Synthesis and Reactions of Some Functionally Substituted Sila- and Germacyclopentadienes

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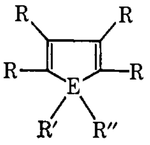
Abstract: The synthesis of a series of halogen-substituted sila- and germacyclopentadienes (I) is described. A survey of the reactions of these compounds shows that the ring structure often provokes a reactivity not expected on the basis of analogy with acyclic silanes and germanes. The formation of anions derived from I is discussed, and equilibrium experiments (reaction 14) indicate that pentaphenylgermole (XIII) is at least 10^6 times more acidic than triphenylgermane. A spectrophotometric determination of the acidity of triphenylgermane in DMSO gave a value of 23.0 for the pK_a. The acidity of the germole, XIII, could not be determined in the same manner, precluding an accurate determination of its pK_a. Several compounds containing σ bonds to transition metal carbonyls (I, R″ = transition metal carbonyl moiety) were synthesized and attempts to rearrange these to π-bonded "sandwich" compounds are reported.

A facile synthesis of halogen-substituted sila- and germacyclopentadienes was sought since much of the derivative chemistry of silicon and germanium proceeds through halogen intermediates. Although sila- and germacyclopentadienes[2] (I) have been previously prepared,[3-6] no halogen-substituted derivatives have been reported except for a preliminary communication of this work in which experimental details were not included.[7]



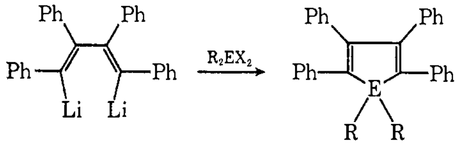
I

This investigator's interest in the siloles and germoles was twofold. First, anions derived from these compounds would contain a six π-electron system and might be expected to exhibit resonance stabilization as found in the cyclopentadienide anion. Such resonance stabilization would presumably involve a partial p_π–p_π bond between silicon or germanium and carbon. In contrast to d_π–p_π bonding,[8] no compounds are known which contain a p_π–p_π bond between carbon and silicon or germanium. Second, it was of interest to determine if "sandwich" compounds could be prepared containing silicon or germanium as a heteroatom in the π-bonded ring. In view of some predictions made by Brown[9] concerning the stabilities of heteroatomic, π-bonded rings, it was hoped that the properties of such sandwich compounds would lead to a better understanding of the relative importance of "back-donation," etc., in the bonding of sandwich compounds in general.

Results and Discussion

Previous[3,4,6] methods of preparing siloles and germoles utilized 1,4-dilithiotetraphenylbutadiene, made from diphenylacetylene and lithium as shown in reaction 1. This procedure was reported[4] to be unsuccessful in preparing halogen-substituted siloles and germoles when REX_3 or EX_4 was used as halide in reaction 1. However, adding the dilithio reagent to the halides REX_3 or EX_4, rather than *vice versa*, does give good yields of halogen-substituted derivatives (reactions 2 and 3).

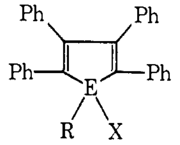
$$2Ph_2C_2 + 2Li \xrightarrow{Et_2O}$$



E = Si, Ge

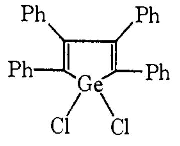
(1)

$Ph_4C_4Li_2 + REX_3 \longrightarrow$



(2)

$Ph_4C_4Li_2 + GeCl_4 \longrightarrow$



II

(3)

Reaction 3 gave the best results when the slurry of $(C_6H_5)_4C_4Li_2$ was added to $GeCl_4$ dissolved in diethyl ether. The product (II) begins to precipitate from the diethyl ether after a fraction of the lithium reagent has

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[2] The trivial names for these compounds are "siloles" and "germoles," respectively.

[3] E. H. Braye, W. Hubel, and I. Caplier, *J. Amer. Chem. Soc.*, **83**, 4406 (1961).

[4] F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

[5] H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 291 (1964).

[6] K. Rühlmann, *Z. Chem.*, **5**, 354 (1965).

[7] M. D. Curtis, *J. Amer. Chem. Soc.*, **89**, 4241 (1967).

[8] (a) M. D. Curtis and A. L. Allred, *ibid.*, **87**, 2554 (1965), and references therein; (b) M. D. Curtis, R. K. Lee, and A. L. Allred, *ibid.*, **89**, 5150 (1967); (c) A. L. Allred and L. W. Bush, *ibid.*, **90**, 3352 (1968).

[9] D. A. Brown, *J. Chem. Soc.*, 929 (1962); *J. Inorg. Nucl. Chem.*, **10**, 49 (1959).

Table I. Sila- and Germacyclopentadienes from the Reaction of $(C_6H_5)_4C_4Li_2$ with REX_3 and $GeCl_4$

Halide	Product	Mp, °C	% yield[a]	Calcd, % C	Calcd, % H	Found, % C	Found, % H
$GeCl_4$	$(C_6H_5)_4C_4GeCl_2$ (II)	197–199	70	67.26	4.04	67.20	4.05
$GeCl_4$	$[(C_6H_5)_4C_4]_2Ge$ (III)	257–260	5				
$C_6H_5GeCl_3$	$(C_6H_5)_4C_4Ge(C_6H_5)Cl$ (IV)	210–211	47	75.39	4.65	74.81	4.58
$C_6H_5GeCl_3$	$[(C_6H_5)_4C_4Ge(C_6H_5)-]_2$[b] (V)	235–236	25	80.68	4.98	80.77	5.16
$C_6H_5SiCl_3$	$(C_6H_5)_4C_4Si(C_6H_5)Cl$ (VI)	181–183	70	82.14	5.07	82.33	5.29
CH_3SiCl_3	$(C_6H_5)_4C_4Si(CH_3)Cl$ (VII)	194–195	58	80.23	5.11	80.70	5.64

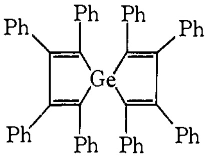
[a] Based on an assumed[4] 80% yield of $(C_6H_5)_4C_4Li_2$. [b] % Ge: Found 14.61 (calcd 14.34).

