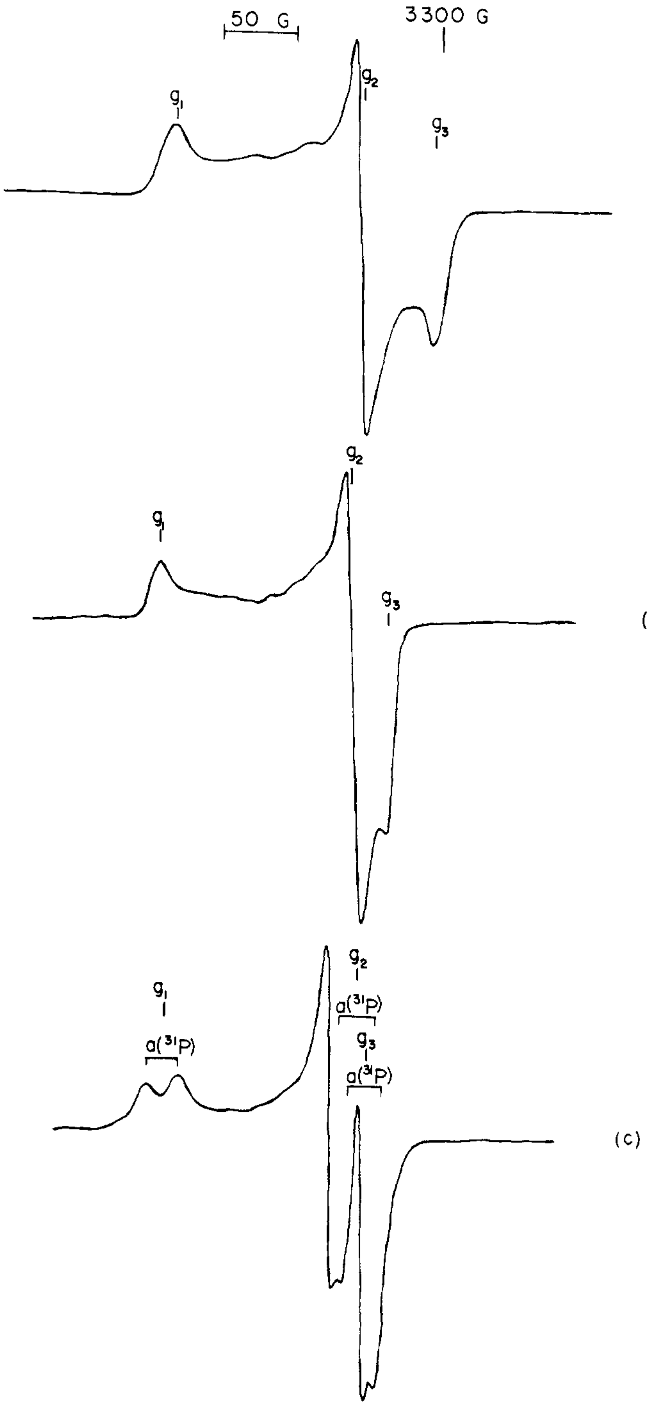

Figure 2. EPR spectra for dioxygen complexes of RhOEP in toluene glass (−160 °C): (a) RhOEP(O_2), (b) RhOEP(O_2) (piperidine), (c) RhOEP(O_2)[P(OBu)$_3$].

with those reported for the complex previously formulated as Rh^{II}TPP (Table I), suggesting that this species is actually the dioxygen complex, RhTPP(O_2). Authentic Rh(II) species with effective D_{4h} symmetry have substantially larger g values ($g_{\parallel} \sim 2.0$, $g_{\perp} \sim 2.3$: $\langle g \rangle \sim 2.2$) associated with the $(d_{xy}{}^2d_{xz,yz}{}^4)d_{z^2}{}^1$ electron configuration.[14,15] Heating a solid sample of the compound that we formulate as RhTPP(O_2) at 150 °C in high vacuum results in sublimation of a diamagnetic RhTPP compound. This species readily reacts with NO to form RhTPP(NO) (ν_{NO} 1658 cm^{-1}) and reacts with O_2 in the presence of donors to regenerate the EPR spectrum that we associate with RhTPP(O_2) complexes. The diamagnetic RhTPP species has NMR and electronic spectral properties as well as reactivity patterns consistent with a Rh^{II}TPP dimer (RhTPP)$_2$. We are presently attempting to grow crystals of RhTPP(O_2) and (RhTPP)$_2$ suitable for X-ray structure determinations.

