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Triphenylgermyl-substituted Ferrocenes. New Syntheses of Ferrocenyl Lithium and Grignard Reagents

by

Dietmar Seyferth, H. P. Hofmann, R. Burton and J. F. Helling

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Massachusetts Institute of Technology
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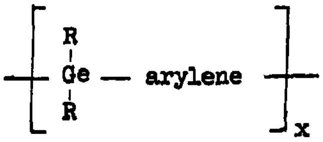
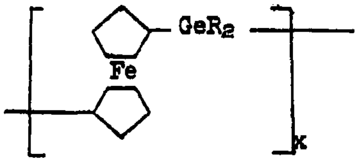
Introduction

The original purpose of this work was to prepare and evaluate polymers of the type



$$\left[-\overset{R}{\underset{R}{\mathrm{Ge}}} - \text{arylene} - \right]_x$$

Of particular interest was the germaniumferrocenylene system:



in view of the interesting properties of ferrocene and its derivatives. At the time this research commenced no satisfactory synthesis of 1,1'-ferrocenylene active metal reagents was available except for the 1,1'-ferrocenylenedisodium reagent. As described in this report, the major product in its reaction with triphenylbromogermane was hexaphenyldigermane. Thus an evaluation of the corresponding dilithium and di-Grignard reagents in this reaction seemed desirable. For this reason syntheses of these reagents were developed. However, in all cases of the reaction of the 1,1'-ferrocenylene active metal reagents with organometallic halides, incomplete reaction leading to monosubstituted ferrocenes in significant amounts was encountered. This apparently general behavior makes impossible syntheses of useful organometallic polymers based on the ferrocene unit, and for this reason this approach will not be pursued further.

(Contribution from the Department of Chemistry of the Massachusetts Institute of Technology, Cambridge 39, Massachusetts)

Triphenylgermyl-substituted Ferrocenes and Related Compounds. New Syntheses of Ferrocenyl Lithium and Grignard Reagents.

By Dietmar Seyferth, Hermann P. Hofmann, Raymond Burton and John F. Helling

The reaction of 1,1'-ferrocenylenedisodium with triphenylbromogermane gave significant amounts of triphenylgermylferrocene in addition to the expected 1,1'-bis(triphenylgermyl)ferrocene. Similar behavior was noted when trimethylchlorosilane was used in place of the germane. Treatment of the disodioferrocene with magnesium bromide in ether represents a new route to the ferrocene di-Grignard reagent, carbonation of which gave 1,1'-ferrocenedicarboxylic acid. However, addition of triphenylbromogermane to the di-Grignard solution resulted in almost none of the disubstituted product, but a 32% yield of triphenylgermylferrocene was realized. A new preparation of ferrocenyllithium and 1,1'-ferrocenylenedilithium by the transmetalation reaction occurring between ethyllithium and the corresponding chloromercuriferrocenes in ether is described. Again, the reaction of 1,1'-ferrocenylenedilithium with trimethylchlorosilane produced significant amounts of the monosubstituted product in addition to 1,1'-bis(trimethylsilyl)ferrocene. The preparation of 1,1'-bis(triphenylgermyl)titanocene dichloride, triphenylgermylmanganese pentacarbonyl and triphenylgermyl-π-cyclopentadienyliron dicarbonyl is described.

During early stages of a study of metal-substituted ferrocenes an attempt was made to prepare 1,1'-bis(triphenylgermyl)ferrocene by the reaction of 1,1'-ferrocenylenedisodium with triphenylbromogermane. It had been reported that metalation of ferrocene with phenylsodium[1] and with n-amylsodium[2] gave, after carbonation, 1,1'-ferrocenedicarboxylic acid in moderate yield; only traces of ferrocenecarboxylic acid were formed. When this sodiation procedure was used in our experiments, the desired 1,1'-bis(triphenylgermyl)ferrocene was obtained in ca. 12-13% yield (based on the ferrocene used; 35% yield based on unrecovered ferrocene), but surprisingly large amounts (4-10%) of the monosubstituted product, triphenylgermylferrocene, also were present. By far the major product was hexaphenyldigermane (53-77%); some hexaphenyldigermoxane (derived from hydrolysis of unreacted triphenylbromogermane) and minor amounts of tetraphenylgermane also were isolated. This mixture of phenylated germanes could be resolved only with difficulty into the pure components by elution chromatography. The bis(triphenylgermyl)ferrocene was identical with an authentic sample prepared _via_ cyclopentadienyltriphenylgermane. Previous workers had observed significant yields of tri-n-hexylsilylferrocene in the preparation of 1,1'-bis(tri-n-hexylsilyl)ferrocene when the disodioferrocene route was used[3]. This was believed due to

