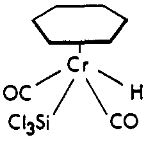
Table I. Properties of Trichlorosilyl Hydrides[a]

Compound	Mp, °C	τ(M–H)[b]	γ(CO), cm^{-1} [c]
1 $(OC)_4Fe(H)SiCl_3$	<0	19.0	2124, 2069, 2058, 2053[d]
2 $C_6H_6(OC)_2Cr(H)SiCl_3$	114–114.5	20.5	1982, 1922
3 $C_5H_5(OC)_2Mn(H)SiCl_3$	82–83	19.7[e]	2028, 1977
4 $C_5H_5(OC)Fe(H)(SiCl_3)_2$	131–132	21.6	2025
5 $C_5H_5(OC)Co(H)SiCl_3$	31–33	23.3	2045

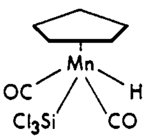
[a] Microanalysis and mass spectrometry support the formulation of all compounds except **1**; the thermal instability and air sensitivity of the latter has prevented us from obtaining meaningful results. For **3** and **4**, [parent − Cl]$^+$ is the heaviest fragment observed. [b] Nmr solvent is cyclohexane for **5**, acetonitrile for other compounds. [c] Infrared carbonyl stretching fundamentals; solvent is *n*-hexane except for **2**, for which low solubility required the use of dichloromethane. [d] Additional bands at 2000 and 2023 cm^{-1} due to $Fe(CO)_5$ grow as the spectrum is measured. [e] Broad.

conditions by ultraviolet irradiation of $Fe(CO)_5$–$HSiCl_3$ mixtures.

We report in this communication the isolation of the anticipated intermediate, *cis*-$(OC)_4Fe(H)SiCl_3$ (**1**) and the extension of this photochemical reaction to other metal carbonyl derivatives. Thus far, reactions with π-$C_6H_6Cr(CO)_3$, π-$C_5H_5Mn(CO)_3$, π-$C_5H_5Fe(CO)_2$-$SiCl_3$, and π-$C_5H_5Co(CO)_2$ have yielded compounds **2–5**. On the basis of these preliminary results, it is clear that a new and broadly applicable route has been opened to this important class of transition metal hydrides.



2



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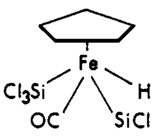

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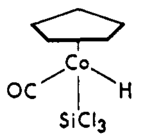

5

The very volatile *cis*-$(OC)_4Fe(H)SiCl_3$ crystallizes from pentane at −78° and melts well below room temperature to an extremely air-sensitive liquid. Its reaction with tetrafluoroethylene was examined with the object of forming a more stable tetrafluoroethyl derivative; instead, the product from a reaction at room temperature is a yellow crystalline solid characterized by analysis and mass spectrum as $[(OC)_4FeSiCl_3]_2$. It is presumably related to the known compound $[(CO)_4RuSi(CH_3)_3]_2$.[4]

Compounds **2–5** are prepared under similar conditions,[5] and, with the exception of **5**, appear stable for long periods in the purified crystalline form. Solutions are much less stable. Fractional sublimation under vacuum is an important purification technique; the work-up procedures, in our opinion, are more exacting than those normally encountered in metal carbonyl chemistry. Yields range from an estimated 10% with **5** to >90% with **2**.

It is scarcely necessary to point out that all of these compounds conform to the 18-electron or effective atomic number rule. Formally, they are derived by replacing an electron-pair-donating carbonyl group with H and $SiCl_3$ as single-electron donors. This formal viewpoint may correspond closely to the mechanism as well. Presumably, a photon ejects a carbonyl group to form a coordinatively unsaturated or 16-electron intermediate, to which the Si–H bond adds.[6]

X-Ray crystallographic studies on some of the compounds are in progress.[7] Analogy with established structures[8] suggests an arrangement in which the metal occupies the apex of a distorted square pyramid, with ligands other than the ring forming the base. We have seen no evidence for the second isomer that is possible in principle for such a structure.[9]

Compound **4** was first obtained as a product of the thermal reaction between Cl_3SiH and $[\pi$-$C_5H_5Fe(CO)_2]_2$.[10] It is a very strong acid (pK_a estimated as 4 in acetonitrile) of which the anion forms stable salts. The acid strength of the other hydrides has not yet been determined.

Acknowledgment. We thank the National Research Council of Canada for financial support and for a bursary to W. J.

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(4) J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *Chem. Commun.*, 965 (1967).

