

**Alicyclic 1,2-디할로폴리플루오르올레핀으로 부터 비닐리튬
 화합물과 Perfluorinated 유기금속화합물의 합성***

朴 達 祚** · 崔 三 權**

미국 콜로라도대학교 화학과
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**The Preparation of Perfluorinated Organometallic
 Compounds via Vinyl lithium Compounds of
 Alicyclic 1,2-Dihalopolyfluoroolefins***

Joseph D. Park** and Sam Kwon Choi**

Department of Chemistry, University of Colorado, Boulder, Colorado U. S. A.

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요 약. 폴리플루오르올레핀리튬 化合物들이 1,2-dihalopolyfluorocycloalkenes 와 알킬리튬試藥
 과의 交換反應에 依하여 合成되었다.

수은, 비소와 디메틸게르마늄할로겐화물과의 여러가지 反應이 著述되어 있고 또 이 化合物들의
 化學的性質에 對하여 考察하였다.

Abstract. Polyfluorocycloalkenyllithium compounds have been prepared by an exchange reaction
 with 1,2-dihalopolyfluorocycloalkenes and alkyl lithium reagents. Their reactions with mercuric,
 arsenic and dimethyl germanium halides are described and the chemistry of these compounds
 discussed.

Introduction

The preparation of vinyl lithium derivative of alicyclic fluorine-containing olefins has been the subject of considerable activity in recent years. In contrast, very little work has been recorded in the literature on the chemistry of the alicyclic polyfluorovinyl lithium derivatives (Fig. 1 and 2).

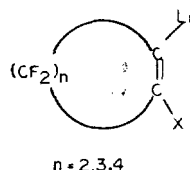


Fig. 1.

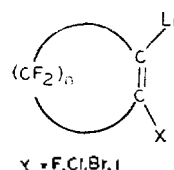


Fig. 2.

It is the purpose of the present work to describe a convenient method for the facile preparation of a number of these fluorinated alicyclic vinyl lithium compounds through halogen-lithium exchange process from the corresponding 1,2-dihalopolyfluorocycloolefins and utilization of these intermediate for the synthesis of

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**The Korea Advanced Institute of Science, Seoul, Korea

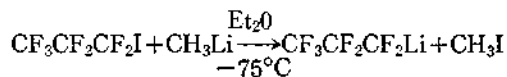
various organometallic compounds bearing di-valent, trivalent and tetravalent metals.

Historical

The utility of organolithium compounds in organic synthesis is a well established fact and needs no further mention.

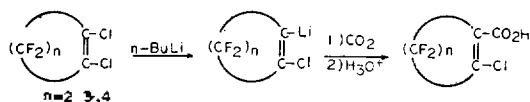
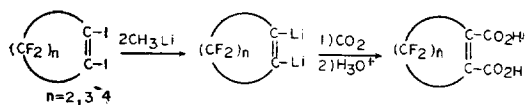
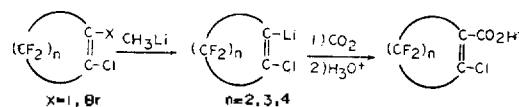
Organolithium derivatives were first prepared in 1917 by Schlenk and Holtz¹ by the reaction of lithium metal on alkyl mercurials. Since this historic discovery, the search for new and novel types of these reagents has continued to be an unceasing challenge.

The initial preparation of a fluorinated organolithium compound was reported by McBee, Pierce, and Judd² who in 1954 found that perfluoro-*n*-propyl iodide and methyllithium at low-temperature interact via halogenlithium inter-conversion to give good yields of perfluoro-*n*-propyllithium.

