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Reactivity of Halogermylenes with Various Transition-Metal Complexes. The First Germylenes with Germanium–Transition-Metal Bonds

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Halogermylenes react readily with some metal carbonyl dimers (M = Fe, Co, Mn) to give the corresponding insertion adducts that have been isolated. In contrast, similar insertions into M^{4B}–transition-metal bonds usually lead to unstable adducts that decompose by an α-elimination process to give the first germylenes with germanium–transition-metal bonds. These new divalent germanium species give specific germylenes reactions. Cycloaddition with 2,3-dimethylbutadiene leads to germacyclopentenes and shows an unusual thermal reversibility. Insertion into the cobalt–cobalt bond of $Co_2(CO)_8$ gives a polymetalated compound.

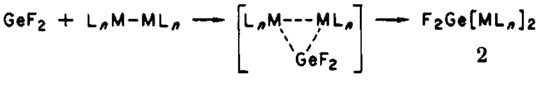
Introduction

Insertion reactions of divalent 4B metal (M^{4B}) species into transition-metal–transition-metal bonds provide an easy route to various polymetalated compounds of the $X_2M^{4B}[ML_m]_2$ type (M = transition metal).[1-3] In the germanium series, because of its high electrophilic reactivity, difluorogermylene, GeF_2, gives numerous insertion reactions and, in particular, inserts into M^{4B}–M^{4B} bonds.[2,4]

Depending on the halogen, the different dihalogermylenes show different reactivity toward transition-metal–transition-metal bonds such as Fe–Fe, Co–Co, and Mn–Mn.[1,3,5] In order to determine the reactivity of difluorogermylene within the series, we have studied its reactions with transition-metal complexes that contain symmetrical or unsymmetrical transition-metal–transition-metal bonds or 4B metal (M^{4B})-transition-metal bonds.

Results and Discussion

Insertion Reactions into Transition-Metal–Transition-Metal Bond. (i) Reaction with Symmetrical Complexes. Various polymetalated compounds have been obtained by insertion reactions of pure difluorogermylene or of its complexes $GeF_2{\cdot}OR_2$ (R_2O = ether, THF, dioxane) into metal–metal bonds of transition-metal complexes as shown in eq 1. The products 2 thus synthesized are shown in Table I.



$$GeF_2 + L_nM{-}ML_n \longrightarrow \left[L_nM{-}{-}{-}ML_n \,(\text{bridged by } GeF_2)\right] \longrightarrow F_2Ge[ML_n]_2 \quad (1)$$

1 2

M = Fe, Co, Mn

Table I. Adducts 2 from the Insertion of GeF_2 into Metal Carbonyl Dimers

products	no.	yield, %
$[F_2Ge[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$[6]	**2a]**	47
$F_2Ge[Co(CO)_4]_2$	**2b**	18
$F_2Ge[Co(CO)_3PPh_3]_2$	**2c**	45
$F_2Ge[Co(CO)_3P(OPh)_3]_2$	**2d**	32
$F_2Ge[Mn(CO)_5]_2$	**2e**	8

In the case of octacarbonyldicobalt the reaction appears more complicated than with the others. Although **2b** could be isolated by sublimation, the reaction proceeds with strong evolution of carbon monoxide to give only a low yield of this product. Difluorogermylene insertion into the Mn–Mn bond of $Mn_2(CO)_{10}$ also is difficult and was observed only after 48 h at 130 °C. No insertion derivative corresponding to the reaction of GeF_2 and $[(\eta\text{-}C_5H_5)(CO)_3Mo]_2$ was isolated or characterized.

Curtis et al.[5] failed to obtain insertion derivatives of dibromogermylene either into the Co–Co bond of $Co_2(CO)_8$ or into the Mn–Mn bond of $Mn_2(CO)_{10}$. These results show that in these reactions difluorogermylene appears to have the greatest reactivity within the halogermylene series, and they also seem to confirm the observation of Patmore et al.[7] that the presence of a bridged carbonyl ligand in the metal–metal bonded complex enhances the facility of insertion reactions of 4B metal (M^{4B}) divalent species into such metal–metal bonds.

