

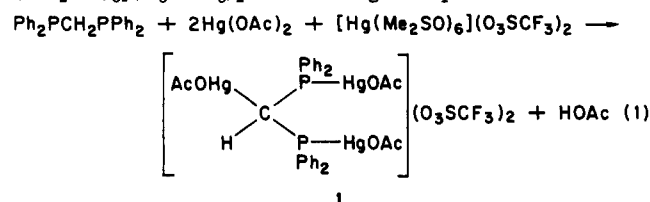
Table I. $\{^1\text{H}\}$ NMR Parameters of $\{(\text{AcOHg})_n\text{CH}_2\text{-}n[\text{PPh}_2(\text{HgOAc})]_2\}^{2+ a}$

n	$\delta(^{31}\text{P})$	$\delta(^{199}\text{HgP})$	$\delta(^{199}\text{HgC})$	$^1J(^{199}\text{Hg}, ^{31}\text{P})$	$^2J(^{199}\text{Hg}, ^{31}\text{P})$	$^3J(^{199}\text{Hg}, ^{31}\text{P})$	T, K
1	34.1	916 d ^b	854 t ^b	8773	265	30	253
2	43.3	889 d ^c	941 t ^c	8648	234	212	273

^a Chemical shifts are in parts per million the low field of 85% H₃PO₄ or aqueous Hg(ClO₄)₂ (2 mmol of HgO/cm³ of 60% HClO₄); coupling constants are in Hz; solvent, MeOH. ^b $^2J(^{199}\text{Hg}, ^1\text{H}) = 260$, $^3J(^{199}\text{Hg}, ^1\text{H}) = 300$; coupling constants determined from a ^1H -coupled ^{199}Hg NMR spectrum. ^c The t/d intensity ratio of **2** is nearly (due to different NOE) doubled compared with that of **1**.

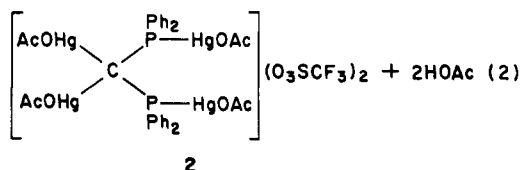
methylene carbon is known only in a few cases.⁸⁻¹² The complexes were generated from the deprotonated ligand and appropriate metal compounds or by deprotonation of the coordinated ligand. We report here further examples of C-substitution in various mercury complexes of dpmm.

The reaction of dpmm with Hg(OAc)₂ and [Hg(Me₂SO)₆](O₃SCF₃)₂¹³ according to eq 1 in methanol at



ambient temperature affords the C-metalated product **1** almost quantitatively within a few minutes.¹⁴ The compound was isolated and crystallized as an Me₂SO solvate.¹⁵ The structure is evidenced by ^{199}Hg and ^{31}P NMR spectroscopy.¹⁶ The $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectrum ($^{199}\text{Hg}, I = 1/2$, abundance 16.8%) of **1** shows two different mercury sites: one doublet attributable to the mercury bound to phosphorus and a 1:2:1 triplet for the carbon-bound mercury being coupled to two equivalent phosphorus atoms via two bonds. This is confirmed by the ^{31}P NMR spectrum. The NMR data are summarized in Table I.

The reaction of one further equivalent of Hg(OAc)₂ according to eq 2 leads under the same conditions almost



quantitatively to the dimercurated product **2**, which was characterized similarly to **1** (Table I).^{14,17} Particular

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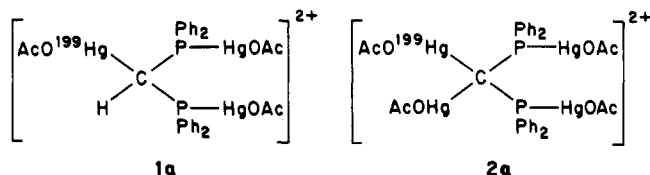
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(14) The use of [Hg(Me₂SO)₆](O₃SCF₃)₂ alone in the reactions 1 and 2 leads to compounds corresponding to **1** and **2** besides other unidentified products; the use of Hg(OAc)₂ alone in the reactions 1 and 2 leads to products corresponding to **1** and **2** that exhibit an increased kinetic lability of the Hg-P bonds and decompose even faster.