Table II. Sila- and Germacyclopentadienides Derived from the Compounds in Table I by Replacement of Chloride

$(C_6H_5)_4C_4E(R)X$ E	R	X	Compd no.	Mp, °C	Selected ir bands, cm^{-1} [c]	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Si	CH_3	OH	VIII	199–202	SiOH: 946	83.61	5.81	83.54	5.84
Ge	C_6H_5	OH	IX	256–257[a]	GeOH: 670	78.05	5.01	78.40	5.23
Ge	C_6H_5	$-O(C_6H_5)GeC_4(C_6H_5)_4$	X	255–257	GeOGe: 875	79.42	4.90	79.72	5.01
Ge	C_6H_5	H	XIII	187–188	GeH: 2056	80.52	5.17	79.87	5.12
Ge	C_6H_5	$Si(CH_3)_3$	XV	178–180	$SiCH_3$: 1250, 850	76.70	5.92	76.91	6.18
Ge	C_6H_5	C_6H_5	XVI	198–199		82.37	5.18	81.97	5.32
Ge	H	H	XVII	192–193	GeH: 2060	78.01	5.15	77.77	5.18
Si	CH_3	H	XVIII	223–224	SiH: 2122	86.94	6.04	86.71	6.20
Si	C_6H_5	H	XIX	198–199	SiH: 2120	88.26	5.67	88.25	5.74
Si	C_6H_5	C_4H_9	XX	145–148		87.97	6.61	87.85	6.67
Si	C_6H_5	$-Fe(CO)_2(C_5H_5)$	XXI	201–203	CO: 1960, 2010	77.12	4.73	76.75	4.82
Ge	C_6H_5	$-Mn(CO)_5$	XXII	144[b]	CO: 2008, 2104	68.31[b]	3.91[b]	68.25	3.94
Ge	C_6H_5	$-Co(CO)_4$	XXIII	165	CO: 2009, 2037, 2096	67.40	3.72	67.77	3.75
Ge	C_6H_5	$-Fe(CO)_2(C_5H_5)$	XXIV	191–193	CO: 1956, 2006	72.09	4.42	72.08	4.44

[a] Shrinks and dehydrates at 186° (see text). [b] This compound occludes toluene on recrystallization. The composition of these crystals is $(XXII \cdot {}^1/_2C_6H_5CH_3)$. [c] Selected as being pertinent to the identification of the compound.

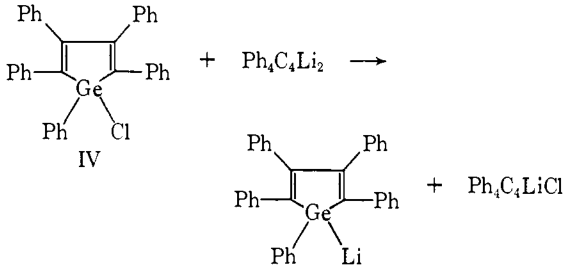
been added. In only one preparation was a small amount (0.5 g) of the known[4] octaphenyl-1,1′-spirobigermole (III) isolated. Apparently, the low solubility of the dichlorogermole (II) in diethyl ether prevents its further reaction with $(C_6H_5)_4C_4Li_2$ to give III.



III

When phenyltrichlorogermane was used as the halide in reaction 2, the desired chlorogermole (IV) was isolated along with a second compound identified as decaphenyl-1,1′-dihydro(1,1′-digermafulvalene) (V). The latter substance undoubtedly arises from a halogen–metal exchange sequence as shown in reactions 4 and 5. No silicon compound corresponding to V was isolated in the synthesis of VI, possibly due to a lower stability of the silyllithium compound (see below). The compounds obtained by reactions 2 and 3 are listed in Table I. All these compounds are yellow to yellow-green, fluorescent solids. Table II lists the compounds derived from the chlorides by the reactions discussed below.

The reactivity of the diene moiety often interferes with the reactions typical of halosilanes and germanes. Treatment of an acetone solution of the methylchlorosilole (VII) with a few drops of 6 *M* KOH gave a near-quantitative yield of tetraphenylbutadiene in 5 min at reflux (eq 6). Under identical conditions the germole IV is cleanly converted to the oxide X (ν_{GeOGe} = 875 cm^{-1}) (eq 7). Although C–Si bonds are generally more susceptible to base cleavage than C–Ge bonds, the C–Si bonds in VII appear to be exceptionally reactive. Thus, VII is cleaved to tetraphenylbutadiene by 1 ml of



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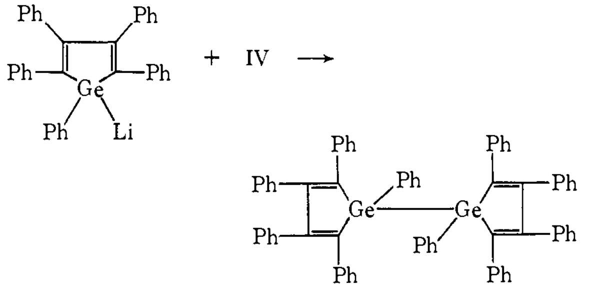
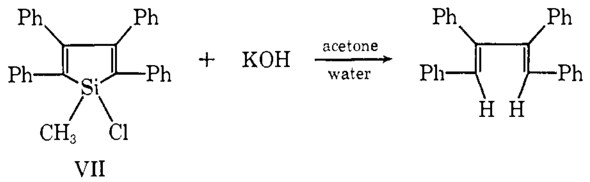


(5)

V

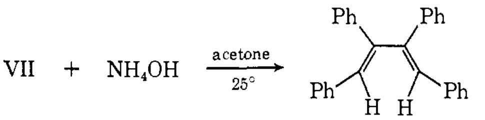


(6)

VII

$$\underset{\text{IV}}{2\text{Ph}_4\text{C}_4\text{Ge(Ph)Cl}} + \text{KOH} \xrightarrow[\text{water}]{\text{acetone}} \underset{\text{X}}{[\text{Ph}_4\text{C}_4\text{Ge(Ph)}\text{—}]_2\text{—O}} \qquad (7)$$

3 *M* NH_4OH in 50 ml of acetone after 15 min at room temperature (eq 8). However, a *two-phase* reaction mixture, consisting of dilute NH_4OH and a solution of the silole or germole in methylene chloride, gives good yields of the corresponding hydroxides.



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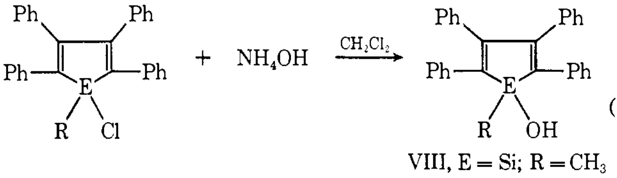


(9)

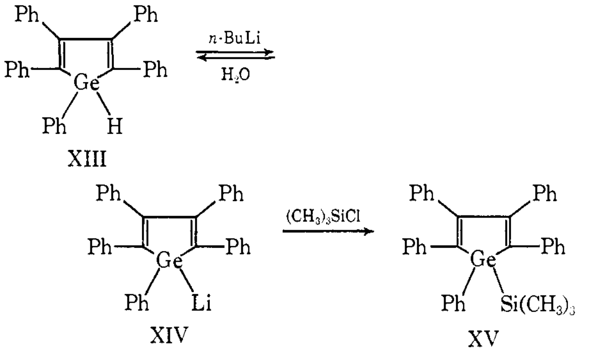
VIII, E = Si; R = CH_3
IX, E = Ge; R = C_6H_5

Both VIII and IX exhibit a strong O–H stretch in the ir, but neither shows an E–O stretch in the commonly quoted ranges.[10,11] However, bands at 946 and 670 cm^{-1} are attributed to the Si–OH and Ge–OH stretching modes, respectively. The melting behavior of IX (shrinks at 186°, then hardens and remelts at 256–257°) suggests that the hydroxide is losing water to form the oxide X. This was confirmed by examining the ir spectrum of the heated material. The Ge–OH band at 670 cm^{-1} was no longer present, and the Ge–O–Ge band at 875 cm^{-1} had appeared.