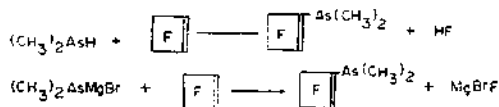


Recently Nakata¹⁷ of this laboratory synthesized mono- and divinyl lithium compounds of polyfluorocycloalkene through halogen-lithium interchange reaction. He found that facile exchange with methyllithium took place when the resident vinylic halogen was iodine or bromine. When *n*-butyllithium was employed as the alkyl lithium agent, however, vinylic chlorine was observed to undergo exchange as well. The utility of these organometallics as intermediates for the preparation of heretofore inaccessible polyfluorocycloalkenes bearing functionally active substituents at the vinylic sites was demonstrated through carbonation as follows:

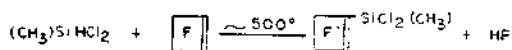
It was established Cullen²² and Hota²³ that perfluorocyclobutenyl derivatives such as $(\text{CH}_3)_2\text{As}-\text{C}=\text{CF}-\text{CF}_2-\text{CF}_2$ can be obtained by re-



acting the hexafluorocyclobutene with suitable arsenicals as follows:



It seemed desirable to try to prepare similar derivatives of other metal and metalloids since at the time of starting this investigation only two silicon containing analogues had been reported.^{24,25}



Haluska²⁵ also claimed to have obtained compounds of the type $\text{CH}_3\text{Cl}_2\text{Si}-\text{C}=\text{CClCF}_2-\text{CF}_2-\text{CF}_2$ from dichloromethyl silane and 1,2-dichloro-hexafluorocyclopentene and stated that the mechanism of reaction appeared to be the addition of the silane across the double bond with subsequent elimination of hydrogen halide.

The previous discussion constitutes a comprehensive survey of the currently existing literature on the subject of polyfluoro aliphatic and other polyfluoro organo metallic compounds.

The literature is conspicuously bereft of accounts dealing with the synthesis of alicyclic fluorine-containing mono or dibridged organo-metallic compounds.

The present study is concerned with attempts to prepare polyfluorocycloolefin derivatives of

mercury, germanium and arsenic and other functional groups.

Results and Discussion

The metallation of 1,2-diiodopolyfluorocycloolefins with methyl lithium and 1,2-dichloropolyfluorocycloolefins with *n*-butyllithium in diethyl ether has been recently reported by Nakata¹⁷ to give mono- and dilithiopolyfluorocycloolefin derivatives. These derivatives were utilized in this program of investigation of the chemistry of the polyfluorocycloalkene organo-mercury compounds. The product of lithiation of polyfluorocycloalkenes in diethyl ether at low temperature was reacted quite straightforwardly with mercuric chloride to give good yields of the desired mono- and dimeric polyfluorocycloalkenes, according to the following equations:

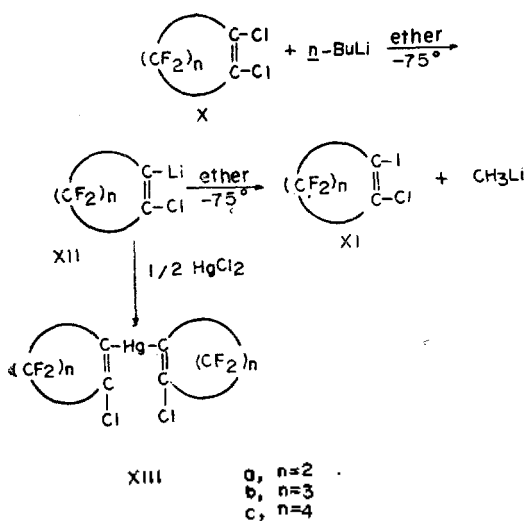
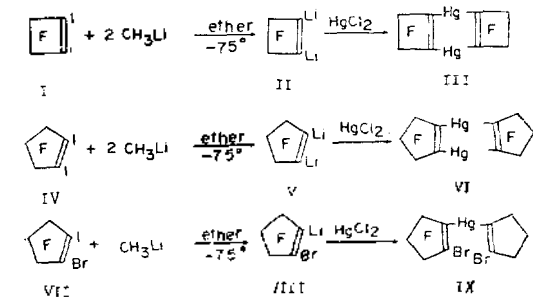


Table 1.