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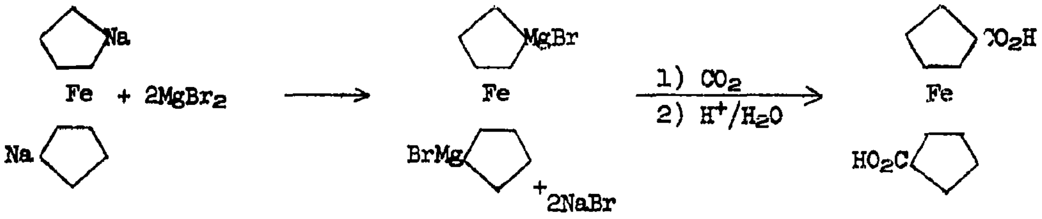
(1) A. N. Nesmeyanov, E. G. Perevalova and Z. A. Beinoravichute, _Doklady Akad. Nauk S.S.S.R._, _112_, 439 (1957); _C. A._, _51_, 13855 (1957).

(2) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beinoravichute and I. L Malygina, _Doklady Akad. Nauk S.S.S.R._, _120_, 1263 (1958); _C. A._, _53_, 1293 (1959).

(3) S. I. Goldberg, D. W. Mayo, M. Vogel, H. Rosenberg and M. Rausch, _J. Org. Chem._, _24_, 824 (1959).

incomplete reaction between the disodioferrocene and tri-n-hexylbromosilane, caused by steric hindrance toward further coupling introduced when one of the sodium atoms attached to the cyclopentadienyl rings was replaced by a bulky R_3Si group. We have made similar observations when the disodioferrocene reagent was characterized using trimethylchlorosilane, except that our mono- to disubstituted product ratio was much larger than that reported by the authors cited above.

Conversion of 1,1'-ferrocenylenedisodium to the 1,1'-ferrocenylene di-Grignard reagent by treatment with magnesium bromide in ether, followed by carbonation, gave 1,1'-ferrocenedicarboxylic acid in ca. 30% yield, accompanied only by traces of the monocarboxylic acid:



This represents a new route to the di-Grignard derivative of ferrocene which is perhaps more convenient than its recently reported[4] synthesis based on the not readily available 1,1'-dihaloferrocenes. The steric factors in the coupling reaction with triphenylbromogermane and trimethylchlorosilane, however, seem to be even more severe in the case of the 1,1'-ferrocenylene di-Grignard reagent, since the monosubstituted compounds were accompanied by only trace amounts

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(4) H. Shechter and J. F. Helling, J. Org. Chem., 26, 1034 (1961).

of the disubstituted products. It is worth noting that in the case of the reaction of the di-Grignard reagent with triphenylbromogermane no hexaphenyldigermane was produced. Attempts to characterize any 1-bromomagnesium-1'-triphenylgermylferrocene present in these solutions before hydrolysis, using reagents of smaller steric requirements such as carbon dioxide and methyl iodide, were unsuccessful insofar as pure products could not be isolated from the reaction mixtures. This may not be taken as proof that such a mono-Grignard reagent does not exist in the reaction mixture.

The interest in ferrocenyl active metal reagents developed during the course of this work led us to work out a new synthetic route to ferrocenyllithium[5] and 1,1'-ferrocenylenedilithium. The available synthesis of these reagents via lithiation of ferrocene was unsatisfactory, since an unresolvable mixture of both reagents was formed under all conditions tried, and since a fairly large excess of n-butyllithium was required for moderate to good conversions of lithioferrocenes.[6-9]

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(5) Preliminary communication: J. F. Helling and D. Seyferth, Chemistry and Industry (London), (1961).