Although no monomeric rhodium(II) porphyrin species has been directly observed, the Rh-Rh bonding in (RhOEP)$_2$ and its reactivity with NO and O_2 are indicative of a half-occupied d_{z^2} in Rh^{II}OEP. The free-radical-like reactivity of the rhodium(II) porphyrin unit is similar to that recognized for other low spin d^7 complexes such as $[Co(CN)_5]^{3-}$ [16] and $Rh(NH_3)_4{}^{2+}$.[6] The reactivity patterns for cobalt(II) and rhodium(II) porphyrins are closely related; however, increased thermal stability of the rhodium(II)-dioxygen complexes and the unique metal-metal bonding are manifestations of the enhanced covalent bonding ability of the second transition series metal.

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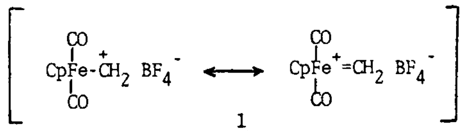
Cyclopropanation of Olefins with a Stable, Iron-Containing Methylene Transfer Reagent[1]

Sir:

A common synthetic transformation is the conversion of olefins into cyclopropanes. The importance of this conversion stems from the occurrence of cyclopropane rings in many natural products and from the utility of cyclopropanes as synthetic intermediates leading to other systems.[2] A disadvantage of many of the previously reported methods for the cyclopropanation of olefins is that the species required for methylene transfer are often quite unstable and cannot be isolated easily if at all. During the past decade, transition metal-carbene complexes have been studied extensively.[3] Although these species have structures that suggest that they may behave as carbene sources of possible use in cyclopropanation,[4] they frequently exhibit quite different patterns of chemical behavior. However, several years ago, Jolly and Pettit reported the apparent generation of the iron-containing species (**1**) which was considered to be a cationic iron–carbene complex

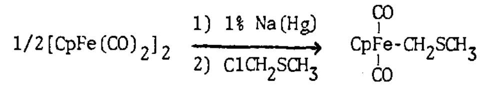


$$\left[\ \mathrm{Cp}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{\mathrm{Fe}}}\text{-}\overset{+}{\mathrm{C}}\mathrm{H_2}\ \mathrm{BF_4}^- \longleftrightarrow \mathrm{Cp}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{\mathrm{Fe}}}{}^{+}{=}\mathrm{CH_2}\ \mathrm{BF_4}^-\ \right]$$

1

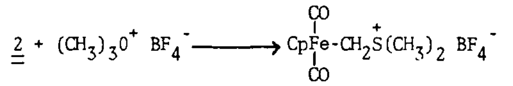
plex and which was reported to react with a few olefins to give cyclopropanes.[5] More recently, **1** and related species (including complexes of other metals) have been subjects of various experimental and theoretical studies.[6] These reports suggested to us that a useful cyclopropanation reagent may be available if a stable precursor of **1** could be prepared. In this communication we are pleased to report our development of a new reagent which fulfills this requirement.

We have found that the sulfide **2** may be obtained in 93% yield (after crystallization) by the procedure of King and Bisnette (eq 1), although these workers had reported a yield



$$1/2[\mathrm{CpFe(CO)_2}]_2 \xrightarrow[\text{2) } \mathrm{ClCH_2SCH_3}]{\text{1) 1\% Na(Hg)}} \mathrm{Cp}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{\mathrm{Fe}}}\text{-}\mathrm{CH_2SCH_3} \qquad (1)$$

2



$$\underline{\underline{2}} + \mathrm{(CH_3)_3O^+\ BF_4^-} \longrightarrow \mathrm{Cp}\overset{\mathrm{CO}}{\underset{\mathrm{CO}}{\mathrm{Fe}}}\text{-}\mathrm{CH_2}\overset{+}{\mathrm{S}}\mathrm{(CH_3)_2\ BF_4^-} \qquad (2)$$

3

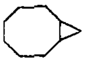
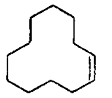
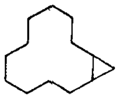
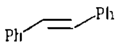
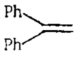
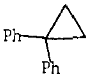
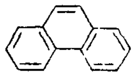
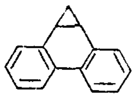
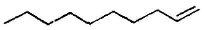
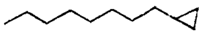
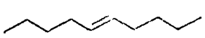
$$\underline{\underline{3}} + \mathrm{R^1CH{=}CHR^2} \longrightarrow$$