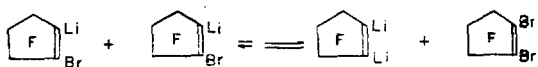
Compound	ν_{C} (cm ⁻¹)	Compound	ν_{C} (cm ⁻¹)
	1533		1580
	1530		1598
	1529		1627

These mono- and dimeric polyfluorocycloalkenes were the only divalent organometallic compounds which were obtained. Attempts to prepare the analogous organometallic compounds of zinc and cadmium were unsuccessful. Even though Zn, Cd, and Hg belong to group II b, (the same as Hg) no general reason was available to explain this failure. Since mercury is an *sp* hybridized, C—Hg—C bond angle in compound II and VI will be somewhat bent due to ring strain.

It was observed that the infrared double bond stretching frequency increased with increase of ring size of bis-(polyfluorocycloalkene)-mercury, which is reverse to the effect of non-substituted dichloropolyfluorocycloalkenes (Table 1).

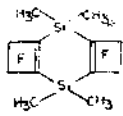
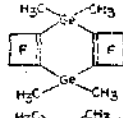
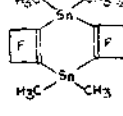
If the back donation of the *d*-electron of mercury to the π^* orbital becomes more significant as ring size decreases, then the bond order of the double bond will be lowered and the stretching vibration will decrease accordingly. This could account for the observed results.

It was further observed that the yield of bis(2-bromohexafluorocyclopenten-1-yl)-mercury (IX) was lower when compared to the yield of compound XIII. This indicated that bromine-lithium interchange took place during the lithiation.



The nucleophilic replacements of the bis-(2-

Table 2

Compound	Chemical shift of H	Compound	Chemical shift	Electro** negativity
	9.49	(CH ₃) ₄ Si	10.00	1.90
	9.31	(CH ₃) ₄ Ge	9.67	2.00
	9.36	(CH ₃) ₄ Sn	9.95	1.93

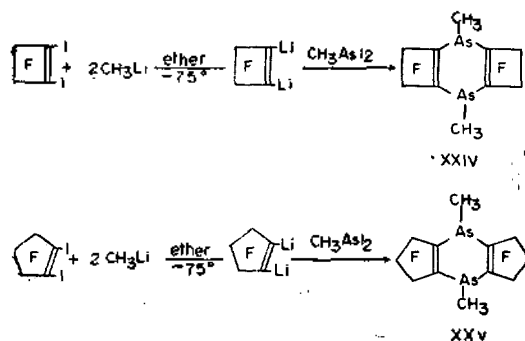
*56 **Mulliken electronegativity

germanium(9.67) and of tin(9.95) (Table 2).

It would thus seem that the chemical shift of the proton in the MCH₃ series increases with decreasing electro-negativity of M (metal).

Although the metals in compound XXIII, XVII and XXII are sp³ hybridized, their geometry is slightly distorted from perfect tetrahedral symmetry due to strain imposed by the rings.

The diarsine-bridged polyfluorocycloalkenes were obtained by carrying out the reaction in ether at -75°C by reacting dilithium polyfluorocycloalkene with methylarsenic diiodide according to the following equation:



The H' NMR spectrum of compound XXIV and XXV showed a singlet at τ 8.41, 8.38 respectively, corresponds to AsCH₃ protons.

Experimental

Preparation of Octafluoro-2,7-dimercuratrycyclo (6.2.0.0^{3,6})deca-1 (8),3(6)-diene (III).

A solution of 9.7 g (0.025 mol) of 1,2-diiodotetrafluorocyclobutene in 75 ml anhydrous diethyl ether in a 250 ml reaction vessel equipped with two reflux condensers (the first topped with a gas inlet tube, the other with a drying tube filled with indicating Drierite), a magnetic stirring assembly, and a serum cap was cooled to -75°C. (dry ice-acetone bath). Methyl lithium (22.5 ml of 2.15 M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes and the temperature was not allowed to rise above -65°C. After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C. and then 6.8 g (0.025mol) of mercuric chloride was

added and stirred for an additional 10 minutes, after which the mixture was allowed to reach gradually to room temperature and drowned with water. The organic layer was separated, dried over anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator. The crude solid product upon recrystallization in *n*-hexane, yielded 11.2g (68% of theory) of octafluoro-2,7-dimercuratricyclo (6.2.0^{3,6}) deca-1(8),3(9)-diene (III). m. p. 100-101 °C. Anal: Calcd. for C₈F₈Hg₂: C, 14.81; F, 23.46; Hg, 61.73.