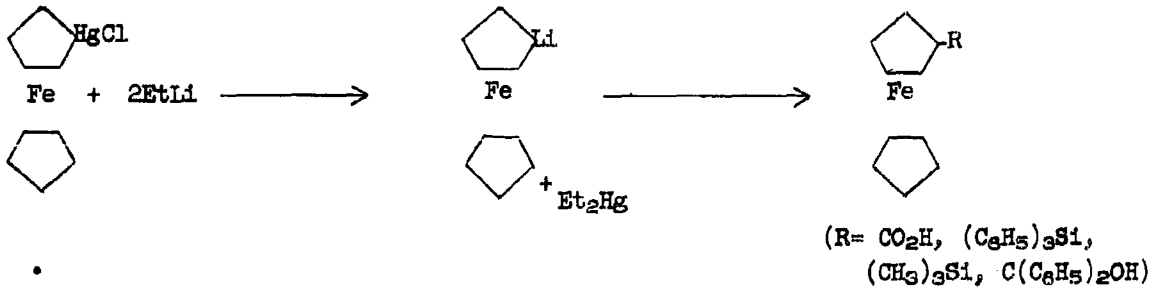
(6) R. A. Benkeser, D. Goggin and G. A. Schroll, J. Am. Chem. Soc., 76, 4025 (1954).

(7) A. N. Nesmeyanov, E. G. Perevalova, R. N. Golovnya and O. A. Nesmeyanova, Doklady Akad. Nauk S.S.S.R., 97, 459 (1954).

(8) M. Rausch, M. Vogel and H. Rosenberg, J. Org. Chem., 22, 900 (1957).

(9) D. W. Mayo, P. D. Shaw and M. Rausch, Chemistry and Industry (London), 1388 (1957).

Our new preparation of ferrocenyllithium reagents uses the transmetalation reaction occurring between chloromercuriferrocene or 1,1'-bis(chloromercuri)ferrocene and alkyllithium reagents. These chloromercuri derivatives are available through the mercuration of ferrocene and can be separated by extraction of the chloromercuriferrocene from the essentially insoluble dimercurated compound.[7] This procedure represents a satisfactory route to ferrocenyllithium essentially free of the dilithiated compound and starting alkyllithium. The reaction produces diethylmercury (when ethyllithium is used) in nearly quantitative yield, and subsequent conversions of the ferrocenyllithium formed gave monosubstituted ferrocenes in yields of 60-65%:



Apparently only trace to very low yields of 1,1'-ferrocenylenedilithium were formed in these reactions. Phenyllithium proved to be much less satisfactory in this application. The use of diferrocenylmercury in place of chloromercuriferrocene did not appear to offer any advantage. Reaction of 1,1'-bis(chloromercuri)ferrocene with four equivalents of ethyllithium, followed by carbonation, gave 1,1'-ferrocenedicarboxylic acid in only 44% yield, although diethylmercury had been formed in high yield. Treatment of the dilithio derivative prepared in this manner with trimethylchlorosilane again produced trimethylsilylferrocene in significant quantity in addition to 1,1'-bis(trimethylsilyl)ferrocene.

Incidental to the synthesis of these germanium-substituted ferrocenes, three other germanium-containing transition metal compounds have been prepared. The reaction of the lithium derivative of cyclopentadienyltriphenylgermane with titanium tetrachloride gave 1,1'-bis(triphenylgermyl)titanocene dichloride in very low yield. The action of $NaMn(CO)_5$ and $NaFe(CO)_2C_5H_5$ on the bromogermane gave $(C_6H_5)_3GeMn(CO)_5$ and $(C_6H_5)_3GeFe(CO)_2C_5H_5$, both stable, crystalline solids, the first compounds containing a germanium-transition metal bond to be reported.

EXPERIMENTAL[10]

<u>Reactions of 1,1'-Ferrocenylenedisodium</u>. (a) <u>With Triphenylbromogermane</u>. - To n-amylsodium in 250 ml. of pentane prepared from 0.075 mole of n-amyl chloride and 0.15 g. atom of sodium dispersion by the procedure of Morton[11] was added 6.0 g. (0.03 mole) of ferrocene. The mixture was heated at reflux for several hr. while vigorous stirring was continued. Triphenylbromogermane (28.8 g., 0.075 mole) was added, and the reaction mixture was refluxed for several hr. The mixture was treated first with 50 ml. of methanol (since unreacted sodium appeared to be present), then with water. The organic phase was evaporated and all solids