(3)

of only 25%.[7] Methylation of **2** (1 equiv of $\mathrm{(CH_3)_3O^+BF_4^-}$,[8] $\mathrm{CH_2Cl_2}$, −20 to +25 °C) gives the sulfonium salt **3** (eq 2) in 82% yield as a yellow, crystalline solid: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.22 (s, 5 H), 2.74 (s, 6 H), 2.45 (s, 2 H). The salt **3** is quite stable in that it undergoes no noticeable change upon storage in the air for several months at room temperature. Although not necessary for use in the reactions reported here, **3** may be purified conveniently by preparing a solution (~0.5 M) in DMF at 25 °C under an inert atmosphere, adding anhydrous diethyl ether (~3 vol.) until the solution just becomes cloudy, cooling the mixture slowly to −20 °C to induce crystallization, and removing the supernatant liquid with a syringe. The recovery is 70–80%.

Most satisfying is that, when **3** is heated at reflux in dioxane (1–2 M solutions, 4–12 h) with olefins under a nitrogen atmosphere, cyclopropanes are produced directly (eq 3). Our results to date are summarized in Table I. The salt **3** appears to meet the goal of being a stable, isolable cyclopropanation reagent that may be used as a routine laboratory item. The isolation of products is generally quite simple: the reaction mixtures are diluted with pentane to precipitate the iron-containing byproducts, and the cyclopropanes are obtained from the pentane solution by distillation or chromatographic procedures. The stereospecificity of the reaction is indicated by the last two entries in Table I; in each case, none of the opposite stereoisomeric cyclopropane[9] could be detected within the limits of sensitivity (<0.1%) of our gas chromatographic equipment. We note, though, that apparently a side reaction (unidentified as yet) occurs during the cyclopropanations which leads to destruction of **3** as indicated by the low conversions of olefins that result from the use of only 1 equiv of **3** in some cases. As a result we generally employ 2 equiv of the reagent in these reactions.

Table I. Cyclopropanation of Olefins with **3**[a]

Olefin	Cyclopropane	Conversion of Olefin (%)[b]	Yield (%)[b]
		96	92
		63	66
	 [c]	62	64
		100	96
		38	82
		81	70
		49	67
		59	87

[a] For these experiments, 2-equiv portions of **3** were employed. [b] All conversions and yields were determined by GLC using internal standards calibrated against pure samples of the cyclopropanes obtained by preparative GLC. The yields are corrected for recovered olefins. None of the yields have been optimized. [c] The stereochemistry of this product was determined by ^{1}H NMR as reported in ref 10.

In our ongoing studies we are attempting to design reagents having modified leaving groups which will permit more efficient conversions of olefins. We are also exploring the extension of these reactions to alkylidene transfer in general and other applications of the types of organometallic reagents described here.

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[1:2,9:10]Bismethano[2.2]paracyclophane

Sir:

Strained hydrocarbons of the cyclophane class have been studied both theoretically and experimentally as a function of the length of the polymethylene chains which connect the π systems.[1] Changes in the electronic and magnetic resonance spectra, as well as in the chemical and thermal behavior of these compounds, have been observed with increasing deformation of the aromatic rings and bond angles, and as a function of the proximity of transannularly located benzene rings.[2] In recent years the possibility of a hyperconjugative effect between the C-C σ bond of the bridge and the aromatic π system has been proposed as an explanation for the anomalous electronic behavior of [2.2]paracyclophane.[3] Further enhancement of the changes might be expected if the benzene rings were bridged not by ethylene, but by cyclopropane rings. Previous attempts to prepare such a system by cyclopropanation of [2.2]paracyclophane-1,4-diene with diazomethane were unsuccessful.[4] This reaction leads to preferential attack on the aromatic double bonds and yields products similar to those observed from the reaction of diazomethane with other [2.2]paracyclophane derivatives.[4,5]

In the preparation of [2.2.2](1,2,4)cyclophane, it was demonstrated that carbon-carbon bond formation via transannular reductive dehalogenation was an effective and efficient means of introducing additional bridges (and additional ring strain) into cycles which already contained benzene rings in a face-to-face configuration.[6] A simple extension of this procedure was used in an attempt to synthesize [1:2,9:10]bismethano[2.2]paracyclophane (1) through a double ring contraction of [3.3]paracyclophane.