Found: C, 14.46; F, 24.00; Hg, 61.30.

The infrared spectrum of compound III contained a sharp absorption at 1,538 cm⁻¹ which corresponds to an olefinic stretching frequency.

The Preparation of Dodecafluoro-2,8-dimercuratricyclo(7.2.0.0^{3,7})dodeca-1(4), 3(7)-diene (VI). A solution of 5.4 g (0.0125 mol) of 1,2-diiodohexafluorocyclopentene in 90 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75 °C. Methylithium (11.3 ml of 2.15 M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes and the temperature was not allowed to rise over -65 °C. After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at -75 °C. and then 3.5 g (0.0125 mol) of mercuric chloride was added. The reaction mixture was stirred for an additional 15 minutes and then allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was subjected to recrystallization from *n*-hexane, to yield 5g (53% of the ory) of dodecafluoro-2,8-dimercuratricyclo (7.2.0.0^{3,7}) dodeca-1(9), 3(7)-diene (VI). m. p. 80.5-81.5 °C.

Anal: Calcd. for C₁₀F₁₂Hg₂: C, 16.04; F, 30.48; Hg, 53.47.

Found: C, 15.72; F, 30.71; Hg, 53.53.

The infrared spectrum of compound VI contained a strong absorption at 1,583 cm⁻¹ which corresponds to an olefinic stretching frequency.

Preparation of Bis-(2-bromohexafluorocyclopenten-1-yl) mercury (IX). A solution of 9.5g (0.025 mol) of 1-iodo-2-bromo-hexafluorocyclopentene in 80 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75 °C. Methylithium (11.3 ml of 2.15M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes and the temperature was not allowed, to rise over -65°C After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75 °C. and then 3.4 g (0.0125 mol) of mercuric chloride was added. After the reaction mixture was stirred for an additional 10 minutes, the reaction mixture was allowed to reach gradually to room temperature and the product was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator. The crude solid product was subjected to recrystallization from *n*-hexane to yield 8.6 g (49% of theory) of bis-(2-bromohexafluorocyclopenten-1-yl)-mercury (IX). m. p.

99-70°C. Anal: Calcd. for Br₂C₁₀F₁₂Hg: Br, 22.59; C, 16.94; F, 32.20; Hg, 28.24.

Found: Br, 22.81; C, 16.87; F, 31.83; Hg, 28.13.

The infrared spectrum of compound IX contained a strong absorption at 1,595 cm⁻¹ which corresponds to an olefinic stretching frequency.

Preparation of Bis-(2-chlorotetrafluorocyclobuten-1-yl) mercury (XIIIa). A solution of 14g (0.05mol) of 1-iodo-2-chlorotetrafluorocyclobutene in 100ml of anhydrous diethyl ether con-

tained in the previously described reaction vessel was cooled to -75°C . Methylithium (11.3 ml of 2.15 *M* in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes and the temperature was not allowed to rise over -65°C . After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 9g (0.025 mol) of mercuric bromide was added. After the reaction mixture was allowed to reach gradually to room temperature, the product was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 16.2g (63% of theory) of bis-(2-chlorotetrafluorocyclobuten-1-yl)-mercury (XIIIa). m. p. $140-141^{\circ}\text{C}$.

Anal: Calcd. for $\text{C}_8\text{Cl}_2\text{F}_8\text{Hg}$: C, 18.40; Cl, 13.60; F, 29.30; Hg, 38.70.

Found: C, 18.25; Cl, 13.40; F, 29.90; Hg, 38.20.

The infrared spectrum of compound XIIIa contained a sharp absorption at $1,580\text{ cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of Bis-(2-chlorohexafluorocyclopenten-1-yl) mercury (XIIIb). A solution of 12.3g (0.05 mol) of 1,2-dichlorohexafluorocyclopentene in 100ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . *n*-butyllithium (20 ml of 2.46 *M* in tetrahydrofuran) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes. After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 6.8g (0.025 mol) of mercuric chloride was added. After the reaction mixture was stirred for an additional 10 minutes,

the reaction mixture was allowed to reach room temperature gradually. After washing with dilute hydrochloric acid, the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was then removed in a rotary evaporator. The solid crude product was then subjected to recrystallization in *n*-hexane yielded 17g (56% of theory) of bis-(2-chlorohexafluorocyclopenten-1-yl)-mercury (XIIIb). m. p. $60-61^{\circ}\text{C}$.