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[10] All reactions involving air or moisture sensitive reagents were carried out under an atmosphere of dry, prepurified nitrogen. Melting points are uncorrected. Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

[11] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little and R. L. Letsinger, J. Am. Chem. Soc., 72, 3785 (1950).

as well as the aqueous phase extracted well with benzene. Evaporation of the benzene extracts left an orange-brown solid from which 4.1 g. of unreacted ferrocene was removed by steam distillation and vacuum sublimation. The residue was chromatographed repeatedly on alumina using heptane-benzene mixtures as eluant and gave, in the order listed, 8.09 g. of hexaphenyldigermoxane, 0.2 g. of tetraphenylgermane, 0.52 g. (3.5% conversion, 10% yield based on unrecovered ferrocene) of triphenylgermylferrocene, 3.5 g. (12% conversion, 38% yield) of 1,1'-bis(triphenylgermyl)ferrocene, and 12 g. of hexaphenyldigermane (53% based on triphenylbromogermane). The first two and the last germanium compounds were identified by m.p., mixed m.p. and infrared spectra. Triphenylgermylferrocene, orange crystals, m.p. 155-156°, showed characteristic bands at 1112 and 1005 cm^{-1} (monosubstituted ferrocene[12]) and at 1080 cm^{-1} (Ge-phenyl linkages[13]).

Anal. Calcd. for $C_{28}H_{24}GeFe$: C, 68.77; H, 4.95; Ge, 14.85; Fe, 11.43.

Found: C, 68.99; H, 5.09; Ge, 14.47; Fe, 11.62.

1,1'-Bis(triphenylgermyl)ferrocene, orange crystals, m.p. 244-245°, had a strong band at 1080 cm^{-1}, but lacked bands at 1112 and 1005 cm^{-1}.

Anal. Calcd. for $C_{46}H_{38}Ge_2Fe$: C, 69.76; H, 4.84; Ge, 18.34; Fe, 7.06.

Found: C, 69.56; H, 4.88; Ge, 17.91; Fe, 7.27.

Another experiment was carried out with 0.06 mole of commercial n-amylsodium (Orgmet), 0.03 mole of ferrocene and 0.06 mole of triphenylbromogermane. Produced were triphenylgermylferrocene in 11% conversion (26% yield), 1,1'-bis(tri-

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(12) M. Rosenblum and R. B. Woodward, J. Am. Chem. Soc., 80, 5443 (1958).

(13) M. C. Henry and J. G. Noltes, J. Am. Chem. Soc., 82, 555 (1960).

phenylgermyl)ferrocene in 13% conversion (30% yield), and hexaphenyldigermane in 77% yield.

(b) With Trimethylchlorosilane. - To 1,1'-ferrocenylenedisodium prepared as described above from 5.2 g. (0.028 mole) of ferrocene was added all at once an excess of trimethylchlorosilane (ca. 7 g.). After having been stirred overnight at room temperature, the mixture was hydrolyzed. The aqueous phase was washed with petroleum ether and the combined organic phase and petroleum ether washings dried over magnesium sulfate. The solvent was removed by careful distillation until the volume of the solution had been reduced to ca. 8 ml. After cooling, the supernatant solution was removed from crystals of unreacted ferrocene with a dropper, and the residual crystals were washed with a few small portions of cold pentane, the washings being added to the solution. The crude ferrocene remaining was sublimed carefully to give 2.28 g. of slightly impure material, m.p. 169-175°. A small amount of oily material remaining in the sublimer bottom was combined with the liquid phase, which then was concentrated under reduced pressure. The residue was diluted to 10 ml. in a volumetric flask with benzene, and 0.15 ml. portions were used for gas chromatographic analysis (Dow Corning 710 Silicone Fluid on firebrick). Approximate and very likely low yields were determined by collection of ferrocene, trimethylsilylferrocene and 1,1'-bis(trimethylsilyl)ferrocene in this order. In terms of 10 ml. of solution, the following yields were obtained: ferrocene 0.43 g.; trimethylsilylferrocene, 0.72 g. (10%); bis(trimethylsilyl)ferrocene, 2.08 g. (23%). Total ferrocene yield was 2.71 g. (52% recovery). The silylferrocenes, both known compounds[8], were identified by their infrared spectra and analyses. Trimethylsilylferrocene, red oil, absorption at 1250, 840 and 756 cm^{-1} (trimethylsilyl group), at 1112 and 1005 cm^{-1} (monosubstituted ferrocene).