Heating the silole hydroxide VIII under vacuum to its melting point caused extensive decomposition but no silole oxide corresponding to X was obtained. Also, only impure resins were obtained when the phenylchlorosilole (VI) was hydrolyzed with either NH_4OH–CH_2Cl_2 or KOH–water–acetone. No tetraphenylbutadiene was observed, even after prolonged reaction times.

The displacement of chloride from VI by *n*-butyllithium is also quite solvent sensitive. In benzene, the reaction between butyllithium and VI gives a good yield of the butyl-substituted derivative, XX. The nmr spectrum of XX consists of two groups of unresolved peaks due to phenyl ($\tau \sim 3$) and butyl ($\tau \sim 8$–10) protons with an area ratio of 2.9 : 1 (calcd 2.8 : 1). On the other hand, in THF solvent, each drop of added butyllithium gives a transient red color (very similar to XIV, see below), and no pure products were isolated. It is probable that in THF, halogen–metal exchange occurs.

As reported previously,[7] the chlorides listed in Table I are readily reduced to the corresponding hydrides with $LiAlH_4$. The only hydride listed in Table II which gives a well-defined lithium salt (XIV) on treatment with *n*-butyllithium is the pentaphenylgermole XIII (eq 10). The germyllithium compound XIV is bright, cherry red in THF solution; and, as indicated in reaction 10, gives back the hydride XIII on treatment with water and reacts with trimethylchlorosilane to produce the silyl derivative XV. The silyl derivative has the characteristic[10] Si–CH_3 frequencies at 1250 and 850 cm^{-1} in its ir spectrum and exhibits a proton resonance at τ 9.77 due to the silyl-methyl groups. The observed area ratio of aromatic : aliphatic proton resonances is 2.8 : 1 (calcd for XV, 2.78 : 1).



XIII

XIV

XV

(10)

The addition of *n*-butyllithium to the tetraphenylgermole XVII produces a very dark green color which is dispelled relatively slowly when excess trimethylchlorosilane is added. The product, mp 239–241°, gives an nmr spectrum consisting of a multiplet at $\tau \sim 3$ and two sharp spikes at τ 4.70 and 9.87. The area ratios (43 : 7 : 9) suggest a dimer, the structure of which is unknown. It is worth noting that diphenylgermane reacts with butyllithium to give a mixture of products, one of which is also a dimer.[12]

$$(C_6H_5)_2GeH_2 + C_4H_9Li \longrightarrow Ph_2Ge(Bu)Li + Ph_2GeBu_2 + [Ph_2Ge(Li)\text{-}]_2 + Ph_2GeLi_2 \qquad (11)$$

The silyl hydrides XVIII and XIX do not form silyllithium derivatives on treatment with *n*-butyllithium.[7] Instead, deep purple colors[6] are formed, and nmr spectra (Figures 1 and 2, and Experimental Section) indicate that butyl groups are incorporated into the molecule. Quenching these reaction mixtures with H_2O or D_2O does not give compounds containing Si–H (Si–D) or Si–O bonds. No esr signals have been observed from these deeply colored solutions, indicating that the colors are not due to radicals formed by one-electron exchange with the butyllithium. By analogy with the known behavior of triphenylsilane toward *n*-butyllithium,[13] it is postulated that the following reactions are occurring to give a highly colored, conjugated C–Li derivative (reactions 12 and 13). Quenching XXI with D_2O would be expected to give a C–D bond, but, unfortunately, the C–D stretching region in the ir was obscured by overtone or combination bands.

In an attempt to duplicate reaction 13, crushed LiH was added to a solution of XX in THF. After several hours at room temperature, no reaction was apparent. However, when the more soluble $LiAlH_4$ is added to XX dissolved in THF, a deep purple color forms very rapidly. Addition of water to this mixture gives a resin whose nmr spectrum is very similar to, but not identical with, the crude product obtained from the reaction of butyllithium with XIX. The failure of bulk LiH to react with XX may be ascribed to the very low solubility of LiH in THF, whereas the LiH formed *in*

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(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 338.

(11) D. Quane and R. S. Bottei, *Chem. Rev.*, **63**, 403 (1963).

(12) R. J. Cross and F. Glockling, *J. Chem. Soc.*, 4125 (1964).

(13) H. Gilman and H. W. Melvin, *J. Amer. Chem. Soc.*, **71**, 4050 (1949).

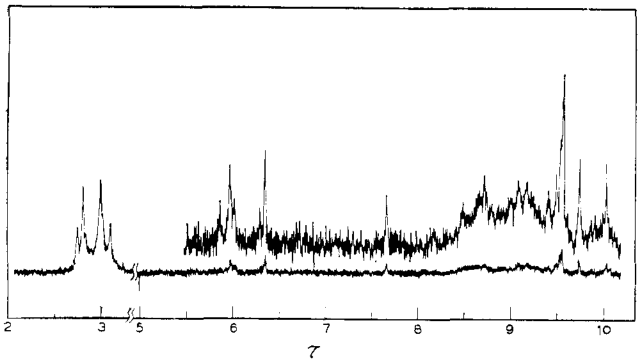
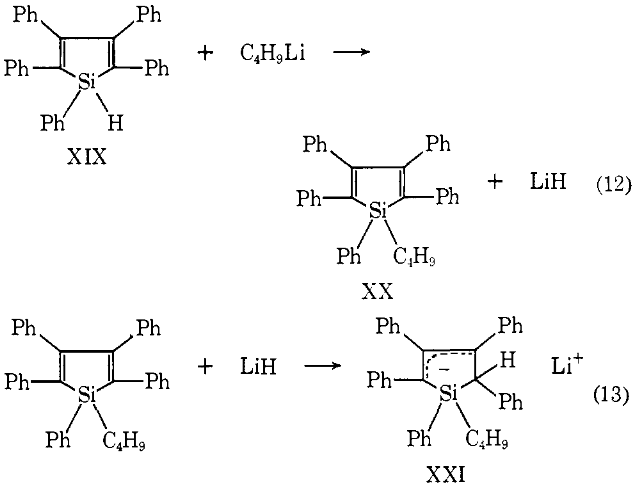
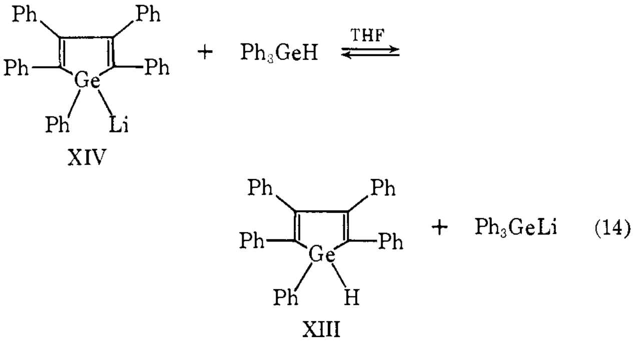