(15) $\{(\text{AcOHg})\text{CH}[\text{PPh}_2(\text{HgOAc})]_2\}(\text{O}_3\text{SCF}_3)_2 \cdot 3\text{Me}_2\text{SO}$: mp 127-133 °C. Anal. Calcd for C₃₉H₄₉F₆Hg₃O₁₅P₂S₃: C, 27.6; H, 2.9; Hg, 35.5. Found: C, 27.4; H, 2.9; Hg, 34.6. The Me₂SO content was also confirmed by integration of the ^1H NMR spectrum.

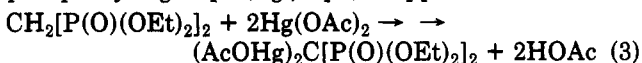
(16) NMR spectra were recorded on a multinuclear Bruker WP-80 spectrometer.

conclusive is the nearly doubled intensity of the ^{199}Hg satellite pattern due to $^2J(^{199}\text{Hg}, ^{31}\text{P})$ in the ^{31}P NMR spectrum according to a statistical abundance of 19.37% for the isotopomer **2a** compared with that of **1a** (11.56%).



The mercury-199 resonance of the C-bound mercury is at high frequency relative to that of **1** in keeping with the results for the series CH_{4-n}(HgX)_n.¹⁸

The occurrence of reactions 1 and 2 under mild conditions is quite interesting since the replacement of hydrogen by mercury (mercuration) in aliphatic compounds is limited to acidic hydrocarbons, i.e., hydrogens α to electron-withdrawing groups¹⁹ such as cyano, diazo, carbonyl, or phosphoryl²⁰ groups (e.g., eq 3). dpmm is not acidic ac-



cording to a pK_a of 29.9,²¹ and deprotonation only succeeds by using very strong bases. We propose that the methylene group of dpmm is activated as a result of the coordination of mercury to the diphenylphosphino groups, i.e., that [PPh₂HgOAc]⁺ acts as an electron-withdrawing group.

Acknowledgment. Thanks are due to the Fonds zur Förderung der Wissenschaft, Vienna, for making available the NMR spectrometer.

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New Tin Heterocycles: Adducts between Acetylenes or Allenes and "Distannacyclopropanes"

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Summary: 1,2,4,5-Tetrastannacyclohexanes react with 1-alkynes and 1,1-dimethylallene in the presence of tetrakis(triphenylphosphine)palladium(0) to give 4-substituted 1,3-distannacyclopentenes and 4-methylene-1,3-distannacyclopentanes, respectively. These compounds are formally adducts between the acetylene or allene and distannacyclopropanes.

Table I. Products, Reaction Conditions, Melting or Boiling Points, and Yields of Distannaheterocycles

compd	R	R'	R''	reactn condtns (°C/h)	mp, °C, or bp °C (mmHg)	isolated yield (% and g)
1a	H	H	CMe ₂ OH	85/15	53	73, 4.95
1b	H	Me	CMe ₂ OH	85/15	<110 (10 ⁻³)	88, 0.94
1c	Me	Me	CMe ₂ OH	85/15	60 (10 ⁻³)	<i>a</i>
1d	Me	Me	CO ₂ Me	60/15	90 (10 ⁻³)	71, 0.76
1e	H	H	CH ₂ NMe ₂	85/15	70 (10 ⁻³)	90, 0.41
2a	H	H		85/15		<i>b</i>
2b	H	Me		85/3	<150 (10 ⁻³)	<i>c</i>
2c	Me	Me		25/48	70 (10 ⁻³)	59, 0.64