(5) Reactions in this work were carried out using a Hanovia Type 30620 lamp placed a few inches from a water-cooled quartz reactor. The solvent was hexane.

(6) Oxidative addition of Si–H to certain square-planar d^8 compounds (which are 16-electron species according to the effective number rule) has been observed: F. de Charentenay, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, *A*, 787 (1968), and references cited.

(7) Professor J. A. Ibers (Northwestern University) is determining the structure of **4**. The structures of **2** and **3** are being studied by Professor M. J. Bennett in this department.

(8) Specifically, those of the types π-$C_5H_5Mo(CO)_3R$ and π-C_5H_5-$Mo(CO)_2LR$; *cf.* M. R. Chruchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967); 7, 953 (1968).

(9) The *trans* placement of basal ligands in the suggested structures **2–4** has not been established. The arrangement in π-$C_5H_5Mo(CO)_2$-$[P(C_6H_5)_3]COCH_3$ is *trans*, however.[8] We have observed that the high-field proton of **4** is equivalently coupled to the *two* silicons (^{29}Si, I = $^1/_2$, 4.7%) with J(H–Fe–Si) = 20 cps. This is consistent with a *trans* geometry, but could also result from time averaging of other structures.

(10) W. A. G. Graham and W. Jetz, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M82. Full details of our study of this reaction will shortly be submitted for publication.

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Polyhedral Carboranes Containing an Arsenic, Antimony, or Germanium Atom in the Cage

Sir:

Recently it was reported that distorted icosahedral boranes containing both a carbon and a phosphorus atom and isoelectronic with $B_{12}H_{12}^{2-}$ could be prepared in reasonable yield by the route described in the following equation.[1]

$$Na_3B_{10}H_{10}CH(C_4H_8O)_2 + PCl_3 \longrightarrow 1,2\text{-}B_{10}H_{10}CHP + 3NaCl + 2C_4H_8O$$

In principle other heavier nonmetal and metalloid elements should be inserted into the carborane frame-

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(1) J. L. Little, J. T. Moran, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 5495 (1967).

Table I. Analytical Data for Carborane Derivatives

Compound	Calculated, %					Found, %				
	C	H	N	B	E[a]	C	H	N	B	E
1,2-$B_{10}H_{10}CHAs$	5.83	5.37	...	52.45	36.34	5.78	5.18	...		
1,7-$B_{10}H_{10}CHAs$	5.83	5.37	...	52.45	36.34	5.82	5.27	...		
1,2-$B_{10}H_{10}CHSb$	4.74	4.38	...	42.74	48.13	5.59	4.34	...	42.02	48.14
1,7-$B_{10}H_{10}CHSb$	4.74	4.38	...	42.74	48.13	5.18	4.28	...	42.83	47.98
1,2-$B_{10}H_{10}CHGeCH_3$	11.0	6.45	...	49.40	33.17	10.91	6.61	...		
$(CH_3)_4N[B_{10}H_{10}CHGe]$	21.58	8.33	5.03	38.98	26.08	21.49	8.61	5.48		

[a] E represents the element As, Sb, or Ge.

work by this type of reaction. We now wish to report the synthesis and preliminary chemistry of three new carborane molecules in which either an arsenic, antimony, or germanium atom has been inserted into the cage structure.

Slow addition of a 10% tetrahydrofuran (THF) solution of arsenic trichloride to a slurry of $Na_3B_{10}H_{10}CH$ in THF at room temperature produced 1,2-$B_{10}H_{10}CHAs$ (I), mp 399–399.5°, in 25% yield. The analytical data for I are given in Table I. The mass spectrum of I at low electron voltage (14 eV) cut off at *m/e* 208, corresponding to a parent ion of composition $(^{11}B_{10}{}^1H_{11}{}^{12}C^{75}As)^+$. In the ^{11}B nmr spectrum of I, the signals of the unique boron atoms (*i.e.*, those opposite the carbon and arsenic in the cage) are clearly found at lowest field. The same is also true for atoms B_9 and B_{12} of 1,2-$B_{10}H_{10}C_2H_2$ and 1,2-$B_{10}H_{10}CHP$.