Figure 1. Nmr spectrum (60 Mc) of the product from adding *n*-butyllithium to XVIII, followed by D_2O.

situ (reaction 12) may be sufficiently reactive to add to the C=C double bonds as indicated in reaction 13.



If delocalization of charge is important in the bonding of the germyllithium compound XIV, then one might expect XIII to be considerably more acidic than triphenylgermane. This effect is demonstrated by the acidities of cyclopentadiene and triphenylmethane which have p*K*'s of 19[14] and 29.[15] In an attempt to obtain an idea of the relative acidities of XIII and triphenylgermane, the equilibrium expressed by reaction 14 was approached from both the left and the right (reaction 14). Upon adding an equimolar amount of Ph_3GeH to the cherry red solution of XIV, no change in color was observed. Adding an equimolar amount of XIII to a very pale yellow solution of triphenylgermyllithium gave immediately the cherry red characteristic of XIV. Rapid addition of trimethylchlorosilane immediately dispelled the red color, giving XV and triphenylgermane. (The pale yellow color of triphenylgermyllithium was also immediately discharged by trimethylchlorosilane in separate experiments.) No XIII or triphenyl(trimethylsilyl)germane were detected.



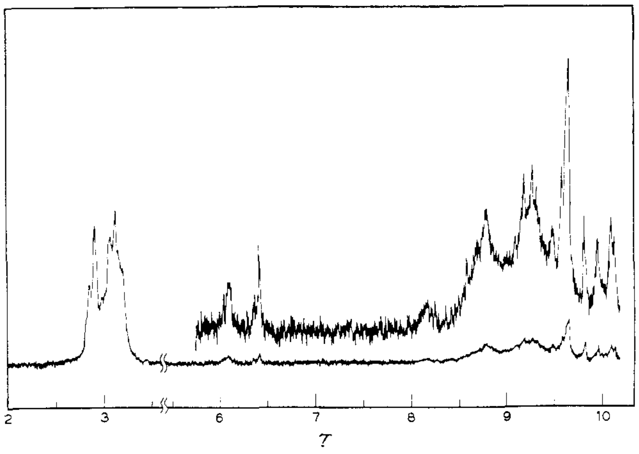


Figure 2. Nmr spectrum (60 Mc) of the product from adding *n*-butyllithium to XVIII, followed by H_2O.

Separate experiments showed that $(C_6H_5)_3GeH$ and $(C_6H_5)_3GeSi(CH_3)_3$ eluted much faster than XIII or XV from alumina, providing a quantitative separation of the triphenylgermanes from the germoles. In this way, the germoles were removed and the triphenylgermanes were examined by 100-Mc nmr spectroscopy. Again, no trace of $(C_6H_5)_3GeSi(CH_3)_3$ was observed. By adding a small, known amount of $(C_6H_5)_3GeSi(CH_3)_3$ to the nmr sample, it was estimated that this compound could have been detected at a concentration of 10^{-3} that of the $(C_6H_5)_3GeH$.

The equilibrium constant for reaction 14 may be expressed as

$$K_{eq} = \frac{K_a^B}{K_a^A}\frac{K_d^A}{K_d^B} \qquad \text{(I)}$$

where $K_a^B = [Ph_3Ge^-][H^+]/[Ph_3GeH]$ and $K_d^B = [Ph_3Ge^-][Li^+]/[Ph_3GeLi]$. The constants K_a^A and K_d^A are the analogous acid dissociation and lithium dissociation constants of the germacyclopentadiene. If it is *assumed* that the amounts of $(C_6H_5)_3GeSi(CH_3)_3$ and XV reflect the relative amounts of corresponding lithium reagents in solution, then (under the condition of equimolar amounts of reactants)

$$\frac{K_a^B}{K_a^A}\frac{K_d^A}{K_d^B} = \frac{[Ph_3GeSi(CH_3)_3]^2}{[Ph_3GeH]^2} \qquad \text{(II)}$$

If the reasonable assumption is made that $K_d^A/K_d^B = 1$, then the square of the molar ratio of $(C_6H_5)_3GeSi(CH_3)$ and $(C_6H_5)_3GeH$ should be a measure of the relative acidities of triphenylgermane and the germole XIII. Since the 100-Mc nmr data indicate that this ratio is less

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[14] F. G. Bordwell, "Organic Chemistry," The Macmillan Co., New York, N. Y., 1963, p 872.

[15] E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, 87, 383 (1965).

than 10^{-3}, one concludes that K_a^A(germole) $\geq 10^6 K_a^B$ (triphenylgermane). It is emphasized that this factor should be regarded as no more than a crude estimate in view of the assumptions inherent in its derivations. Although Birchall and Jolly have shown that inductive effects play a large role in the acidities of germanes,[16] a factor of 10^6 in relative acidities strongly suggests that the germole lithium compound, XIV, is in fact resonance stabilized.