^a Not determined: 100% = 0.31 g. ^b Product contaminated with ca. 30% unknown impurity. ^c Not determined: 100% = 0.36 g. Product mixture contained ca. 40% (¹¹⁹Sn NMR) **2b**. The Sn NMR parameters of the main product are as follow (δ values in CDCl₃): Sn^a 18.8, Sn^b, Sn^c -72.9, Sn^d -21.7. Sn^a shows coupling constants (Hz) of 30.5 (³⁺⁵J) and 77.5 (²J) to Sn^{b,c} and 128.5 (³⁺⁵J) to Sn^d, Sn^{b,c} of 3339.3 (¹J) and couplings to a and d, and Sn^d of 22.9 (³⁺⁵J) and 73.9 Hz (²J) to Sn^{b,c} and coupling to Sn^a. Distillations were carried out by using a Kugelrohr apparatus.

Table II. Tin-119 NMR Data for Compounds of Type 1 and 2 (Chemical Shifts (in CDCl₃) in ppm vs. Me₄Sn and Coupling Constants in Hz)

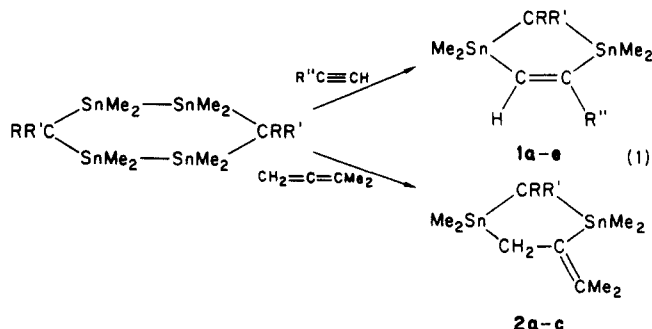
compd	R	R'	R''	δ (Sn)	²⁺³ J(¹¹⁹ Sn- ¹¹⁹ Sn)
1a	H	H	CMe ₂ OH	58.5, 78.5 ^a	260.4
1b	H	Me	CMe ₂ OH	55.2, 69.0 ^a	437.4
1c	Me	Me	CMe ₂ OH	44.7, 56.9 ^a	718.9
1d	Me	Me	CO ₂ Me	54.2, 57.2 ^a	500.8
1e	H	H	CH ₂ NMe ₂	54.3, 65.0 ^a	273.3
2a	H	H		8.8, 66.0 ^b	54.9
2b	H	Me		5.8, 61.5 ^b	183.7
2c	Me	Me		-2.5, 52.2 ^b	382.5

^a High-Field signal corresponds to tin trans to R''.

^b High field signal corresponds to vinylic tin.

We have recently reported on the addition of hexamethylditin to 1-alkynes¹ and allenes.² Following the initial report by Gielen,³ we have also prepared a series of 1,2,4,5-tetrastannacyclohexanes⁴ and determined the crystal structure of one of them, *cis*-1,1,2,2,3,4,4,5,5,6-decamethyl-1,2,4,5-tetrastannacyclohexane.⁵ We felt it would be interesting to study the reaction of these tin heterocycles with acetylenes and allenes, since a double addition across the tin-tin bonds should lead to 10-membered rings containing four tin atoms. Tetrastannamacrocycles have been recently reported in the literature.⁶

We find, however, that five-membered rings are formed rather than the larger rings originally expected (eq 1). The



structural proof for the products **1a-e** and **2a-c** is based,

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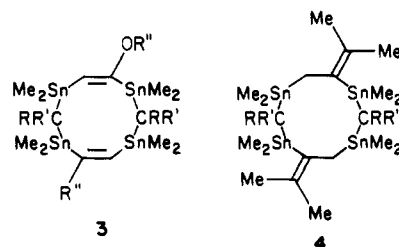
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first, on the cryoscopically determined molecular weight of **1a**, the only solid, and, second, on NMR spectroscopic evidence: the tin chemical shifts (-53 to -79 ppm) of the tetrastannacyclohexanes are in the usual range for ditins but shifted in each case ca. 30 ppm to the low field of the corresponding hexaalkylditins (e.g., Me₆Sn₂, -109 ppm). The product molecules **1** and **2** absorb in the range 0-75 ppm: the range of 45-75 ppm for **1a-e** is completely atypical for stannylalkenes (shifts of -40 to -70 ppm being typical), while the vinylic tin nucleus of the adducts between hexamethylditin and allenes also absorbs to high field vs. Me₄Sn.² Furthermore, the signals exhibit only one tin-tin coupling constant, while the originally expected 10-membered rings (for example, **3** or **4**) would contain