Anal: Calcd. for $\text{C}_{10}\text{Cl}_2\text{F}_{12}\text{Hg}$: C, 19.40; Cl, 11.50; F, 36.70; Hg, 32.40.

Found: C, 19.60; Cl, 10.90; F, 37.00; Hg, 32.00.

The infrared spectrum of compound XIIIb contained a sharp absorption at $1,598\text{ cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of Bis-(2-chlorooctafluorocyclohexen-1-yl) mercury (XIIIc). A solution of 15 g (0.05 mol) of 1,2-dichlorooctafluorocyclohexene in 100ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled at -75°C . *n*-butyllithium (20 ml of 2.46 *M* in tetrahydrofuran) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes. After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 6.8g (0.025 mol) of mercuric chloride was added. After the reaction mixture was stirred for an additional 10 minutes, the reaction mixture was allowed to reach room temperature, and then washed with dilute hydrochloric acid solution. The organic layer was separated and dried over anhydrous magnesium sulfate, the solvent was removed in a rotary evaporator. The crude solid product upon recrystallization from *n*-hexane yielded 22 g (60% of theory) of bis-(2-chlorooctafluorocyclohexen-1-yl)-mercury (XIIIc). m. p. $88-89^{\circ}\text{C}$.

Anal: Calcd. for $C_{12}Cl_2F_{16}Hg$: C, 20.20; Cl, 9.70; F, 42.30; Hg, 27.50.

Found: C, 20.10; Cl, 9.50; F, 43.00; Hg, 28.00.

The infrared spectrum of compound XIIIc contained a sharp absorption at $1,627\text{ cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of 2-Chlorohexafluorocyclopenten-1-yl Mercuric Bromide (XV). A solution of 6.2 g (0.01 mol) of bis-(2-chlorohexafluorocyclopenten-1-yl)-mercury in 70 ml of anhydrous diethyl ether in a 250ml reaction vessel equipped with a reflux condenser and a magnetic stirring assembly was cooled to -60°C . (dry ice-acetone bath). A solution of 0.8 g (0.01 mol) hydrogen bromide in 30ml anhydrous ether (gaseous HBr was dissolved in ether at -40°C) was added drop-wise by means of a dropping funnel. The addition took one minute. After the addition was completed, the reaction mixture was stirred for three hours at -40°C . and then allowed to reach the room temperature gradually. The reaction mixture was washed with water and the organic layer was separated and dried over anhydrous manesium sulfate. The solvent was removed in a rotary evaporator and the crude solid product subjected to recrystallization from *n*-hexane yielded 4g (80% of theory) of 2-chlorohexafluorocyclopenten-1-yl mercuric bromide (XV). m. p. $92.5-93.5^\circ\text{C}$.

Anal: Calcd. for BrC_5ClF_6Hg : Br, 16.35; C, 12.27; Cl, 7.23; F, 23.31; Hg, 40.84.

Found: Br, 16.13; C, 12.50; Cl, 7.05; F, 23.40; Hg, 40.82.

The infrared spectrum of compound XV contained a sharp absorption at $1,620\text{ cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of 2-Chloro-tetrafluorocyclobuten-1-yl-mercuric Bromide (XVI). A solution of 5.5g (0.01mol) of bis-(2-chlorotetrafluorocyclobuten-1-yl)-mercury in 70 ml of anhydrous

diethyl ether in a 250 ml reaction vessel equipped with a reflux condenser, a magnetic stirring assembly was cooled to -60°C . (dry ice-acetone bath). A solution of 0.8g (0.01mol) hydrogen bromide in 30ml of anhydrous ether (gaseous HBr was dissolved in ether at -40°C .) was added drop-wise by means of a dropping funnel. The addition took one minute. After the addition was completed, the reaction mixture was stirred for three hours at -40°C . and then allowed to reach gradually to room temperature. The reaction mixture was washed with water. The organic layer was separated and dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was subjected to recrystallization from *n*-hexane to yield 3.5g (79% of theory) of 2-chlorotetrafluorocyclobuten-1-yl-mercuric bromide (XVI). m. p. $89-90^\circ\text{C}$.