Since the relative acidities derived from the above data rest upon several severe assumptions, a more exact determination of these acidities was undertaken using a spectrophotometric titration of the germanes with potassium dimsyl (KCH_2SOCH_3) in dimethyl sulfoxide (DMSO) solvent.[17,18] The acidity of triphenylgermane was determined by titrating the anion of triphenylpropene with a DMSO solution of the germane

$$I^- + HA \longrightarrow HI + A^- \qquad (15)$$

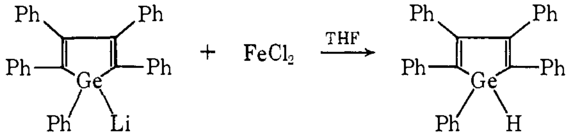
where HI = 1,1,3-triphenylpropene and HA = triphenylgermane. The concentration of indicator anion

$$pK_{HA} = pK_{HI} + \log\frac{[I^-]}{[HI]} - \log\frac{[A^-]}{[HA]} \qquad (III)$$

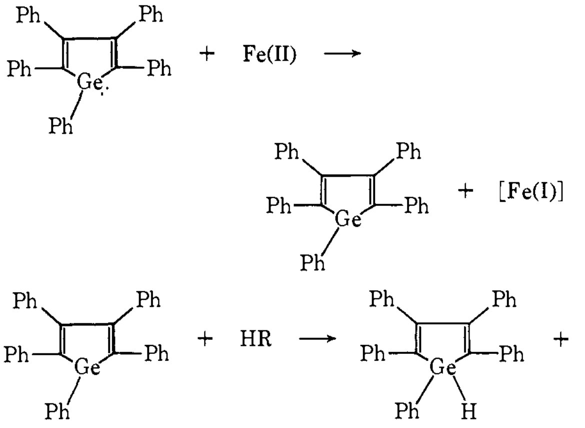
was determined from its absorption at 578 nm. The concentrations of HI, HA, and A^- are then fixed by stoichiometry. Under conditions where $[A^-]/[HA]$ ranged from 8.167 to 0.313, the calculated pK_{HA} varied from 22.89 to 23.00 with an average value of 23.0 ± 0.02 (average deviation). pK_{HI} was taken as 23.1, relative to a standard state in aqueous solution.[17]

The acidity of the germole XIII could not be determined in the same manner because the corresponding anion has an absorption peak at 453 nm, in the same region as the indicator anions. An attempt was made to determine the acidity of XIII using a basicity function[15,17] technique in which the anion of XIII is titrated with methanol. In the mixed solvent system methanol–DMSO, the germole (XIII) did not behave as a simple protic acid. Unknown side reactions preclude a determination of the acidity of XIII using the basicity function technique. Experiments are in progress to determine the acidity of XIII and other substituted germanes using Ritchie's potentiometric method.[18]

As stated in the introduction, a second goal of this research was the preparation of "sandwich" compounds containing the sila- or germacyclopentadienide rings π bonded to a transition metal. In an attempt to prepare an analog of ferrocene, the germyllithium derivative XIV was allowed to react with anhydrous iron(II) chloride. The only organogermane isolated was the hydride XIII (reaction 16). It is believed that the hydride XIII is produced by a series of reactions involving a one-electron transfer to give a germyl free radical which abstracts a hydrogen atom from the solvent (reactions 17 and 18). Reactions such as (17) and (18) have been previously postulated for several organometallic systems.[19]



XIV XIII (16)

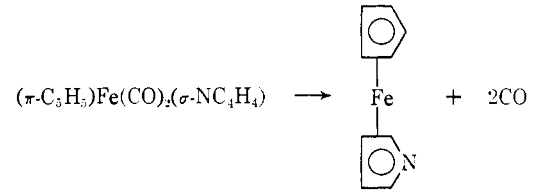


(17)

(18)

The next approach consisted of first synthesizing a σ-bonded derivative of the heterocyclopentadiene and attempting to rearrange the σ-bonded compound to a π-bonded "sandwich" structure. This approach is based on analogy with the known rearrangements of (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5)[20] and (π-C_5H_5)Fe(CO)$_2$(σ-NC_4H_4)[21] (reactions 19 and 20). The σ-bonded derivatives, XXI to XXIV (Table II), were synthesized by allowing the appropriate metal carbonyl anion to react with a chloro-substituted heterocyclopentadiene (reaction 21). The reactions of the chlorosiloles, VI and VII, with the anions $Mn(CO)_5^-$, $Co(CO)_4^-$, and $(C_5H_5)Mo(CO)_3^-$, did not lead to the formation of Si–metal bonds. These observations agree with those of previous workers.[22]

$$(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5) \longrightarrow (\pi\text{-}C_5H_5)_2Fe + 2CO \qquad (19)$$



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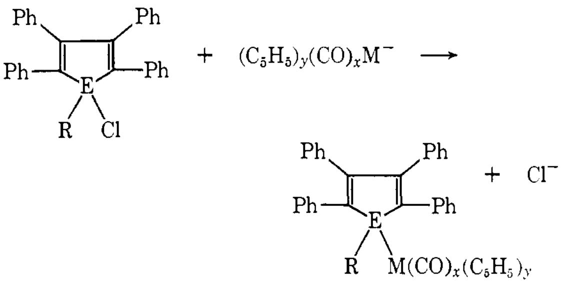

(21)

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[16] T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

[17] (a) E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, **85**, 3054 (1963); (b) E. C. Steiner and J. D. Starkey, *ibid.*, **89**, 2751 (1967).

[18] C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 1721 (1967).

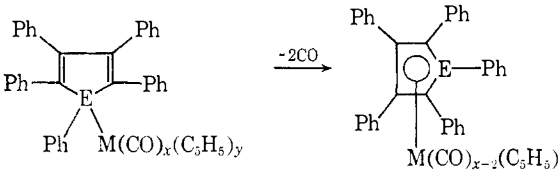
[19] (a) R. E. Dessy, W. Kitching, and T. Chivers, *ibid.*, **88**, 453 (1966); (b) R. E. Dessy and R. L. Pohl, *ibid.*, **90**, 2005 (1968).

[20] B. F. Hallam and P. C. Pauson, *J. Chem. Soc.*, 3030 (1956).

[21] P. L. Pauson and A. R. Qazi, *J. Organometal. Chem.*, **7**, 321 (1967).

[22] H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

The CO stretching frequencies of the carbonyl derivatives are nearly identical with those of corresponding acyclic compounds, indicating no perturbation of metal–CO bonding by the ring structure. The compounds XXI–XXIII were subjected to pyrolysis on a vacuum line to determine if they would rearrange to a π-bonded structure (reaction 22). The carbonyls are thermally stable up to their melting points, at which point they darken and a very slow CO evolution occurs. The rate of CO evolution does not become appreciable until the temperature is raised 40–60° above the melting point, at which point the compounds become dark and viscous. In the case of XXI, ferrocene sublimed to cooler portions of the apparatus. Chromatography of the intractable resins remaining after pyrolysis gave unidentified hydrocarbons (one appeared to be an α,β-unsaturated ketone from its ir band[10] at 1670 cm^{-1}), but no transition metal organometallics.



(22)

Attempts to cause rearrangements to π-bonded structures by ultraviolet photolysis of solutions of XXI–XXIV were also unsuccessful. Apparently, most of the light is absorbed by the organic portion of the molecule and this leads to destruction of the ring systems. Irradiation of XXIV gives a new peak (2060 cm^{-1}) in the CO stretching region, but only ferrocene could be isolated from the reaction mixture by elution chromatography. The other products of the reaction stick tenaciously to silica gel and could not be eluted.

