from water to methanol. The intermediate terminal epoxides **8** were now opened by methoxide ion to give the end-differentiated monoether triols **14–17**.[5b] These are HPLC separable. Each of the diastereomers **14** and **17** arising from the two modes of cascade in the major triepoxide **13** retains the high level of optical purity of their common precursor.

During the cascade process the *meso*-triepoxides **5** and **5′** each gave a racemic mixture of the C_2-tetrols **10** and **11** which were easily distinguished by ^{1}H NMR from their unsymmetrical partners **9** and **12**. However, there was no basis for assigning which of the two C_2 samples had a pair of cis- (i.e., **10**) and which had a pair of trans-disubstituted (i.e., **11**) THF rings. This issue was settled by an alternative synthesis that used an "inside-out" process. Thus, L-(2*R*,3*R*)-(+)-diethyl tartrate was processed in eight steps to the (4*S*,5*S*)-dioxolane **18**. The chiral Sharpless reaction of **18** using L-(+)-diethyl tartrate provided **19** which underwent deprotection and acid-catalyzed opening to give *cis-cis*-**10**, but not its enantiomer. This "inside-out" process therefore complements the "end-to-end" cascade of the *meso*-triepoxides since the latter gives racemates, but by the proper combination of L- and D-diethyl tartrate as starting material and Sharpless catalyst, any of the individual tetrols (**10**, **11**, or their enantiomers) is available optically pure from the former scheme.

We are currently applying many of the above reactions and ideas to three other isomers of dodeca-2,6,10-triene-1,12-diol and will report later on those efforts.

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Synthesis of 1,1-Dilithio-2,2,3,3-tetramethylcyclopropane

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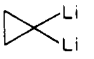
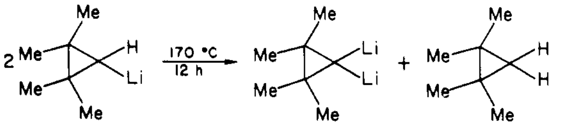
Since the prediction by Schleyer, Pople, and co-workers that 1,1-*gem*-dilithiocyclopropane monomers[1] were prime candidate molecules for observation of planar tetracoordinate carbon, these species have become intriguing synthetic target molecules and work directed toward their synthesis has proceeded in several laboratories. They are interesting species as reagents for further synthetic work whether they prove to be planar or tetrahedral. Schleyer and Pople have predicted higher stability for the planar form by at least 7 kcal/mol. Our laboratory has developed a very facile synthesis for such species. The method involves pyrolysis of 1-lithio-2,2,3,3-tetramethylcyclopropane and produces a dilithio compound in higher yield over a 10–12-h time period:



planar

tetrahedral



We have not yet been successful in applying this reaction technique directly to cyclopropyllithium for there is a problem with elimination of lithium hydride. The starting material 1-lithio-2,2,3,3-tetramethylcyclopropane was prepared by the reaction of 1-bromo-2,2,3,3-tetramethylcyclopropane and lithium in diethyl ether[2] but is contaminated with lithium bromide. This compound, 1-lithio-2,2,3,3-tetramethylcyclopropane, has excellent thermal stability and sublimes at 140 °C under high vacuum (10^{-5} torr). Sublimation of this crude material (~2-g scale) at 140 °C for 12 h usually gives about 50% yield of crystalline 1-lithio-2,2,3,3-tetramethylcyclopropane, leaving a slightly yellowish residual solid. The residual solid (mainly lithium bromide) was found also to contain 1,1-dilithio-2,2,3,3-tetramethylcyclopropane, and this was confirmed by the hydrolysis with D_2O.

Typically, 1.04 g (10 mmol) of 1-lithio-2,2,3,3-tetramethylcyclopropane was placed in a round-bottom flask coupled with a small distillation apparatus and heated to 170 °C under dry and oxygen-free argon for 10 h. Rapid stirring of the powdered sample with a magnetic stirring bar is required when larger quantities are desired. The 1,1,2,2-tetramethylcyclopropane generated was collected in a receiver cooled with an ice bath. The system was then evacuated and 1,1,2,2-tetramethylcyclopropane (0.46 g; 94%) was isoalted, using a vacuum line. The residual solid was carefully hydrolyzed by introducing an excess of D_2O. Through the vacuum line, the products were fractionated through a −45 °C bath (to trap excess D_2O) and a −196 °C bath. A mixture of 1,1-dideuterio-2,2,3,3-tetramethylcyclopropane (94%), dideuterioacetylene (4%), and tetradeuteriopropyne (2%) was obtained from the −196 °C bath.[3] The yield of 1,1-dideuterio-2,2,3,3-tetramethylcyclopropane (0.45 g) was calculated to be 90% based on the starting monolithio compound used. When the pyrolysis was performed at 210 °C, followed by the deuterolysis, a mixture of 1,1-dideuterio-2,2,3,3-tetramethylcyclopropane (41%), dideuterioacetylene (45%), and tetradeuteriopropyne (14%) was obtained. Pyrolysis at 240 °C for 15 min resulted in $(C_2D_2)_n$ (75%) and $(C_3D_4)_n$ (25%) after the deuterolysis. As indicated by the above experiments, 1,1-dilithio-2,2,3,3-tetramethylcyclopropane decomposed into C_2Li_2 and C_6Li_4 as did dilithiomethane[4] and 1,1-dilithioneopentane.[5]