Anal. Calcd. for $C_{13}H_{18}SiFe$: C, 60.46; H, 7.03. Found: C, 60.37; H, 7.28.

1,1'-Bis(trimethylsilyl)ferrocene, red oil, absorption characteristic for the trimethylsilyl group, no absorption near 1112 and 1005 cm^{-1} (1,1'-disubstituted ferrocene[12]).

Anal. Calcd. for $C_{16}H_{26}Si_2Fe$: C, 58.16; H, 7.93. Found: C, 58.37; H, 8.12.

(c) Carbonation. - To check our procedure for 1,1'-ferrocenylenedisodium, and to set a limit on the yields one might expect in reactions involving this reagent, the disodio derivative prepared from 4.0 g. of ferrocene by this procedure was carbonated. The carboxylic acids were isolated using previously described procedures[4,6] ; 3.22 g. (54.5% conversion) of the 1,1'-ferrocenedicarboxylic acid and 0.25 g. (5% conversion) of ferrocenecarboxylic acid were obtained. In addition, 38.5% of the ferrocene was recovered; thus 97.5% of the original ferrocene is accounted for.

Reactions of the 1,1'-Ferrocenylene di-Grignard Reagent. (1) Carbonation. - 1,1'-Ferrocenylenedisodium was prepared from 0.028 mole of ferrocene as before. The pentane was removed in a stream of dry argon and the residue covered with 250 ml. of ether. To this mixture was added a solution of anhydrous magnesium bromide prepared from 10.8 g. (0.057 mole) of 1,2-dibromoethane and 1.37 g. (0.057 g. atom) of magnesium. Within a few minutes the red color of the disodioferrocene was replaced by the yellow color of the di-Grignard reagent. Stirring was continued for one hr. Powdered solid carbon dioxide was added to the mixture. After the excess carbon dioxide had evaporated, the usual workup procedure[4,6] resulted in 1.72 g. of crude ferrocenecarboxylic acids and 2.53 g. of recovered ferrocene. Extraction of the crude acid with benzene gave ca. 70 mg. of the monocarboxylic acid. The products were identified by m.p., mixed m.p. and their infrared spectra. A yield of ca. 30% of the dicarboxylic acid was obtained.

(b) *With Triphenylbromogermane*. - To a solution of the di-Grignard reagent prepared as above from 0.028 mole of ferrocene was added 22 g. (0.057 mole) of triphenylbromogermane. The mixture was stirred overnight, hydrolyzed with 150 ml. water and evaporated. Unreacted ferrocene was removed from the residue by steam distillation, giving after sublimation 2.56 g. (49%) of impure ferrocene, m.p. 170-176°. The residue from this procedure was extracted with 600 ml. chloroform; the extracts were dried and evaporated, leaving a dark brown residue. This was taken up in pentane (four 50 ml. portions). The oily residue obtained on removing the pentane was chromatographed on alumina using hexane:benzene (9:1). Isolated were: ferrocene, 0.76 g.; tetraphenylgermane, m.p. 228-231°, 0.2 g.,; triphenylgermylferrocene, m.p. 150-154°, 0.66 g.; 1,1'-bis(triphenylgermyl)ferrocene, m.p. 231-236°, 0.42 g. The residue from the pentane extraction consisted of 15.74 g. of dark brown solid. A 3 g. portion of this was crystallized from toluene to give 2.12 g. of hexaphenyldigermoxane, m.p. 184-186°. The mother liquor was evaporated to dryness and the residue purified by chromatography to give 0.71 g. of triphenylgermylferrocene, m.p. 150-153°. The total yield of the monosubstituted compound thus was 4.38 g. (32%).

(c) *With Trimethylchlorosilane*. - Ferrocene (0.028 mole) was converted to the di-Grignard reagent and treated with 7 g. of trimethylchlorosilane. The procedure used before gave 0.36 g. of trimethylsilylferrocene (5% yield; *via* preparative gas chromatography) and only a trace of bis(trimethylsilyl)ferrocene. Refluxing the reaction mixture overnight did not improve the yield.