Irradiation of XXII produced similar observations. All carbonyl-containing substances stick to alumina or silica gel; but a yellow, waxy hydrocarbon of unknown structure does elute.

The failure to isolate sandwich compounds in the above experiments does not necessarily mean that they are incapable of existence. The σ-bonded derivatives are so stable that the drastic conditions necessary for their decomposition might preclude the isolation of the possible π-bonded structures. Also, Pauson, *et al.*,[20,23] have shown that phenyl substitution on the cyclopentadienyl ring makes reaction 19 more difficult. It has been found[24] that the siloles and germoles reported here react directly with such metal carbonyls as Fe(CO)$_5$, Fe$_3$(CO)$_{12}$, and M(CH$_3$CN)$_3$(CO)$_3$ (M = Mo, W) to give products possibly containing π-bonded heterocyclopentadienes.

The synthesis of functionally substituted siloles and germoles has made possible the study of the derivative chemistry of this interesting class of compounds. This paper has reported the results of a survey of some reactions which these siloles and germoles undergo. Further studies are planned to clarify the extent of resonance stabilization of the anions and the effect of the heteroatom on the ability of these compounds to form "sandwich" complexes with transition metals.

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were obtained on a Varian A-60 instrument and chemical shifts are relative to internal tetramethylsilane in CCl$_4$ solvent. Ir spectra were routinely obtained as KBr disks on a Beckman IR 9; exceptions are the CO stretching frequencies of the carbonyl derivatives which were obtained in CH$_2$Cl$_2$ solvent. The 1,4-dilithiotetraphenylbutadiene was prepared according to the directions of Braye, *et al.*[3] A nitrogen atmosphere was maintained during all manipulations of reactive intermediates, *e.g.*, organolithiums.

1,1-Dichlorotetraphenyl-1-germacyclopentadiene (II). An ethyl ether suspension of 1,4-dilithiotetraphenylbutadiene, from 8.5 g (0.047 mole) of diphenylacetylene and excess lithium, was added portionwise to 5.0 g (0.029 mole) of GeCl$_4$ dissolved in 200 ml of ether with rapid stirring. After stirring for 0.5 hr, the ether was stripped and the residue treated with CH$_2$Cl$_2$. The suspension was filtered giving a white solid (LiCl) and a yellow filtrate which was concentrated and cooled to −10°. Scratching produced a crop of brilliant yellow crystals which were recrystallized twice from CH$_2$Cl$_2$–hexane, giving 5.3 g of product, II. Concentration of the mother liquors gave a small amount of yellow solid which was recrystallized from CH$_2$Cl$_2$–hexane. This solid, mp 257–260°, was identified by its melting point as III (lit.[4] mp 258–260°).

1-Chloropentaphenyl-1-germacyclopentadiene. (C$_6$H$_5$)$_4$C$_4$Li$_2$, from 17.4 g (0.098 mole) of diphenylacetylene and excess Li, was added portionwise to 10.0 g (0.039 mole) of phenyltrichlorogermane in 200 ml of THF. After the addition was complete (about 0.5 hr), the mixture was stirred at room temperature for 1.5 hr. Then the THF was stripped at reduced pressure and the residue extracted with 200 ml of hot toluene The toluene solution was filtered and then concentrated; subsequent cooling to 0° gave 18.9 g of crude product, mp 195–200°. Several recrystallizations from toluene gave 10.0 g of pure IV. From the mother liquor of the first recrystallization about 5 g of yellow crystals, mp 235–236°, were obtained and identified as V by elemental analysis.

The siloles VI and VII were prepared by an exactly analogous procedure.

1-Methyl-1-hydroxytetraphenyl-1-silacyclopentadiene (VIII) and 1-Hydroxypentaphenyl-1-germacyclopentadiene (IX). A 0.25-g sample of VII was dissolved in about 30 ml of CH$_2$Cl$_2$ and stirred at reflux with 20 ml of water containing a few drops of concentrated NH$_4$OH. At first, the CH$_2$Cl$_2$ layer became cloudy, but after about 20 min the cloudiness disappeared. At this point, the layers were separated and the CH$_2$Cl$_2$ was replaced by hot toluene. Cooling the toluene to 25° gave 0.20 g of yellow crystals of VIII, mp 199–202°. IX was prepared in an identical fashion from 0.4 g of VI in 40 ml of CH$_2$Cl$_2$, yield 0.3 g.

Bis(pentaphenylgermole) Oxide (X). A 0.2-g sample of the chloride IV was dissolved in 30 ml of acetone and the solution brought to reflux; 2 *M* KOH was added dropwise until a total of about 1 ml had been added. The mixture was refluxed for 20 min and then allowed to cool to room temperature giving 0.15 g of product. Recrystallization from toluene gave pure X (0.1 g).

Reaction of VII with KOH. A 0.4-g sample of VII was dissolved in 50 ml of acetone and treated with KOH as above. Within 5 min, the solution was colorless and white crystals separated. These were collected and identified as tetraphenylbutadiene: mp 184–185° (lit.[25] mp 183–195°); yield 0.3 g, 89%. *Anal.* Calcd for C$_{28}$H$_{22}$: C, 92.85; H, 7.15. Found: C, 92.90; H, 6.98.

Under identical conditions, no reaction was observed between XVI or XVII and KOH.

Tetraphenylbutadiene was also obtained when 0.5 g of VII in 50 ml of acetone was treated with about 1 ml of 3 *M* NH$_4$OH. After standing at 25° for 15 min, the bright yellow color of the silole had faded and colorless crystals of (C$_6$H$_5$)$_4$C$_4$H$_2$ separated.

Hydrolysis of 1-Chloropentaphenyl-1-silacyclopentadiene (VI). A 0.5-g sample of VI was dissolved in 20 ml of CH$_2$Cl$_2$ and treated with dilute, aqueous NH$_4$OH as above. After stirring at room temperature for 1 hr, the layers were separated and the CH$_2$Cl$_2$ was replaced by petroleum ether (bp 40–60°). Cooling to room temperature gave a yellow oil. Several attempts were made to crystallize this oil by triturating it with several solvents with no success. After standing for several weeks, the oil solidified to a waxy solid.

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[23] S. McVey and P. L. Pauson, *J. Chem. Soc.*, 4312 (1965).

[24] M. D. Curtis, unpublished results.

[25] A. N. Nesmeyanov, A. E. Borisov, and I. S. Savel'eva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1034 (1959); *Chem. Abstr.*, 54, 1366*i* (1960).

Treating VI (0.5 g) in 30 ml of refluxing acetone with aqueous KOH for 0.5 hr also gave a yellow oil on work-up. This oil also solidified on standing for several weeks. Both solids had what appeared to be a large number of partially resolved bands in the region 1000–1100 cm^{-1}. The four strongest peaks occurred at 1020, 1070, 1110, and 1130 cm^{-1}, although none of these was completely resolved and each band appeared to have a large number of shoulders. The solids were not characterized further.