In addition, pure 1,1-dilithio-2,2,3,3-tetramethylcyclopropane was obtained when 1-lithio-2,2,3,3-tetramethylcyclopropane was pyrolyzed under an inert atmosphere at 170 °C (yield 40%). At this temperature, the reaction proceeded slowly and 8–10 h were required for completion.

The ^{1}H NMR spectrum of 1-lithio-2,2,3,3-tetramethylcyclopropane in hexadeuteriobenzene consisted of singlets at δ 1.28 and 1.40 due to the methyl groups and a singlet at δ −2.59 due to the ring proton, while the ^{1}H NMR of 1,1-dilithio-2,2,3,3-tetramethylcyclopropane in hexadeuteriobenzene contained only a singlet at δ 1.13 from the methyl groups. (The equivalence of the four methyl groups indicates a symmetrical structure of the dilithio compound.) Absence of the peak at δ −2.59 is good evidence for geminal lithium substitution on the cyclopropane ring. The methyl-substituted cyclopropane ring enhanced the solubility of the compound in organic solvents, compared with dilithiomethane which is only very slightly soluble in most organic solvents.

Mass spectral analysis of the lithiated cyclopropane after deuterolysis showed a molecular ion at m/e 100 and a base peak at m/e 85, corresponding to $C_7H_{12}D_2$ and $C_6H_9D_2$, respectively. ^{1}H NMR of this compound contained only a singlet at δ 1.21, due to the methyl groups, indicating deuteration at two sites on the cyclopropane ring. Elemental analysis for $C_7H_{12}Li_2$. Calcd: C, 76.36%; H, 10.91%. Found: C, 76.18%; H, 10.87%.

Flash vaporization mass spectroscopy of the new *gem*-dilithiotetramethylcyclopropane shows that only monomers and dimers are present in the gas phase. Thus, the bulky methyl groups and cyclopropyl ring prevent extensive polymerization such as exists in dilithiomethane.[6] The structure of the dimer (and the

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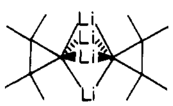
monomer) will soon be investigated in collaboration with Josef Michl and we predict a dimer with four equivalent and orthogonal bridging lithiums:



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Synthesis, Insertion, and Reductive Elimination Reactions of a Hydridoalkoxyiridium Complex

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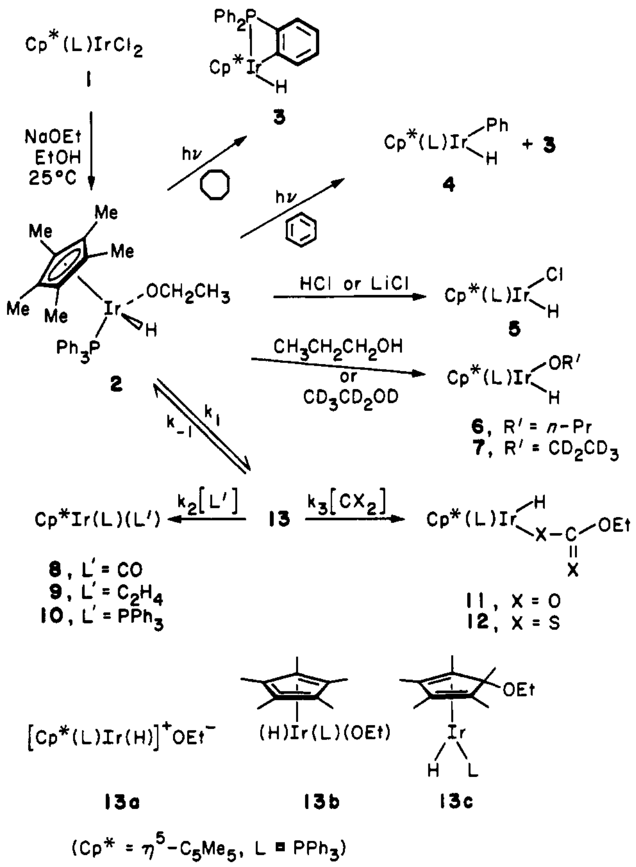
Low-valent, mononuclear late-transition-metal alkoxides, once very rare, are becoming increasingly well-known.[1] Recent studies have demonstrated that such complexes exhibit interesting insertion chemistry, although mechanistic information is still quite sparse.[2] We wish to report here the isolation and some reactions of a mononuclear late-transition-metal alkoxy hydride.[3] Preliminary mechanistic studies of apparent insertion and reductive elimination reactions demonstrate some surprising contrasts with analogous reactions of the corresponding alkyl hydrides.[4]

