Cyclopropane formation from the reaction of (.gamma.-haloalkyl)iron compounds with silver(1+)

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The variable-temperature ¹H NMR spectrum of **3** is shown in Figure 2. The −9.23 ppm resonance shows the same splitting at both 400 and 500 MHz indicating that the two hydride ligands have the same chemical shift and that the splitting pattern is second order. The ³¹P{¹H} NMR spectrum of **3** exhibits resonances due to two inequivalent sets of phosphine donors, while the hydride-coupled spectrum reveals that only one of these sets has significant phosphorus–hydride coupling. From these results and other spectroscopic characterization,[12] complex **3** is formulated as the μ-phenylsilylene hydride $Rh_2H_2(\mu\text{-}SiPhH)(CO)_2(dppm)_2$.

A satisfactory fit of the hydride resonance of **3** at −70 °C was obtained assuming an AA′MM′XX′ pattern with the following parameters: $J_{AA'}$ = 5 Hz, $J_{AM} = J_{A'M'}$ = 143 Hz, $J_{AX} = J_{A'X'}$ = 21.7 Hz, $J_{AM'} = J_{A'M}$ = 14 Hz, $J_{AX'} = J_{A'X}$ = −8.6 Hz, $J_{MM'}$ = 144 Hz, $J_{MX} = J_{M'X'}$ = 93 Hz, $J_{M'X} = J_{MX'}$ = −24 Hz, $J_{XX'}$ = 61 Hz. On the basis of this fit with its one large hydride-phosphorus coupling and the crystallographically determined structure of **2**, complex **3** is proposed to have a cradlelike structure with terminal hydrides and a single μ-SiPhH bridge.
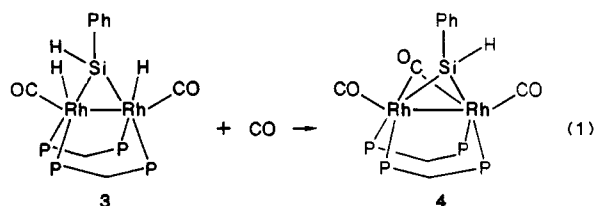

3
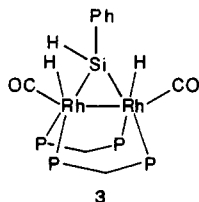
The fluxional process of Figure 2 involves exchange of the hydrogen atoms bound to rhodium and silicon. If the basic cradle structure is preserved throughout the exchange, then the dppm CH₂ protons coalesce from four resonances into two as is readily seen. From the coalescence temperatures of the two sets of dppm methylene protons and the Rh–H/Si–H exchange, $\Delta G^{\ddagger}$ for the process is calculated to be 12 ± 1 kcal/mol at both −30 and 25 °C, indicating a virtually negligible $\Delta S^{\ddagger}$ for the fluxional process. Harrod et al. have observed a similar exchange, but in their case the equilibration was between μ-SiPhH₂ and μ-H hydrogen atoms.[3] The fluxionality for **3** may be due to rapid reductive elimination and oxidative addition of Si–H bonds via a $Rh_2H(SiH_2Ph)(CO)_2(dppm)_2$ intermediate.

The reaction of **3** with $PhSiH_3$ leading to the stable bis μ-SiPhH product **2** undoubtedly proceeds by loss of H₂. This is supported by trapping the resultant intermediate with CO yielding the complex $Rh_2(\mu\text{-}SiPhH)(\mu\text{-}CO)(CO)_2(dppm)_2$ (**4**), which contains a bridging carbonyl ligand with ν_{CO} of 1770 cm⁻¹.[13] Complex **4** can also be prepared in high yield by reaction of $Rh_2(CO)_3(dppm)_2$ with $PhSiH_3$ in C_6H_6 at 25 °C for 24 h. On the basis of the fact that the dppm methylene protons of **4** exhibit four different resonances and that the μ-SiPh*H* resonance appears as a triplet of triplets with the larger J_{PH} similar to that seen for **2**, the structure of **4** is presumed to be of the cradle-type as shown in eq 1.