1-Butylpentaphenyl-1-silacyclopentadiene (XX). A 1.5-g (3.0 mmoles) sample of VI was dissolved in 10 ml of dry benzene. A 1.9-ml sample of 1.6 *M* *n*-butyllithium in hexane was diluted with 30 ml of benzene and this solution was then added dropwise to the solution of VI. After addition was complete, the mixture was refluxed for 1.5 hr. The mixture was then hydrolyzed with 30 ml of 0.1 *M* H_2SO_4. The benzene layer was separated, dried, and the benzene replaced with hexane. Cooling to 0° gave a crop of orang crystals which was recrystallized from toluene–hexane, yield 1.0 g (65%).

When this reaction is performed in an identical manner with the exception that THF was used as the solvent, a transient red color was observed after each drop of added *n*-butyllithium. The THF was stripped and the residue dissolved in toluene. After filtering off the LiCl, the toluene solution was concentrated and cooled to 0°. Only a small amount of resinous material separated. The product also would not crystallize from hexane, hexane–pentane, or pentane. Finally, all solvent was removed under vacuum giving a glassy solid. An nmr spectrum of the solid gave an aromatic: aliphatic proton ratio of 25:4. This material was not further characterized.

1-Lithiopentaphenyl-1-germacyclopentadiene (XIV). To 0.5 g of XIII, dissolved in 50 ml of dry THF, was added 0.41 ml of *n*-butyllithium (2.4 *M* in hexane) with stirring at 78°. A bright red color develops immediately.

Reaction with $(CH_3)_3SiCl$. To the above solution was added 0.5 ml of trimethylchlorosilane. The red color was immediately discharged to give a yellow solution. The THF was stripped at reduced pressure and the residue dissolved in hot toluene. The LiCl was removed by filtration and the toluene solution concentrated. Addition of hexane gives 0.4 g (80%) of XV.

Reaction with Water. To a solution of XIV, prepared as above from 0.25 g of XIII, was added 1.0 ml of water with stirring. The mixture was worked up as above to give 0.20 g (80%) of hydride XIII, identified by melting point and ir.

***n*-Butyllithium and XVII.** The addition of 0.48 ml of 2.4 *M* *n*-butyllithium in hexane to 0.50 g of tetraphenylgermole, XVII, in 50 ml of THF at −78° gave a dark green color. A 1.0-ml sample of trimethylchlorosilane was added and in about 1 min the green color faded to yellow. The usual work-up gave 0.20 g of pale orange crystals, mp 239–241°, from hexane. The ir spectrum gave peaks at 1248 and 848 cm^{-1} ($SiCH_3$) and the nmr spectrum consisted of a broad multiplet at $\tau \sim 3$ and sharp spikes at τ 4.70 and 9.87 with area ratios of 43:7:9, respectively. There was no peak in the Ge–H stretching region in the ir spectrum, mol wt (vpo in benzene), 923.

Anal. Found: C, 73.42; H, 6.04; total oxide (Ge + Si), 33.57.

***n*-Butyllithium and Siloles.** A 0.52-ml sample of 2.4 *M* *n*-butyllithium in hexane was added with stirring to 0.50 g of XVIII dissolved in 100 ml of THF at −78°. A very intense purple color developed immediately. A 0.5-ml sample of D_2O was then added and the color rapidly faded to yellow. Removal of the THF, followed by extraction with toluene, gave a yellow solution from which no crystalline product could be obtained. After stripping off all solvent under vacuum, a yellow resin remained. The nmr spectrum of this resin is given in Figure 1. The aromatic:aliphatic proton ratio is 20:11.

An identical procedure, with the exception of using H_2O in place of D_2O, gave a yellow resin whose ir spectrum was identical with that of the D_2O-quenched product. The nmr spectrum (Figure 2) shows an aromatic:aliphatic proton ratio of 20:12.

Identical procedures with the phenylsilole XIX gave very similar nmr results. The aliphatic:aromatic proton ratio for the D_2O-quenched product was 25:10.7 and 25:11.2 for the H_2O-reaction product.

LiH and $LiAlH_4$ with XX. A 0.5-g sample of XX was dissolved in THF and stirred under nitrogen with 0.5 g of crushed lithium hydride at room temperature. No reaction was evident after 2 hr. A 0.1-g sample of XX reacted immediately with 0.05 g of $LiAlH_4$ in 20 ml of THF, giving a deep purple color. After 0.5 hr, water was added and the solution worked up by stripping solvent (and water), then extracting the residue with hot hexane. No crystalline product could be obtained, so all hexane was stripped giving a yellow resin.

Equilibrium Study (Reaction 14). A. A 0.180-g (1.60 mmoles) sample of XIII was dissolved in 50 ml of THF at −78°. A 1.0-ml sample of 1.6 *M* *n*-butyllithium was added; after 10 min, 0.489 g (1.60 mmoles) of triphenylgermane was added. No change in color was observed. After stirring at −78°, 1.0 ml of trimethylchlorosilane was rapidly added with vigorous stirring (the disappearance of the red color is instantaneous on mixing the reagents). After warming to room temperature, the THF was stripped and the residue dissolved in methylene chloride and filtered to remove LiCl. Removal of solvent gave a yellow, viscous oil. A small portion of this oil was examined by 100-Mc nmr using the chloroform peak (solvent) as the internal lock signal. The sharp signal at +136 cps (upfield) from $CHCl_3$ is due to Ge–H (triphenylgermane) and the sharp spike at +670 cps is due to $SiCH_3$ protons of XV. A small amount of added $(C_6H_5)_3GeSi(CH_3)_3$ gave an easily resolvable peak at +662 cps. Since a weak signal from $(C_6H_5)_3GeSi(CH_3)_3$ might be obscured at the base of the 670-cps peak, the remainder of the oil was chromatographed from alumina (Merck) using redistilled petroleum ether (bp 30–40°) as eluent. Under these conditions, $(C_6H_5)_3GeH$ and $(C_6H_5)_3GeSi(CH_3)_3$ elute rapidly, XV and XIII much more slowly. The first fraction taken consisted of everything that eluted up to the point that the yellow band approached the bottom of the column. Removal of solvent from this fraction gave a clear oil, the 100-Mc nmr spectrum of which consisted of the Ge–H peak at +136 cps, a series of very weak absorptions near +576 cps (impurity in petroleum ether?), but no hint of a peak at +662 cps.