Preparation of Ferrocenyllithium. (a) *via Ethyllithium.* - A Schlenk tube containing 1.77 g. (4.2 mmole) of chloromercuriferrocene (prepared according to the method given in ref. 7 as modified by Helling[14]) was evacuated and filled with argon. Ether (9 ml.) and ethyllithium (9.3 mmole, 9.2 ml. of 1.01M solution) in ether were added in succession at 27°. The mixture was stirred for 45 min., cooled to 0° and poured onto ethereal Dry Ice. The mixture was hydrolyzed with water. Acidification of the aqueous layer with 3N hydrochloric acid gave ferrocenecarboxylic acid (0.62 g., 64%) as an orange precipitate. After recrystallization from ether-petroleum ether, it melted at 199-203° (dec.); lit.[7] m.p. 192-205°. The ether layer was dried and treated with 2.3 g. (8.4 mmole) of mercuric chloride in ether. Ethylmercuric chloride crystallized and was filtered. After recrystallization from aqueous methanol and sublimation, 1.34 g. of pure material, m.p. 192-193°, was isolated; lit.[15] m.p. 192-193°. Concentration of the mother liquor gave an additional 0.76 g. of crude ethylmercuric chloride; total yield: 2.0 g. (90%). In another experiment on the same scale the reaction mixture was hydrolyzed and the ether layer treated with mercuric chloride (5 mmoles). Two g. (90%) of ethylmercuric chloride, m.p. 186-189°, and 0.19 g. of less pure material was isolated.

(b) *via n-Butyllithium.* - Similar procedures were used in the reaction of 4.4

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(14) J. F. Helling, Ph.D. Thesis, The Ohio State University, 1960.

(15) C. S. Marvel, C. G. Ganerke and E. L. Hill, *J. Am. Chem. Soc.*, *47*, 3009 (1925).

mmoles of chloromercuriferrocene with 9.7 mmoles of n-butyllithium in ether and of 2.7 mmoles of diferrocenylmercury[7] with 6 mmoles of n-butyllithium. Ferrocenemonocarboxylic acid was isolated in yields of 50% and 43% respectively, in addition to ferrocene in 25% and 19% yield.

(c) <u>via Phenyllithium</u>. - Chloromercuriferrocene, 3.37 g. (8 mmoles), in 10 ml. ether was treated with 19 mmoles of 0.41M phenyllithium solution at 0°. The reaction mixture was stirred at room temperature for 90 min., cooled to 0° and poured over crushed Dry Ice in ether. After hydrolysis, a tan precipitate (0.08 g.) was filtered off. The aqueous layer was acidified with 3N HCl to give a yellow-white precipitate. Vacuum sublimation of the latter resulted in 0.8 g. of benzoic acid and left as a residue 1.08 g. (58%) of ferrocenecarboxylic acid. Concentration of the aqueous layer followed by ether extraction gave more benzoic acid, m.p. 120-122°, a total yield of 0.97 g. (42% based on phenyllithium). The original ether solution was dried and evaporated. Vacuum sublimation of the residue produced diphenylmercury (1.81 g., 63%), m.p. 124-125°, mixed m.p. undepressed. The sublimation residue was a red-orange oil which appeared to decompose slowly at elevated temperature.

<u>Reactions of Ferrocenyllithium</u>. - (a) <u>With Triphenyl- and Trimethylchlorosilane</u>.- Ferrocenyllithium was prepared from 4.2 mmoles of chloromercuriferrocene and 10.4 mmoles of ethereal ethyllithium. Solid triphenylchlorosilane (Dow Corning Corp.), 3.42 g. (11.6 mmoles), was added after 1 hr. The mixture was stirred overnight and the solution then filtered through alumina and evaporated. The residue was taken up in hot heptane. Elution chromatography on alumina using petroleum ether as eluant gave 0.06 g. of ferrocene (8%) and 1.23 g. (65%) of triphenylsilylferrocene, m.p. 144-145° (from heptane); lit.[6] m.p. 142-143°. Elution with benzene

gave additional 0.17 g. of unidentified orange solid, melting range 91-140°. Similar experiments in which trimethylchlorosilane was used produced trimethylsilylferrocene in yields of 50-54%; since these were determined by gas chromatography as described above, they very likely are lower than the actual yields. No trace of 1,1'-bis(trimethylsilyl)ferrocene was observed in the gas chromatogram. Ferrocene was obtained in 12-20% yield in these reactions.

