca. 30% upon the irradiation of 365-nm light. The change in the conductivity occurs almost concomitantly with the photoisomerization of azobenzene. The reversible changes of the conductivity can be repeated more than ten times. The results show that the photoisomerization of azobenzene occurring in the hydrophobic part controls the conductivity associated with the TCNQ moiety located in the hydrophilic part. A tentative explanation is that the trans-to-cis photoisomerization causes a change in the cross sectional area of azobenzene, enhancing the ordering of the TCNQ column, and hence the conductivity of the LB film.

The increase in the conductivity accompanying trans-to-cis isomerization was examined by time-resolved conductivity measurements. It proved that the process was completed within 100 μs after the flash (XeF excimer laser, 351 nm, pulse duration 30 ns, pulse energy 3.8 mJ $\mathrm{cm^{-2}}$), which is the limit of the time-resolving power under the experimental conditions used.[18]

These results indicate that the conductivity of LB films can be reversibly controlled by the photoinduced conformational change in the hydrophobic part. This system demonstrates a new method of controlling the conductivity of organic conductors and the feasibility of fabricating the molecular switching devices.

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