When $EtSiH_3$ is used as the substrate in reaction with **1** under similar conditions, exactly analogous chemistry is observed with sequential formation of $Rh_2H_2(SiEtH)(CO)_2(dppm)_2$ (**5**) and $Rh_2(SiEtH)_2(CO)_2(dppm)_2$ (**6**).

$$\textbf{3} + CO \longrightarrow \textbf{4} \qquad (1)$$

Characterization of **5** and **6** is by ¹H and ³¹P NMR and IR spectroscopies.[14] Complex **6** has also been isolated.[15] From the characterization data, **5** contains a bridging ethylsilylene ligand and terminal hydrides and exhibits fluxional behavior similar to that of **3** in which Si–H/Rh–H interchange is occurring.

The present study thus shows that primary silanes can react with **1** to form μ-SiRH species and that if hydride ligands are also present, rapid exchange of the hydrides with Si–H occurs. These results suggest that Si–H bonds of silylene bridges are relatively labile, a feature which is under continuing investigation.

Supplementary Material Available: Tables of refined positional and thermal parameters, calculated hydrogen positional parameters, and complete bond distances and angles for **2** (11 pages); a tabulation of observed and calculated structure factor amplitudes for the structure determination of **2** (32 pages). Ordering information is given on any current masthead.

(14) **Spectroscopic data for 5:** ¹H NMR (C_6D_6, 298 K, ppm) 7.62 (s, 8 H), 7.22 (s, 8 H), 6.85–6.65 (m, 24 H), 4.29 (AB q, J = 10 Hz, 2 H), 3.10 (AB q, J = 10 Hz, 2 H), 2.15 (br s, 2 H), 1.92 (t, J = 8 Hz, 3 H), −3.8 (very br); ³¹P{¹H} NMR ($CDCl_3$, −55 °C, H_3PO_4 reference, ppm) 17.6 (symmetric mult), 28.98 (symmetric mult). **Spectroscopic data for 6:** ¹H NMR (C_6D_6, 298 K, ppm) 7.87 (s, 8 H), 7.12 (s, 8 H), 6.93 (t, J = 7 Hz, 10 H), 6.79 (t, J = 7 Hz, 2 H), 6.65 (t, J = 7 Hz, 2 H), 6.56 (t, J = 7 Hz, 10 H), 5.47 (symmetric mult, 2 H), 4.58 (m, 2 H), 3.25 (m, 2 H), 2.00 (br s, 4 H), 1.37 (t, J = 7 Hz, 6 H); ³¹P{¹H} NMR (C_6D_6, H_3PO_4 reference, ppm) 32.61 (symmetric mult); IR (CH_2Cl_2) ν_{SiH} = 2054 cm⁻¹, ν_{CO} = 1932 cm⁻¹.
(15) Anal. Calcd for $Rh_2P_4Si_2O_2C_{56}H_{56}$: C, 58.6, H, 4.9. Found: C, 57.8, H, 5.1. The structure of **6** has been determined crystallographically and is virtually identical with that of **2**. Wang, W.-D.; Eisenberg, R., to be submitted for publication.

Cyclopropane Formation from the Reaction of (γ-Haloalkyl)Iron Compounds with Silver(1+)

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Summary: Reaction of $C_5H_5(CO)_2Fe(CH_2)_3Br$ with $AgBF_4$ in benzene leads to formation of cyclopropane in 73% yield.