(b) With Benzophenone. - Ferrocenyllithium solution (from 4.2 mmoles of chloromercuriferrocene) was treated with 4.6 mmoles of benzophenone at 0°. The mixture was stirred overnight at room temperature. Water and 10 ml. of benzene were added; the solution was filtered, and the organic layer dried, concentrated and chromatographed on alumina. Elution with petroleum ether removed ferrocene (0.03 g., 4%), with benzene, ferrocenyldiphenylcarbinol (1.0 g., 65%), m.p. 133-136°; lit.[1] m.p. 130-131°. Continued elution with 1:1 benzene-ether gave a red-orange oil (0.35 g.), which was crystallized from hexane. Further recrystallization from heptane gave m.p. 165-169°. The infrared spectrum suggested the presence of a 1,1'-disubstituted ferrocene, possibly impure 1,1'-bis(diphenylhydroxymethyl)ferrocene (lit.[16] m.p. 179-181°).

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(16) R. Riemschneider and D. Helm, Chem. Ber., 89, 155 (1956).

Preparation of 1,1'-Ferrocenylenedilithium. - To 2.76 (4.2 mmoles) of 1,1'-bis-(chloromercuri)ferrocene[7,14] in 9 ml. ether was added 18.1 mmole of 0.99M ethyllithium solution. The reaction mixture was stirred at room temperature for 1 hr. and then was carbonated. Water was added, and the mixture was filtered. The aqueous layer was acidified with 3N HCl to give a brown precipitate of 1,1'-

ferrocenedicarboxylic acid (0.51 g., 44%), no m.p. below 250°; lit.[7] no m.p. below 250°. Attempts to obtain further products from the colored aqueous mother liquor resulted in decomposition. The original ether layer was treated with 3.4 g. of mercuric chloride. A white precipitate of ethylmercuric chloride (3.91 g., 88%), m.p. 184-187°, was isolated. Sublimation raised the m.p. to 190-192°.

Characterization of the lithium reagent solution with trimethylchlorosilane gave 1,1'-bis(trimethylsilyl)ferrocene in 36% yield and trimethylsilylferrocene in 8% yield.

Preparation of 1,1'-Bis(triphenylgermyl)ferrocene via Cyclopentadienyltriphenylgermane. - Cyclopentadienylsodium was prepared in tetrahydrofuran from 3.45 g. (0.15 g. atom) of sodium and 13.2 g. of freshly distilled cyclopentadiene. To this solution was added 57.5 g. (0.15 mole) of triphenylbromogermane. The resulting mixture was stirred for several hr. at room temperature, filtered and evaporated. The residue was extracted with ca. 800 ml. of hot heptane. Evaporation of the heptane left 47 g. of air and/or moisture sensitive solid. No attempt was made to purify the crude product. To 7.4 g. of this material in 150 ml. ether was added ca. 0.03 mole of n-butyllithium in ether. The mixture was heated at reflux for 1 hr. and then added to a suspension of ferrous chloride (prepared from 0.2 g. of iron powder and 1.1 g. of ferric chloride) in tetrahydrofuran. The reaction mixture was refluxed overnight, hydrolyzed and evaporated. The residue was taken up in benzene, filtered through alumina to remove tars and chromatographed on alumina to give 2.6 g. of 1,1'-bis(triphenylgermyl)ferrocene, identical in all respects with the material from the disodioferrocene reaction.

Preparation of 1,1'-Bis(triphenylgermyl)titanocene Dichloride. - Crude cyclopentadienyltriphenylgermane (7.4 g., 0.02 mole) was metalated with ca. 0.025 mole of ethereal n-butyllithium. The resulting solution was added to a solution of 1.85 g. (0.01 mole) of titanium tetrachloride in 20 ml. ether (prepared at -60°). After 3 hr. at room temperature, the solvent was removed at reduced pressure and the residue extracted with benzene. A small amount of red-violet crystals was obtained on careful concentration of the benzene solution. Recrystallization from benzene gave ca. 30 mg. of pure product, which on heating began to decompose at 244°.

Anal. Calcd. for $C_{46}H_{38}Cl_2Ge_2Ti$: C, 64.63; H, 4.48. Found: C, 64.86; H, 4.72. The presence of Ge-phenyl links was shown by strong absorption in the infrared spectrum at 1080 cm^{-1}.