B. The equilibrium (reaction 14) was approached from the other direction by adding 1.0 ml of 1.6 *M* *n*-butyllithium in hexane to 0.489 g (1.6 mmoles) of triphenylgermane in 50 ml of THF at −78°. The pale yellow color of $(C_6H_5)_3GeLi$ was produced. A 0.810-g sample of XIII was then added and the red color of XVI appeared immediately. This solution was worked up as in A and gave identical results in the nmr experiments.

The yellow color of $(C_6H_5)_3GeLi$, prepared as above, disappeared as fast as the reagents mixed when trimethylchlorosilane was added at −78°. Removal of solvent gave an essentially quantitative yield of $(C_6H_5)_3GeSi(CH_3)_3$.

Acidity Measurements. The method of determining the acidity of weak acids in DMSO has been described previously.[15,17] The apparatus used for the titrations (exclusion of air and moisture) was designed by Dr. E. C. Steiner.

Reaction of XIV and $FeCl_2$. A 1.0-g (2.0 mmoles) sample of XIII was converted to the lithium derivative with 0.82 ml (2.0 mmoles) of 2.4 *M* *n*-butyllithium in hexane. A 0.3-g (*ca.* 3 mmoles) sample of anhydrous $FeCl_2$ (Alfa Inorganics) was added at −78°. After 1 hr, the mixture was allowed to warm gradually to room temperature and the color began to darken. After 2 hr, the color appeared to be a dark green. After stirring overnight, a dark green, cloudy suspension had formed. The THF was stripped at reduced pressure and the residue taken up in toluene. Filtration of the toluene solution gave a tan powder (inorganic—discarded) and an orange solution. Concentration of the toluene (under vacuum) to a volume of 10 ml, followed by the addition of 20 ml of hexane, gave 0.6 g of yellow crystals, identified as XIII by ir (ν_{Ge-H} 2056 cm^{-1}) and elemental analysis: C, 80.15; H, 5.17; Ge, 14.41 (calcd C, H (Table II); Ge, 14.32. No further product could be obtained from the mother liquors.

σ-Bonded Carbonyls (XXI–XXIV). The procedure consists of reducing a metal carbonyl dimer in THF with sodium amalgam.[26] Since they are all similar, only one preparation is given in detail.

A 0.5-g (1.4 mmoles) sample of $[(C_5H_5)Fe(CO)_2]_2$ in 20 ml of THF was stirred with sodium amalgam prepared from 4 ml of Hg and *ca.* 0.5 g of Na. After 1 hr, this murky brown solution was transferred by syringe to a stirred solution of 1.5 g (2.8 mmoles) of IV in 40 ml of THF. After stirring for 0.5 hr, the THF was stripped under reduced pressure, the residue taken up in toluene, and filtered. The toluene solution was reduced in volume to 10 ml under reduced pressure, and the addition of 20 ml of hexane caused large crystals to separate. The solution was slowly cooled to −10° and filtered to give 1.4 g (74%) of product, mp 191–193°.

Similar procedures employing $Mn_2(CO)_{10}$, $[(C_5H_5)Fe(CO)_2]_2$, and $Co_2(CO)_8$ as the sources of the carbonyl anions gave, upon

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(26) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965.

reaction with the appropriate halide, XXI (60%), XXII (89%), and XXIII (65%).

Pyrolysis of σ-Bonded Carbonyls. The pyrolyses were performed on a vacuum line and standard techniques were used to measure the amount of gases, etc. A 0.2932-g (0.418 mmole) sample of XXII was placed in a Pyrex tube attached to the vacuum line. A sand bath was used for heating. As the temperature was raised to 100°, a slow gas evolution occurred, which soon stopped. The total pressure rise corresponded to 2.1×10^{-4} mole. The gas was easily liquefied and was identified by ir as toluene. Heating was continued up to the melting point (*ca.* 160°) with no further gas evolution. At 180° a very slow gas evolution was observed, but the pressure rise up to 240° was only 0.1 mm (in a *ca.* 180-ml volume). At 280°, the compound suddenly turned dark and gas evolution became rapid. After 1.5 hr at this temperature, the gas was evolving extremely slowly. Heating was discontinued and the volume of gas was accurately measured, giving 3.04 moles of CO evolved/mole of XXII. (CO was identified by ir.) Chromatography, under nitrogen, of the residue from alumina gave a yellow, waxy solid (hexane:benzene 2:1 eluent), and an orange solid (benzene:ether 1:2). Neither of these solids contained metal-carbonyl groups (ir), but the solid eluted with ether had a strong band at 1670 cm^{-1}. A dark band remained at the top of the column and would not elute.

With XXI, CO evolution was very slow until the temperature reached 270–280°. After 3.5 hr, 1.05 moles of CO/mole of XXI had evolved, and orange crystals had sublimed to the cooler portion of the pyrolysis tube. The orange crystals were identified as ferrocene by ir and mp (172–173°). Chromatography of the residue gave, in order of elution: unidentified hydrocarbons, starting material, and an unidentified organosilicon compound which did not contain iron (KSCN test). Again, a dark band stuck to the top of the column. Pyrolysis of XXIII gave 2.3 moles of CO/mole of XXIII after 2.5 hr at 200°. The residue was an intractable black tar.

Photolysis of σ-Bonded Carbonyls. A General Electric UA-11A photochemical lamp was employed with a Pyrex filter which absorbs most of the light with wavelengths less than about 320 nm. A nitrogen atmosphere was maintained during the photolysis and a water jacket kept the temperature of the reactant near 23°. A 0.5-g sample of XXIV in 50 ml of CH_2Cl_2 was photolyzed for 3.5 hr, after which time it was calculated from the decrease in absorbance at 2006 cm^{-1} that *ca.* 75% of the starting material had reacted. A new peak at 2060 cm^{-1} appeared during the photolysis. Chromatography (under nitrogen) of the reaction mixture from silica gel gave ferrocene and a waxy hydrocarbon, not containing Ge or Fe. A yellow band would not elute from the column.

Photolysis of XXII (0.30 g in 50 ml of toluene) for 8 hr caused new bands to appear at 1975 and 1920 cm^{-1} with a concomitant decrease in the peaks due to starting material. Concentration of the toluene and subsequent addition of hexane caused a tan powder ($\sim$0.05 g) to precipitate. This powder had an extremely broad and intense band at 1970 cm^{-1}, but no absorptions due to phenyl groups. No crystalline material could be obtained, so the material was chromatographed from silica gel giving a waxy, yellow, unidentified hydrocarbon and a yellow-orange band that would not elute.

Photolysis of XXIII (0.50 g in 50 ml of benzene) gave a red solution, which decomposed extensively on silica gel. No solid products were isolated.

Acknowledgment. The author is indebted to Mr. Robert Imes for determining the acidity of the germanes in DMSO and to Dr. E. C. Steiner for helpful comments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.