isotopomers showing ²J and ³J(Sn-Sn) and the five-membered rings show a coupling that is (at least approximately) the algebraic sum of a two-bond and a three-bond coupling.⁷ Since the latter is almost certainly positive, while the former can change sign,⁸ the magnitude of the observed coupling can change greatly.

Table II shows the tin-119 NMR data for the compounds so far prepared. ²J(Sn-Sn) has the following values: in Me₃SnCH₂SnMe₃ -287, in Me₃SnCHMeSnMe₃ -162, and in Me₃SnCMe₂SnMe₃ +19 Hz.⁸ In (*Z*)-Me₃SnCH=C(CMe₂OH)SnMe₃ ³J(Sn-Sn) is +446 Hz,⁹ while in Me₃SnCH₂C(SnMe₃)=CMe₂ (in which the dihedral angle subtended by the Me₃Sn residues at the C-C single bond is probably ca. 90°) the value is +118 Hz.² The trend in ²J shown above for related open-chain compounds and the values of ²⁺³J in the distannaheterocycles indicate that both the carbon-carbon double bond in the distannacyclopentenes and the single bond in the methylenedistannacyclopentanes are twisted considerably from the ideal "eclipsed" structures. We hope to be able to obtain more exact information by means of X-ray crystallography.

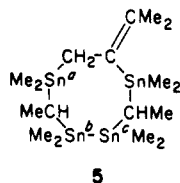
The reactions studied so far are in general remarkably clean: however, product **2b** was surprisingly formed in only

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ca. 40% yield (^{119}Sn NMR), the main product being one in which one allene unit reacts with one tin-tin bond of the six-membered ring to give molecule 5. This structure



follows from the tin-119 NMR data, which are given in a footnote to Table I: most important is the presence of a one-bond tin-tin coupling, though it is surprising that the two tin nuclei b and c are isochronous.

A typical experimental procedure was as follows: 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane (5.51 g, 8.9 mmol) and 3-methyl-1-butyne-3-ol (1.64 g, 19.5 mmol) in xylene (10 mL) were heated for 15 h at 85 °C in the presence of 0.5 mol % tetrakis(triphenylphosphine)-palladium(0), after which time the proton NMR spectrum indicated complete consumption of the tetrastannacyclohexane. The xylene and any low-boiling materials were removed at the water pump, leaving an oil that underwent sublimation to give a colorless solid (4.95 g, 73%), mp 53 °C. In all other cases, the reaction products were obtained as oils that were purified by Kugelrohr distillation. The methylenedistannacyclopentanes are extremely air sensitive, the distannacyclopentenes much less so.

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Registry No. 1a, 93061-62-2; 1b, 93061-63-3; 1c, 93061-64-4; 1d, 93061-65-5; 1e, 93061-66-6; 2a, 93061-67-7; 2b, 93061-68-8; 2c, 93061-69-9; 5, 93061-70-2; $\text{HOMe}_2\text{CC}\equiv\text{CH}$, 115-19-5; $\text{MeOCOC}\equiv\text{CH}$, 922-67-8; $\text{Me}_2\text{NCH}_2\text{C}\equiv\text{CH}$, 7223-38-3; $\text{CH}_2=\text{C}=\text{CMe}_2$, 598-25-4; 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane, 89748-39-0; 1,1,2,2,3,3,4,4,5,5,6,6-decamethyl-1,2,4,5-tetrastannacyclohexane, 93061-71-3; 1,1,2,2,3,3,3,4,4,5,5,6,6-dodecamethyl-1,2,4,5-tetrastannacyclohexane, 93061-72-4; tetrakis(triphenylphosphine)palladium(0), 14221-01-3.