In addition, 3.2 g. of a noncrystallizable red-brown oil was obtained. Attempted purification of the latter by elution chromatography failed.

Preparation of Triphenylgermylmanganese Pentacarbonyl. - Sodium pentacarbonylmanganate (-1) was prepared from 1.95 g. of manganese pentacarbonyl and 200 g. of 1.5% sodium amalgam in 130 ml. of air-free tetrahydrofuran[16] under nitrogen and subsequently added to 3.8 g. (10 mmoles) of triphenylbromogermane in 100 ml. tetrahydrofuran. A colorless precipitate and a red-orange solution were formed. The mixture was stirred at room temperature for several hr., filtered and evaporated in vacuum. The light yellow, crystalline residue was taken up in ca. 80 ml. of anhydrous acetone. Addition of water to the point of turbidity and chilling to 0° overnight led to formation of white crystals. These were washed with

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(16) W. Hieber and G. Wagner, Z. Naturforschg., 13b, 339 (1958).

chilled acetone and dried in vacuum to give 1.8 g. (40%) of $(C_6H_5)_3GeMn(CO)_5$, m.p. 162-164°.

<u>Anal</u>. Calcd. for $C_{23}H_{15}O_5GeMn$: C, 55.37; H, 3.03. Found: C, 55.42; H, 3.23. The product appeared to be air-stable in the solid state, but decomposed in solution. Its infrared spectrum in the carbonyl region (KBr disk) showed a sharp band at 2100 cm^{-1} and very broad, strong absorption centered at 1995 cm^{-1}. A similarity to the published spectra of methyl- and benzylmanganese pentacarbonyls[17] is apparent.

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(17) W. Beck, W. Hieber and H. Tengler, <u>Chem. Ber</u>., <u>94</u>, 862 (1961).

<u>Preparation of Triphenylgermyl-π-cyclopentadienyliron Dicarbonyl</u>. - A solution of 3.0 g. (0.0085 mole) of $[C_5H_5Fe(CO)_2]_2$ in 250 ml. tetrahydrofuran was stirred overnight with 6 g. of 4% sodium amalgam.[18] The solution of $C_5H_5Fe(CO)_2Na$ was decanted from the excess of amalgam and filtered into a second flask. To this solution was added slowly with stirring 4.65 g. (0.012 mole) of triphenylbromogermane in 40 ml. tetrahydrofuran. The mixture was refluxed 1 hr., filtered and evaporated at reduced pressure. The residue was extracted with ether and the solvent removed from the filtered extracts to leave a slightly oily yellow crystalline residue. The latter was washed several times with small amounts of pentane, and the product then was treated in a sublimer at 125°/0.2 mm. to remove a small amount of red oily material. This procedure left 4.61 g. (79%) of crude $(C_6H_5)_3GeFe(CO)_2C_5H_5$, m.p. 159-162°, which was chromatographed on alumina, and then sublimed at 135°/0.001 mm. to give pure, pale yellow material, m.p. 160-

161°.

Anal. Calcd. for $C_{25}H_{20}O_2GeFe$: C, 62.44; H, 4.19; Fe, 11.61.

Found: C, 62.47; H, 4.39; Fe, 11.31

The compound appears to be stable to air and moisture in the solid state. This is in marked contrast to the instability toward atmospheric oxygen of $(CH_3)_3SiFe(CO)_2C_5H_5$[19]. The germanium compound showed two strong bands in the carbonyl region of the infrared spectrum (KBr disc) at 1995 and 1940 cm^{-1}. Similar absorptions were observed at 2000 and 1940 cm^{-1} in the silicon derivative.[19]

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(18) T. S. Piper and G. Wilkinson, J. Inorg. Nuclear Chem., 3, 104 (1956).

(19) T. S. Piper, D. Lemal and G. Wilkinson, Naturwissenschaften, 43, 129 (1956).

This inclosed report is sent to you at the request of Wright Air Development Center, Air Research and Development Command, United States Air Force.

Any comment or correspondence concerning the material contained in this report should be directed to:

Commander
Wright Air Development Center
Attn: WCLTR-2
Wright-Patterson Air Force Base, Ohio

Dietmar Seyferth

Dietmar Seyferth

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