Our results are summarized in Scheme I. Addition of $Cp^*Ir(PPh_3)Cl_2$ (**1**, $Cp^* = C_5Me_5$)[5] to a solution of sodium ethoxide in dry ethanol forms an orange slurry which leads to the formation of a new, soluble complex as detected by ^1H NMR. After removal of the solvent in vacuo and extraction into pentane, yellow microcrystals of $Cp^*IrPPh_3(OEt)H$ (**2**) are obtained from a concentrated pentane solution at −40 °C in 79% yield. Compound **2** exhibits a characteristic Ir–H absorption at 2035 cm^{-1} in the infrared as well as a resonance at δ −13.20 in the ^1H NMR spectrum. The diastereotopic methylene protons in the ethoxy ligand exhibit a complex pattern at δ 3.79 in the ^1H NMR. The complex was further characterized by ^{13}C NMR and elemental analysis.[6]

Hydrido(ethoxy) complex **2** undergoes reaction with a wide range of substrates under mild conditions. Irradiation of **2** in cyclooctane leads to cyclometalation product **3**, the same material obtained upon photolysis of $Cp^*PPh_3IrH_2$ in cyclooctane.[4a,b] Irradiation in benzene leads to a mixture of **3** and $Cp^*(L)Ir(Ph)(H)$ (**4**), products which are also observed on photolysis of $Cp^*(PPh_3)IrH_2$. Photochemical activation therefore appears to induce reductive elimination and extrusion of ethanol from the coordination sphere of the metal, in analogy to the thermal activation of $Cp^*(L)Ir(R)(H)$.[4b–d] Few other reactions of **2**, however, find direct precedent in the chemistry of the (superficially) closely related hydridoalkyliridium complexes. For example, on heating in benzene, a complex mixture of products is formed, in which $Cp^*(L)IrH_2$ is the major (and at present only identified) product. More tractable chemistry is observed in the presence of ligands such as CO, ethylene, and phosphines. Under these conditions, ethanol and the corresponding iridium(I) adducts **8–10** are produced.[6] Although these appear to be direct reductive elimination reactions, mechanistic studies (see below) indicate they are more complicated.

Scheme I



Treatment of the hydridoalkoxy complex with alkyl halides does not lead to haloalkoxy complexes; rather, displacement of the alkoxy ligand is observed. Thus, treatment of **2** with 0.5–1.0 equiv of carbon tetrachloride or chloroform in benzene forms mixtures of the corresponding hydridochloroiridium and dichloroiridium complexes **5** and **1**, in ratios that depend upon the amount of halogenating agent used. Treatment of **2** with either HCl or lithium chloride also leads to **5** (97% and 74% yield, respectively). This reactivity is consistent with electrophilic attack on ethoxide (or incipient ethoxide; see below) ion by the substrate.

Further indication of the reactivity of the alkoxy group is provided by exchange studies with other alcohols. For example, dissolution of **2** in 1-propanol, or treatment with 1 equiv of sodium *n*-propoxide in tetrahydrofuran, leads to the hydrido(*n*-propoxy)iridium complex **6** in 73% yield (NMR).[7] Surprisingly, alkoxy exchange occurs without hydride loss, even in protic sol-

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(6) See supplementary material. Complex **9** was synthesized independently by William D. McGhee of this group.

(7) Attempts to isolate pure samples of this material have been frustrated so far by cocrystallization with nonstoichiometric amounts of solvent. Its identification has been made on the basis of spectroscopic (^1H, ^{13}C, ^{31}P NMR; IR) data.

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