The reaction of electrophilic carbene complexes with alkenes leads to formation of cyclopropanes in high yield.[1,2] One mechanism for cyclopropane formation involves electrophilic attack of the carbene carbon on the alkene which produces an intermediate with an electro-

(13) **Spectroscopic data for 4:** ¹H NMR (C_6D_6, 298 K, ppm) 8.48 (d, J = 7 Hz, 2 H), 7.90 (m, 4 H), 7.73 (m, 4 H), 7.28 (t, J = 7 Hz, 2 H), 7.09 (m, 8 H), 6.9–6.5 (m, 25 H), 5.31 (tt, J_{PH} = 23, 7 Hz, 1 H), 4.20 (dt, J = 15, 9 Hz, 2 H), 3.72 (AB q, J = 10 Hz), 3.28 (dt, J = 15, 9 Hz), 2.47 (AB q, J = 10 Hz); ³¹P{¹H} NMR (C_6D_6, H_3PO_4 reference, ppm) 24.06 (symmetric mult), 44.86 (symmetric mult); IR (CH_2Cl_2) ν_{CO} = 1946, 1770 cm⁻¹, ν_{SiH} = 2012 cm⁻¹.

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philic carbon γ to the metal center.[3,4] This intermediate is then converted to cyclopropane either directly or via a metallocyclobutane. The best evidence for a carbocation γ to a metal center as an intermediate in cyclopropane formation comes from Brookhart's observation that *cis*-β-deuterio-*p*-methoxystyrene reacts with $C_5H_5(CO)_2Fe=$ $CHCH_3^+$ to form a cyclopropane with partial loss of stereochemistry attributed to bond rotation in a carbocation intermediate.[5]
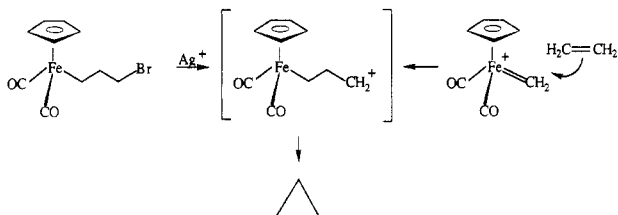
As an alternative means of generating an electrophilic carbon center γ to iron, we have studied the reactions of (γ-haloalkyl)iron compounds with Ag^+ and we now report that this provides an efficient route to cyclopropanes.

The starting materials for our studies are the (ω-haloalkyl)iron compounds $C_5H_5(CO)_2Fe(CH_2)_nX$, first prepared by Moss[6] as precursors to compounds in which two metals are linked by a hydrocarbon chain.[7] A solution of C_5-$H_5(CO)_2Fe(CH_2)_3Br$ (1; 13.5 mg, 0.045 mmol) in 0.25 mL of benzene-d_6 containing hexamethylbenzene as an internal ^1H NMR standard was added to a suspension of $AgBF_4$ (15 mg, 0.077 mmol) in 0.20 mL of benzene-d_6 at liquid-nitrogen temperature.[8] When the mixture was warmed to room temperature and shaken, red insoluble iron species and silver bromide were produced immediately. Integration of the ^1H NMR spectrum indicated that cyclopropane (δ 0.13) was formed in 73% yield as the only detectable organic product. The identity of cyclopropane was confirmed by comparison of its gas chromatographic retention time (Carbowax 20 M, 30 °C) and of its mass spectrum with that of an authentic sample. Similarly, reaction of the related chloride $C_5H_5(CO)_2Fe(CH_2)_3Cl$ (2; 15.5 mg, 0.061 mmol) with $AgBF_4$ (23 mg, 0.118 mmol) in benzene-d_6 led to the formation of cyclopropane in 68% yield as the only organic product detected by ^1H NMR.