Supplementary Material Available: Tables of elemental analyses and ^{13}C NMR data (4 pages). Ordering information is given on any current masthead page.

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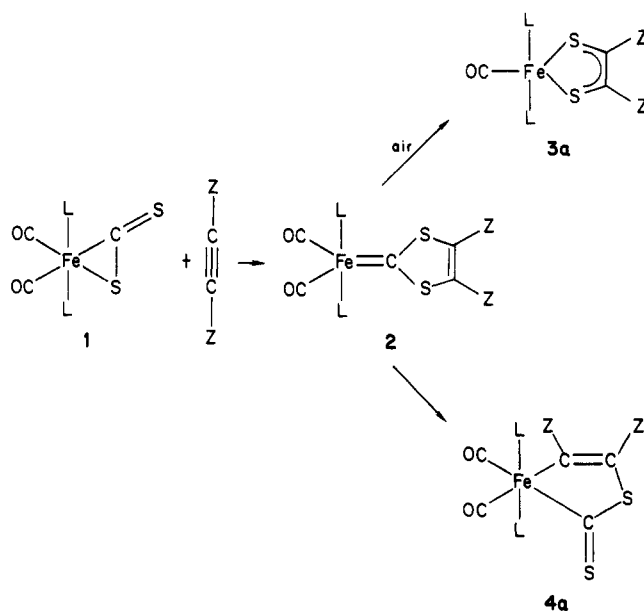
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Summary: The new mixed bimetallic carbene complex $\text{Cl}_2\text{HgFe}(\text{CS}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{CO})_2(\text{PMe}_2\text{Ph})_2$ (5) has been obtained by addition of HgCl_2 to the reactive intermediate $\text{Fe}(\text{CS}_2\text{C}_2(\text{CO}_2\text{Me})_2)(\text{CO})_2(\text{PMe}_2\text{Ph})_2$ (2a). The donor-acceptor adduct 5 has been characterized by single-crystal X-ray diffraction methods that establish the position of the HgCl_2 unit trans to the carbene ligand.

Scheme I



a. L = PMe_2Ph ; Z = CO_2R

Eighteen-valence-electron transition-metal complexes, when they are basic enough, are known to form donor-acceptor adducts with Lewis acids such as HgX_2 ^{1,2} or with 16-electron organometallic species.³ Although these donor-acceptor compounds are well documented, to our knowledge they have not been made for the purpose of trapping unstable, 18-electron intermediates. Here we report that the formation of a metal-mercury(II) bond can be successfully used to stabilize an electron-rich, highly reactive metal-carbene complex.

We have already shown that the (1,3-dithiol-2-ylidene)iron intermediates 2 can be readily obtained by cycloaddition of activated alkynes to the $\eta^2\text{-CS}_2$ ligand of complexes 1⁴ (Scheme I). However, these electron-rich iron(0) complexes are very air-sensitive and decompose to give (dithiolene)iron derivatives 3⁵ and tetrathiafulvalenes.^{5,6} Alternatively, when the phosphorus group L is a basic phosphine (L = PMe_2Ph , PMe_3), they rapidly isomerize into stable metallocyclic iron(II) complexes 4⁴ (Scheme I). Consequently, we were not able to characterize structurally an iron-carbene complex of type 2. We now show that the intermediate 2a reacts with HgCl_2 to give a crystalline adduct and that the formation of the $\text{Fe}\rightarrow\text{HgCl}_2$ bond, in the position trans to the carbene ligand, prevents the transformation of the adduct into complex 3a or 4a and allows the X-ray structure determination of the first carbene iron-mercury(II) complex.

The yellow solution of 0.43 mmol (0.20 g) of 1a (L = PMe_2Ph), in 40 mL of anhydrous ether, was stirred with 1 equiv of dimethyl acetylenedicarboxylate at room temperature under an inert atmosphere. After a few minutes, 1 equiv (0.45 mmol, 0.13 g) of HgCl_2 was added to the

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