Ana: Calcd. for BrC_4ClF_4Hg : Br, 18.18; C, 10.91; Cl, 7.81; F, 17.27; Hg, 45.55.

Fond: Br, 18.03; C, 10.79; Cl, 7.35; F, 17.41; Hg, 45.83.

The infrared spectrum of compound XVI contained a sharp absorption at $1,580\text{ cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of 2-Chlorooctafluorocyclohexen-1-yl-mercuric Bromide (XVII). A solution of 7g (0.01mol) of bis-(2-chlorooctafluorocyclohexen-1-yl)-mercury in 80ml of anhydrous diethyl ether contained previously described reaction vessel was cooled to -60°C . A solution of 0.8g (0.01mol) hydrogen bromide in 30ml of anhydrous ether (gaseous HBr was dissolved in ether at -40°C) was added through a dropping funnel. The addition took one minute. After the addition was completed, the reaction mixture was stirred for 2 hours at -40°C and then allowed to reach gradually to room temperature. The reaction mixture was washed with

water, separated, dried over anhydrous magnesium sulfate, and the solvent removed in a rotary evaporator. The crude product was recrystallized from *n*-hexane, to yield 3.3g (63% of theory) of 2-chlorooctafluorocyclohexen-1-yl mercuric bromide. m. p. 65-66°C.

Anal: Calcd. for $\text{BrC}_6\text{ClF}_8\text{Hg}$: Br, 14.84; C, 13.35; Cl, 6.50; F, 28.20; Hg, 37.16.

Found: Br, 14.48; C, 6.28; Cl, 6.28; F, 28.53; Hg, 37.37.

The infrared spectrum of compound XVII showed sharp absorption at $1,630\text{cm}^{-1}$ which corresponds to an olefinic stretching frequency.

Preparation of Octafluoro-2, 7-tetramethyldigermanatricyclo (6. 2. 0. 0^{3,6}) deca-1 (8), 3 (6)-diene (XVIII). A solution of 9.7g (0.025 mol) of 1,2-diiodotetrafluorocyclobutene in 80 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . Methyl lithium (22.5ml of 2.15 M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes and the temperature was not allowed to rise over -65°C . After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 4.4g (0.025mol) of dimethylgermaniumdichloride was added. The reaction mixture was stirred for an additional 10 minutes and allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate, filtered, and the solvent removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 7.1g (63% of theory) of octafluoro-2, 7-tetramethyldigermana (6. 2. 0. 0^{3,6}) -deca-1 (8), 3 (6)-diene (XVIII). m. p. 161-162°C.

Anal: Calcd. for $\text{C}_{12}\text{F}_8\text{Ge}_2\text{H}_{12}$: C, 31.78; F, 33.54; Ge, 31.85; H, 2.63.

Found: C, 31.79; F, 33.69; Ge, 31.94; H, 2.61.

The infrared spectrum of compound XVII showed a strong absorption at $1,527\text{cm}^{-1}$ which corresponds to an olefinic stretching frequency.

The ^1H NMR spectrum showed sharp singlet at τ 9.31 due to $\text{As}(\text{CH}_3)$ protons.

Preparation of Dodecafluoro-2, 8-tetramethyldigermanatricyclo (7. 2. 0. 0^{3,7}) -dodeca-1 (9), 3 (7)-diene (XIX). A solution of 5.4g (0.125 mol) of 1,2-diiodohexafluorocyclopentene in 90 ml of anhydrous diethyl ether contained as previously described reaction vessel was cooled to -75°C . Methyl lithium (11.3ml of 2.15M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes. The temperature was not allowed to rise over -65°C . After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at -75°C . and then 2.2g (0.0125mol) of dimethyl germanium dichloride was added. The reaction mixture was stirred again for 15 minutes and then allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was subjected to recrystallization from *n*-hexane, to yield 4.7g (68% of theory) of dodecafluoro-2, 8-tetramethyldigermanatrieyclo (7. 2. 0. 0^{3,7}) -dodeca-1 (9), 3 (7)-diene (XIX). m. p. 115-116°C.