The secondary (γ-bromoalkyl)iron compound $C_5H_5(C-O)_2FeCH_2CH_2CH(CH_3)Br$ (3;[9] 18.5 mg, 0.059 mmol) reacted with $AgBF_4$ (24 mg, 0.123 mmol) in benzene-d_6 containing hexamethylbenzene as an internal ^1H NMR standard to produce methylcyclopropane in 70% yield.[10]

The identity of methylcyclopropane was confirmed by comparison of its gas chromatographic retention time and mass spectrum with that of an authentic sample.[11]

In contrast to the efficient production of cyclopropanes from (γ-haloalkyl)iron compounds 1–3, formation of cyclobutane and cyclopentane from the corresponding (ω-haloalkyl)iron compounds was slow and inefficient. For example, the (4-bromobutyl)iron compound $C_5H_5(CO)_2$-$Fe(CH_2)_4Br$ (4; 16.2 mg, 0.052 mmol) and $AgBF_4$ (17 mg, 0.087 mmol) in benzene-d_6 failed to produce any detectable cyclobutane; instead, slow decomposition to insoluble material occurred over several hours. The (5-bromopentyl)iron compound $C_5H_5(CO)_2Fe(CH_2)_5Br$ (5) reacted slowly over several hours with $AgBF_4$ in benzene-d_6 to produce cyclopentane (8%) in addition to small amounts of pentenes detected by ^1H NMR and GC–MS. For comparison, 1-bromopropane rearranged slowly to 2-bromopropane upon treatment with $AgBF_4$ in benzene-d_6.
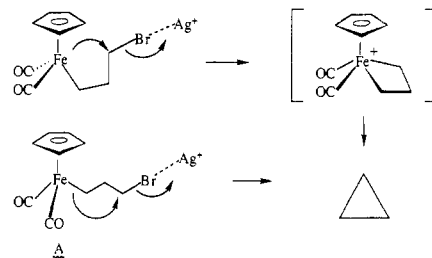
The reaction of $AgBF_4$ with (γ-haloalkyl)iron compounds 1–3 to produce cyclopropanes is therefore much more rapid than the reactions of primary alkyl bromides or (δ-haloalkyl)- or (ϵ-haloalkyl)iron compounds. This provides strong evidence for iron participation in the cleavage of the γ-carbon–halogen bond in 1–3. In addition, the Lewis acid Ag^+ complexes to the halogen atom and accelerates the loss of halide. There are two possible mechanisms for iron participation in cyclopropane formation. First, backside attack of iron d electrons at the γ-carbon could accelerate loss of bromide and lead to a cationic ferracyclobutane which then reductively eliminates cyclopropane. The closest precedent for this mechanism is the recently reported formation of platinacyclobutanes from the reaction of diazoalkanes with platinum alkene complexes.[12] A second mechanism involves the W-shaped conformation A in which the back side of the Fe–C σ bond nucleophilically displaces bromide and produces cyclopropane directly. This mechanism has precedent in the cyclopropane forming reactions of alkyltin compounds bearing a leaving group in the γ-position.[13,14] Davis has demonstrated that cyclopropane formation occurs via a double-inversion process of a W-shaped conformation of the tin derivative.[15] The two mechanisms for cyclopropane formation from 1–3 can be distinguished by determining the stereochemistry at the carbon center α to iron. The ferracyclobutane mechanism requires retention of stereochemistry at the α-carbon while the W-shaped transition state requires inversion of stereochemistry at the α-carbon. We are currently attempting to synthesize stereochemically labeled (γ-haloalkyl)iron compounds to

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(8) All reactions were performed in a similar manner. For example, a benzene-d_6 solution of 1 and hexamethylbenzene as an internal NMR standard was prepared in a drybox and capped with a septum. One portion of the solution was syringed into an NMR tube and sealed under vacuum for use as a standard. A second portion of the solution was syringed into an NMR tube containing a frozen suspension of $AgBF_4$ (2 equiv) in benzene-d_6 at liquid-nitrogen temperature. The tube was sealed under high vacuum, warmed to room temperature, and shaken. A ^1H NMR was taken within 15 min, and the yield of cyclopropane was calculated by comparison of NMR integrations of the reaction mixture and the standard solution using the hexamethylbenzene peak as a standard.

