for example, **4a** (Nu = OBn) is a precursor in carbohydrate, terpene, and alkaloid chemistry,[10c] and **4a** (Nu = SPh) has been used to prepare insect pheromones.[10b]

In summary, opening of (*R*)- and (*S*)-glycidyl derivatives catalyzed by BF_3 etherate is highly efficient and proceeds with excellent regio- and stereoselectivity. The results summarized in Table I with hexadecanol, oleyl alcohol, and petroselinyl alcohol as nucleophiles show that glycidyl derivatives **1–3** are precursors to optically active ether-linked lipids, an important class of biologically active compounds.[11] Many previous syntheses of ether-linked lipids involved D-mannitol or its derivatives as starting material and were thus lengthy.[12] Optically active glycidol has been used as a lipid precursor but gives *unprotected* monoglycerides in low yield on ring opening.[4h,13] In contrast, the route reported in this communication is a practical, short synthesis of the enantiomers of alkyl lipids and other chiral 1,2-monoprotected diols.

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Synthesis and Reactivity of $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(CH_2)$: A Monomeric (Pentamethylcyclopentadienyl)iridium Methylene Complex

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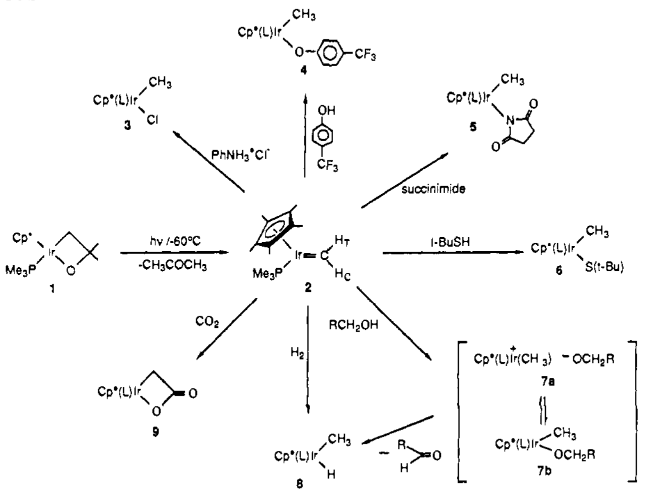
Since their discovery in 1964 by Fischer, transition-metal carbene complexes have been studied extensively.[1] Although a large number of dinuclear cyclopentadienyl and pentamethylcyclopentadienyl cobalt, rhodium, and iridium bridging alkylidene complexes are known,[2] no *monomeric* alkylidene complex in this well-studied series has ever been made.[3] We now report the generation of such a complex in an experimentally simple photoextrusion reaction. This species is remarkable for two reasons: (a) it is indefinitely stable in solution at −40 °C, showing no tendency to give a stable dimer before undergoing slow decomposition upon concentration or warming to higher temperatures; and (b) preliminary investigations of its chemistry indicate that the methylene carbon is exceptionally basic.

Scheme I



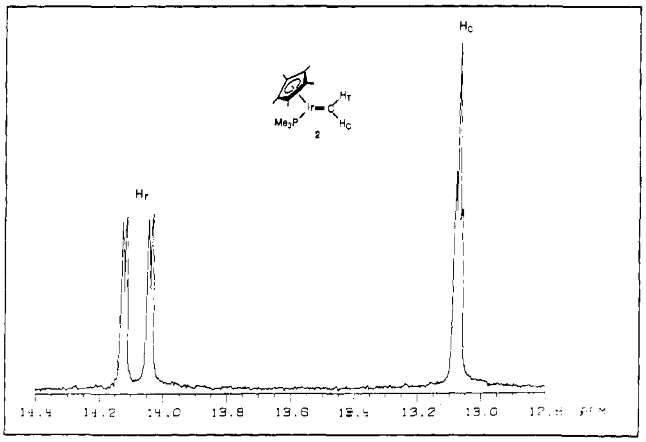


Figure 1. Low field region of the ^1H NMR spectrum of **2** at −45 °C in toluene-d_8.

Irradiation of a toluene solution of 2-oxametallacycle **1**[4] at −70 °C for 8 h leads to the disappearance of starting material and the generation of 1 equiv of acetone (δ 1.54 ppm) and a single, new organometallic species as determined by NMR spectrometry. The new species exhibits typical absorptions in both the ^1H and ^{13}C NMR spectra due to simple PMe_3 and η^5-coordinated pentamethylcyclopentadienyl ligands. The only other resonances observable confirm the identity of this species as the methylidene complex **2** (Scheme I).[5] As shown in Figure 1, the signals for two protons are evident in the ^1H NMR spectrum at very low field (14.08 and 13.08 ppm). These hydrogens are coupled weakly to one another. One exhibits a large trans coupling to phosphorus ($J(H_TP)$ = 24 Hz) and the other a smaller cis coupling ($J(H_CP)$ = 3 Hz). The $^{13}C\{^1H\}$ NMR spectrum shows a single low field resonance at 189.9 ppm; a proton-coupled spectrum establishes this as a carbon to which two hydrogens are attached (J_{CH} = 146, 134 Hz). The chemical shifts of these hydrogen and carbon resonances (as well as the reactivity of the species; see below) confirm the existence of **2** as a monomer; bridging CH_2, CHR, and CR_2 groups in dinuclear transition-metal complexes uniformly resonate at substantially higher field.[6] GC analysis of the volatile

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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 ^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H 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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