Anal: Calcd. for $\text{C}_{14}\text{F}_{12}\text{Ge}_2\text{H}_{12}$: C, 30.32; F, 41.15; Ge, 26.36; H, 2.16.

Found: C, 30.27; F, 41.10; Ge, 26.27; H, 2.12.

The infrared spectrum contained a strong absorption at $1,575\text{cm}^{-1}$ ascribable to an olefinic stretching frequency.

The ^1H NMR spectrum showed sharp singlet at τ 9.2 due to two $\text{Ge}(\text{CH}_3)_2$ protons.

The Preparation of Bis-(2-chlorooctafluorocyclohexen-1-yl)-dimethyl Germane (XX). A

solution of 7.4g (0.025 mol) of 1,2-dichlorooctafluorocyclohexane in 90ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . *n*-butyllithium (11ml of 2.46 M in tetrahydrofuran) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes and the temperature was not allowed to rise over -65°C . After the addition was completed, the reaction mixture was stirred for an additional 60 minutes at -75°C . and then 2.2g (0.0125 mol) of dimethyl germanium dichloride was added. The reaction mixture was allowed to reach gradually to room temperature and the product was washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 9.5g (64% of theory) of bis-(2-chlorooctafluorocyclohexen-1-yl)-dimethyl germane (XX). m. p. $53\sim 54^{\circ}\text{C}$.

Anal: Calcd. for $\text{C}_{14}\text{Cl}_2\text{F}_{16}\text{GeH}_6$: C, 27.02; Cl, 11.42; F, 48.91; Ge, 11.66; H, 0.98.

Found: C, 27.22; Cl, 11.19; F, 49.13; Ge, 11.41; H, 1.05.

The infrared spectrum of compound XX displayed a sharp absorption at $1,612\text{cm}^{-1}$ which corresponds to an olefinic stretching frequency.

The ^1H NMR spectrum showed a sharp singlet at τ 9.02 due to $\text{Ge}(\text{CH}_3)_2$ protons.

Preparation of Bis-(2-Chlorohexafluorocyclopenten-1-yl)-dimethyl Germane (XXIa) A solution of 8.4g (0.025 mol) of 1-iodo-2-chlorohexafluorocyclopentene in 90 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . Methylolithium (11.3ml of 2.15M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes and the temperature was not allowed to

rise above -65°C . After the addition was completed, the reaction mixture was stirred for another additional 60 minutes at -75°C . and then 2.2g (0.0125mol) of dimethyl germanium dichloride was added. The reaction mixture was stirred for an additional 15 minutes and allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 8.7g (68% of theory) of bis-(2-chlorohexafluorocyclopenten-1-yl)-dimethyl germane (XXIa). m. p. $34\sim 35^{\circ}\text{C}$.

Anal: Calcd. for $\text{C}_{12}\text{Cl}_2\text{F}_{12}\text{GeH}_6$: C, 27.69; Cl, 13.46; F, 43.84; Ge, 13.84; H, 1.15.

Found: C, 28.13; Cl, 13.58; F, 43.62; Ge, 13.25; H, 1.10.

The infrared spectrum of compound XXIa displayed a strong absorption at $1,600\text{cm}^{-1}$ ascribable to olefinic stretching frequency.

The ^1H NMR spectrum showed sharp singlet at τ 9.07 due to $\text{Ge}(\text{CH}_3)_2$ protons.