(9) $C_5H_5(CO)_2FeCH_2CH_2CH(CH_3)Br$ (3): ^1H NMR (200 MHz, benzene-d_6) δ 3.98 (s, C_5H_5), 3.85 (m, CH), 1.86 (m, CH_2), 1.52 (d, J = 6.6 Hz, CH_3), 1.17 (m, $FeCH_2$); ^{13}C NMR (126 MHz, benzene-d_6) δ 217.6 (CO), 85.3 (d, J = 180 Hz, C_5H_5), 55.2 (d, J = 150 Hz, CH), 49.5 (t, J = 128 Hz, CH_2), 25.8 (q, J = 129 Hz, CH_3), −0.78 (t, J = 135 Hz, $FeCH_2$); IR (hexane) 2011 (s), 1964 (sh), 1968 (s) cm^{-1}.

(10) $CH_3CHCH_2CH_2$: ^1H NMR (200 MHz, benzene-d_6) δ 0.94 (d, J = 5.7 Hz, CH_3), 0.58 (m, CH), 0.37 (m, 2 H), −0.06 (m, 2 H). See also: Crawford, R. J.; Erickson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 3907.

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distinguish between these two mechanisms.

Synthesis and Molecular Structure of Lithium Tri-*tert*-butylberyllate, Li[Be(*t*-C$_4$H$_9$)$_3$]

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*Summary:* Di-*tert*-butylberyllium, (*t*-C$_4$H$_9$)$_2$Be, and *tert*-butyllithium, (*t*-C$_4$H$_9$)Li, react in pentane to produce clear, colorless needlelike crystals of Li[Be(*t*-C$_4$H$_9$)$_3$] in high yield. A single-crystal X-ray diffraction study at −149 °C has established the trigonal-planar arrangement of the *tert*-butyl groups around beryllium.

We have recently initiated a survey of the organometallic chemistry of beryllium and report herein the synthesis and structural characterization of a new crystalline organoberyllium compound, lithium tri-*tert*-butylberyllate, Li[Be(*t*-C$_4$H$_9$)$_3$]. Structures for the related compounds LiBeH$_3$[1] and Li$_2$[Be(CH$_3$)$_4$][2] have previously been deduced from X-ray powder diffraction data. The dynamics of the Be(CH$_3$)$_2$/LiCH$_3$ system in diethyl ether has been studied by IR and variable-temperature ^{1}H NMR spectroscopy and was shown to be very fluxional at ambient temperature.[3] The structure of [NaBe(C$_2$H$_5$)$_2$·O(C$_2$H$_5$)$_2$]$_2$ has also been determined by single-crystal X-ray diffraction.[4,5] This structure has a nominally trigonal-planar arrangement around beryllium with two Be–C bonds and a hydrogen-bridged Be–Be bond.

In a typical synthesis utilizing a glass high vacuum system, 550 mg (4.47 mmol) of di-*tert*-butylberyllium, (*t*-C$_4$H$_9$)$_2$Be, prepared by the method of Head, Holley, and Rabideau[6] was condensed onto a frozen (−196 °C) solution of 286 mg (4.47 mmol) of freshly sublimed *tert*-butyllithium, (*t*-C$_4$H$_9$)Li, in 5 mL of dry pentane. The reaction vessel was sealed and allowed to warm to ambient temperature. The two reactants mixed by diffusion only. Colorless needle-shaped crystals of the title compound began to form after a few minutes. After 5 h the product was collected by filtration, washed with pentane, and dried under vacuum. Yield: 669 mg (3.60 mmol, 80.5% of theory). NMR spectra in C$_6$D$_6$: ^{1}H, δ = 1.01 ppm; ^{9}Be, δ = 19.5 ppm; ^{7}Li, δ = −2.30 ppm; ^{13}C, δ = 32.6 ppm (q, *J* = 15 Hz, 9 C), δ = 17.3 ppm (s, 3 C).