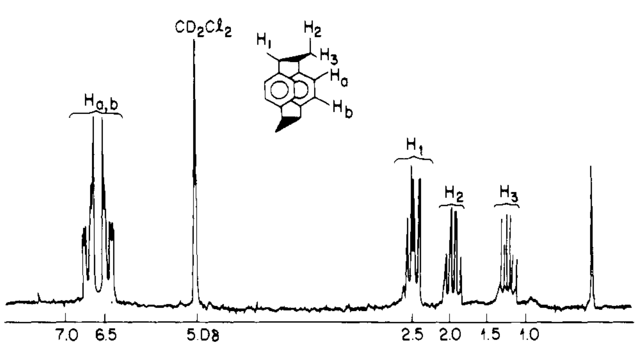
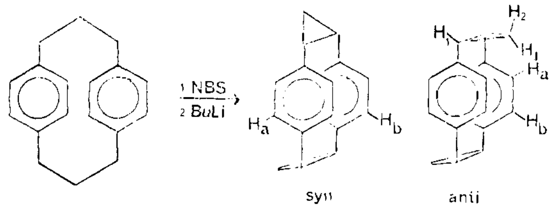


Figure 1.



II

I

The starting material was prepared by the method of Longone, Küsefoglu, and Gladysz.[7] Treatment of [3.3]paracyclophane (0.4 g) with 5 equiv (1.5 g) of recrystallized *N*-bromosuccinimide in refluxing carbon tetrachloride with a trace of benzoyl peroxide yielded 0.9 g (95%) of a material with approximate composition $C_9H_9Br_2$, mp >300 °C.[8] No attempt was made to separate the numerous isomers, but an NMR spectrum of this (barely soluble) material in tetrahydrofuran-d_8 gave a multiplet at $\delta \sim 5$ (Me_4Si), indicative of the presence of a secondary benzylic bromide. A dilute solution of the brominated material in tetrahydrofuran was treated with excess butyllithium, added dropwise over a period of 30 min at −70 °C under argon. After the usual workup in water-dichloromethane, the organic residue was subjected to thin layer chromatography (first on silica gel-chloroform, then several times on alumina-hexane) which resulted in the isolation of ~5% (based on [3.3]paracyclophane) of a crystalline, sparingly soluble colorless solid which sublimes readily and melts on rapid heating at 246-250 °C.

The composition of this material is $C_{18}H_{16}$ according to the mass spectrum (precise mass 232.1237, calcd 232.1223) which also indicated major fragments at m/e^+ 115, 117 (probably C_9H_9, a characteristic fragment of [3.3]paracyclophane[9]), and 128. The ultraviolet spectrum (ethanol, 2×10^{-5} M) indicates substantial perturbation of the π system: λ_{max} (ϵ) 230 (15 000), 260 (5000, sh), 304 (900).[10] The carbon magnetic resonance spectrum (22.62 MHz, CD_2Cl_2, Me_4Si) confirmed the presence of the cyclopropane rings (137.45 (quaternary carbon),[11] 134.10 (C_B), 128.11 (C_A), 23.90 (C_1), and 4.10 (C_{23})) in the ratio 0.3:2:2:2:1, respectively. A proton magnetic resonance spectrum of the material (CD_2Cl_2, 90 MHz, Me_4Si) is shown in Figure 1. Aromatic protons H_b and H_a appear at δ 6.74 and 6.51 ($J_{ab} = 8.0$, $J_{ab'} = 1.8$ Hz). Cyclopropane protons appear at δ 2.49 (H_1), 1.96 (H_2), and 1.20 (H_3) ($J_{12} = 5.7$, $J_{13} = 7.9$, $J_{23} = 6.6$ Hz). A computer simulation based on these data generated a spectrum essentially identical with the one shown in Figure 1. Aromatic coupling constants in the range of 7-9 Hz are characteristic of ortho splittings in previously isolated cyclophanes, while meta coupling constants are on the order of 1-2 Hz.[5] For the syn isomer of 1, protons H_a and H_b are meta (or para) to one another, and therefore a large aromatic coupling would not be expected. For the anti isomer of 1, however, H_a and H_b should give rise to an AB quartet further complicated by meta coupling as was observed in the proton spectrum of 1. On the basis of these data we have assigned to compound 1 the structure *anti*-[1:2,9:10]bismethano[2.2]paracyclophane.

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