Preparation of Bis-(2-bromohexafluorocyclopenten-1-yl)-dimethylgermane (XXIb) A solution of 10.8g (0.025mol) of 1-iodo-2-bromohexafluorocyclopenten in 90 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . Methylolithium (11ml of 2.16 M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 4 minutes and the temperature was not allowed to rise above -65°C . After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 2.2g (0.0125 mol) of dimethyl germanium dichloride was added. The reaction mixture was stirred for another additional 15 minutes and allowed to reach gradually to room temperature. The product was washed with water, separated, dried

over anhydrous magnesium and the solvent removed in a rotary evaporator. The crude solid product was subject to recrystallized from *n*-hexane, to yield 7g (47% of theory) of bis-(2-bromohexafluorocyclopenten-1-yl) -dimethylgermane (XXIb). m. p. 47-48°C.

Anal: Calcd. for $\text{Br}_2\text{C}_{12}\text{F}_{12}\text{GeH}_6$: Br, 26.23; C, 23.60; F, 37.38; Ge, 11.80; H, 0.98.

Found: Br, 26.09; C, 23.67; F, 37.59; Ge, 11.58; H, 1.02.

The infrared spectrum of compound XXIb contained a strong absorption at $1,592\text{cm}^{-1}$ ascribable to an olefinic stretching frequency.

The ^1H NMR spectrum showed a sharp singlet at τ 9.08 due to $\text{Ge}(\text{CH}_3)_2$ protons.

Preparation of Octafluoro-2,7-dimethyldiarsenatricyclo (6.2.0.0^{3,6}) deca-1(8), 2(6)-diene (XXIV). A solution of 9.5g (0.025mol) of 1,2-diiodotetrafluorocyclobutene (I) in 80ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . Methyl lithium (22.5ml of 2.15M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 10 minutes and the temperature was not allowed to rise above -65°C . After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 9.0g (0.025mol) of methylarsenic diiodide was added. The reaction mixture was then stirred for an additional 15 minutes and allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 5.3g (52% of theory) of octafluoro-2,7-dimethyldiarsenatricyclo-(6.2.0.0^{3,6})-deca-1(8), 3(6)-diene (XXIV). m. p. 127-128°C.

Anal: Calcd. for $\text{As}_2\text{C}_{10}\text{F}_8\text{H}_6$: As, 35.03; C,

28.03; F, 35.51; H, 1.40.

Found: As, 35.18; C, 27.94; F, 35.42; H, 1.28.

The infrared spectrum of compound XXIV contained a strong absorption at $1,523\text{cm}^{-1}$ which corresponds to an olefinic stretching frequency.

The ^1H NMR spectrum showed sharp singlet at τ 8.41 due to $\text{As}-\text{CH}_3$ protons.

Preparation of Doedcafluoro-2,8-dimethyldiarsenatricyclo (7.2.0.0^{3,7})-dodeca-1(9), 3(7)-diene (XXV). A solution of 5.4g (0.0125 mol) of 1,2-diiodohexafluorocyclopentene in 90 ml of anhydrous diethyl ether contained in the previously described reaction vessel was cooled to -75°C . Methyl lithium (11.3ml of 2.15 M in diethyl ether) was added in a drop-wise manner by means of a syringe. The addition took 7 minutes and the temperature was not allowed to rise above -65°C . After the addition was completed, the reaction mixture was stirred for an additional 50 minutes at -75°C . and then 4.5g (0.0125mol) of methyl arsenic diiodide was added. The reaction mixture was stirred for an additional 15 minutes and then allowed to reach gradually to room temperature. The product was washed with water, separated, dried over anhydrous magnesium sulfate and the solvent removed in a rotary evaporator. The crude solid product was recrystallized from *n*-hexane, to yield 4g (60% of theory) of doedcafluoro-2,8,-dimethyl diarsenatricyclo(7.2.0.0^{3,7})-dodeca-1(9), 3(7)-diene (XXV). m. p. 112-113°C.

Anal: Calcd. for $\text{As}_2\text{C}_{12}\text{F}_{12}\text{H}_6$: As, 28.40; C, 27.27; F, 43.18; H, 1.13.

Found: As, 27.27; C, 27.60; F, 43.07; H, 1.02

The infrared spectrum of compound XXV contained a sharp absorption at $1,538\text{cm}^{-1}$ which corresponds to an olefinic stretching frequency.

The ^1H NMR spectrum showed sharp singlet at τ 9.1 due to $\text{As}(\text{CH}_3)$ protons.

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