Solid Li[Be(*t*-C$_4$H$_9$)$_3$] fumes in air but appears to be very stable under vacuum or in an inert atmosphere. It exhibits good solubility in benzene, toluene, tetrahydrofuran, glyme,
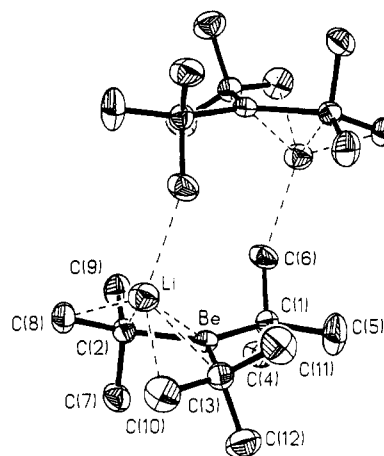
Figure 1. ORTEP plot (50% probability thermal ellipsoids) of Li[Be(*t*-C$_4$H$_9$)$_3$] showing the trigonal-planar arrangement of the three *tert*-butyl groups around beryllium and the dimeric orientation of the molecules in the unit cell.

and diethyl ether and is slightly soluble in pentane. When heated at 70 °C under high vacuum, it sublimes with little decomposition. A low-temperature ^{1}H NMR study in a toluene-d_8/CF$_3$Br mixed solvent (ca. 50/50) system showed only a single resonance down to −140 °C. The room-temperature ^{13}C NMR spectrum (C$_6$D$_6$) shows resonances characteristic of *tert*-butyl groups. In ethereal solvents such as THF, glyme, or ethyl ether, di-*tert*-butylberyllium etherate, (*t*-C$_4$H$_9$)$_2$Be·O(C$_2$H$_5$)$_2$, and *tert*-butyllithium react readily to produce a clear, colorless solution. The ^{9}Be NMR spectra of these solutions exhibit signals which are shifted about 2 ppm upfield from the resonances for the title compound in ether-free solvents.

A single-crystal X-ray diffraction study of lithium tri-*tert*-butylberyllate at −149 °C revealed that the molecule crystallizes in the triclinic space group P$\bar{1}$ with *a* = 8.515 (2) Å, *b* = 8.546 (2) Å, *c* = 11.293 (3) Å, α = 72.90 (2)°, β = 70.49 (2)°, γ = 62.08 (2)°, *V* = 675.2 (3) Å^3, and *Z* = 2. Diffraction data was collected on a Nicolet diffractometer using Mo Kα radiation. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, and positional parameters of the hydrogen atoms were refined with fixed isotropic thermal parameters. Final least-squares refinement gave *R* = 4.1% and R_w = 5.0% using 1380 reflections having *F* > 5.0σ(*F*). Lithium tri-*tert*-butylberyllium crystallizes solvent-free from pentane solutions as a dimeric unit having C_i symmetry as shown in Figure 1. The geometry around the beryllium atom is trigonal planar with the beryllium atom and the three tertiary carbon atoms (from the *tert*-butyl groups) lying in one plane. The planarity of this unit is clearly indicated by the fact that the sum of the three C–Be–C angles is 359.9°. The lithium atom resides above this plane in a cavity having close contacts with Be, C(2), C(3), C(8), C(10), H(8B), H(8C), and H(10B) and with C(6A), H(6A) and H(6B) of the second molecule. The Be–C(1) distance is 1.812 (4) Å, which is similar to Be–C distances in [NaBe(C$_2$H$_5$)$_2$·O(C$_2$H$_5$)$_2$]$_2$[4,5] and Li$_2$[Be(CH$_3$)$_4$].[2] The distances Be–C(2) and Be–C(3) are longer at 1.854 (4) Å and 1.864 (3) Å, respectively, apparently due to interaction with the Li atom. The Be–Li distance is 2.227 (6) Å and the four C–Li distances within the molecular unit average 2.228 Å. This value is similar to LiC distances in methyllithium (2.30 Å)[7,8] and ethyllithium (2.18 Å).[9] The Li–C(6A)

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