Although reaction of $B_{10}H_{10}CH^{3-}$ with antimony trichloride gave an unusually exothermic reaction, the desired neutral carborane was not obtained. Slow addition of an antimony triiodide–THF solution to $Na_3B_{10}H_{10}CH$ in THF at ice-bath temperatures produced 1,2-$B_{10}H_{10}CHSb$ (II) in 30% yield. The molecular composition of II was confirmed by elemental analysis (Table I), osmometric molecular weight, and measurement of the parent ion at *m/e* 256.0837 (calculated for $^{11}B_{10}{}^1H_{11}{}^{12}C^{123}Sb^+$: 256.0833). Both I and II could be transformed in sealed tubes at 505 and 450°, respectively, into isomeric species III and IV. The ^{11}B nmr spectra of these two thermal products were nearly identical but too complex to be attributed to the 1,12 isomer. Thus III and IV appear to be 1,7-$B_{10}H_{10}CHAs$ (mp 351–352°) and 1,7-$B_{10}H_{10}CHSb$ (mp 403.5–404.5°), respectively. Unlike the phospha- and arsacarboranes, there is considerable decomposition in the thermal rearrangement of 1,2-$B_{10}H_{10}CHSb$. Only a 20% yield of 1,7-$B_{10}H_{10}CHSb$ was obtained. Heating I at 575° produced a mixture of III and 1,12-$B_{10}H_{10}CHAs$ (V). The 1,12 isomer was purified by column chromatography, mp 335.5–337.0°, and its composition determined by measurement of the parent ion at *m/e* 208.1011 (calculated for $^{11}B_{10}{}^1H_{11}{}^{12}C^{75}As$: 208.1004). The ^{11}B nmr spectrum of V consisted of two overlapping doublets of equal area at +7.5 (J_{BH} = 160 cps) and +8.2 (J_{BH} = 175 cps) ppm externally referenced to $BF_3 \cdot (C_2H_5)_2O$. The relative gas chromatographic retention times (SE-30 Silicone on Chromosorb P column) of the arsacarboranes increase in the order V, III, and I, paralleling the expected increase in polarity of the isomers (*i.e.*, 1,12- < 1,7- < 1,2-$B_{10}H_{10}CHAs$).

Reaction of $Na_3B_{10}H_{10}CH$ with CH_3GeCl_3 in THF at reflux produced a sublimable solid (VI) which could be recrystallized from cyclohexane (mp 216–217°). The parent peak in the mass spectrum of VI appeared at *m/e* 224 which corresponds to the $(^{11}B_{10}{}^1H_{14}{}^{12}C_2{}^{76}Ge)^+$ ion. The ^1H nmr spectrum of VI in $CDCl_3$ solution contained two singlets at τ 7.45 (1 H, broad) and 7.95 (3 H) which are assigned to the hydrogen atoms bonded to the carborane carbon and the methyl group, respectively, of the $B_{10}H_{10}CHGeCH_3$ molecule. Treatment of VI with piperidine at reflux generated an anion (VII) which was isolated and characterized as the tetramethylammonium salt. The ^1H nmr spectrum of VII in dimethyl-d_6 sulfoxide contains only two singlets at τ 6.88 (12 H) and 8.0 (1 H, broad). The ^{11}B nmr spectrum envelope of VII was quite similar to that of $B_{10}H_{10}CHGeCH_3$, indicating that the cage structure was still intact. These data suggest that piperidine demethylates VI to produce the $B_{10}H_{10}CHGe^-$ ion (VII). Indeed reflux of VII with excess methyl iodide in THF regenerates $B_{10}H_{10}CHGeCH_3$ in good yield. Both germacarboranes (VI and VII) were extensively decomposed after short exposure at 450°.

Reaction of I, II, or III with 4 equiv of piperidine in benzene solution abstracts one boron atom from each type of cage structure to give in moderate yield piperidinium salts of $B_9H_{10}CHE^-$ ions (E = As or Sb). Similar results were obtained with the phosphacarboranes.[2] When a large excess of piperidine was allowed to react with 1,2-$B_{10}H_{10}CHSb$, a substantial amount of the $B_{10}H_{12}CH^-$ ion[3] was formed. The phosphorus and arsenic analogs did not appear to undergo this type of degradation in concentrated piperidine solution.

Transition metal complexes of the 7,8- and 7,9-$B_9H_9CHAs^{2-}$ ions[4] have been prepared and appear to be similar to the recently reported phosphacarborane–transition metal complexes.[2] This work and further studies on the heteroatom carboranes are now in progress and will be reported later.

Acknowledgment. This work was generously supported by the Office of Naval Research and the National Science Foundation under Grant GP-7878.

(2) L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker, and C. R. Peterson, *J. Am. Chem. Soc.*, 90, 4489 (1968).

(3) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, 6, 2229 (1967).

(4) The numbering system employed in this article follows the new nomenclature rules which recently appeared in *Inorg. Chem.*, 7, 1945 (1968). A different numbering system was used in ref 2.

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