In these insertion reactions, direct electrophilic attack of difluorogermylene on a transition-metal–transition-metal bond probably occurs through the formation of a bridged intermediate, 1 (eq 1), on the route to the observed adducts. However, $Co_2(CO)_8$ has more labile carbonyl ligands, and in its reaction with the nucleophilic germanium center of the $F_2Ge{\cdot}THF$ complex, displacement of carbonyl ligands takes place and the reaction leads, after $[(CO)_3(F_2Ge)Co]_2$ decomposition, to the stable cluster $Co_4(CO)_{12}$.

The less reactive organohalogermylenes also give insertion derivatives in thermally induced reactions. However, under these conditions, a secondary reaction, redistribution of ligands on germanium, was observed that was probably caused by the instability of the initial adduct.

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(1) Satgé, J.; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1.

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(3) Mackay, K. M.; Nicholson, B. K. In "Comprehensive Organometallic Chemistry"; Pergamon Press: Elmsford, NY, 1982; Vol. 6, part 43.

(4) Castel, A.; Escudié, J.; Rivière, P.; Satgé, J.; Bochkarev, M. N.; Maiorova, L. P.; Razuvaev, G. A. *J. Organomet. Chem.* **1981**, *210*, 37.

(5) Scibelli, J. V.; Curtis, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 399 and references therein.

(6) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Denisov, F. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 142.

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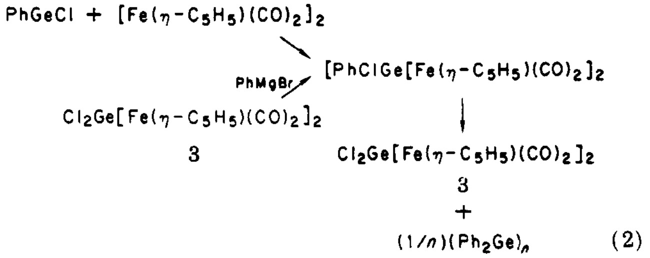
Thus, monophenylation of stable $Cl_2Ge[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$,[8] leads to a similar symmetrization reaction.

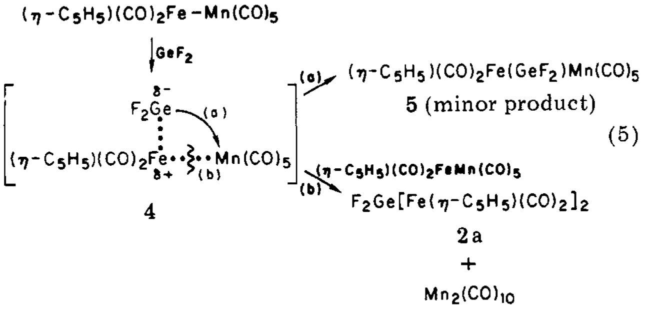


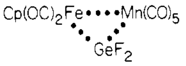
(ii) Reaction with Unsymmetrical Complexes. To date, insertion reactions of germylenes into unsymmetrical transition-metal–transition-metal bonds have not been reported. Difluorogermylene, however, reacts with such complexes to give only symmetrical derivatives as described above (eq 1).

$$GeF_2 + 2(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}Mn(CO)_5 \rightarrow F_2Ge[Fe(\eta\text{-}C_5H_5)(CO)_2]_2 + Mn_2(CO)_{10} \quad (3)$$

$$GeF_2 + 2(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}MoCp(CO)_3 \rightarrow F_2Ge[Fe(\eta\text{-}C_5H_5)(CO)_2]_2 + \text{viscous polymers} \quad (4)$$

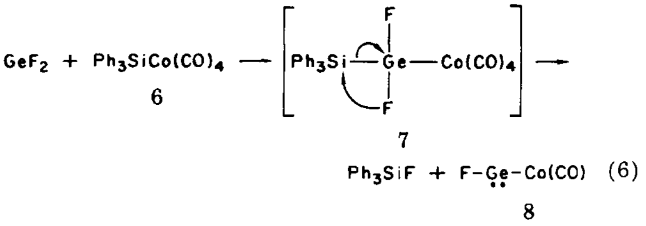
Since some unsymmetrical complexes with germanium–transition-metal bonded complexes do exist,[9,10] we think that the redistribution reaction observed is probably due to the favored decomposition of reaction intermediate 4, formed by the initial attack of the germylene on the transition-metal–transition-metal bond (eq 5). In eq 5, reaction a, the interaction between germanium and manganese in 4 would lead, through a bridged intermediate





to the unsymmetrical adduct 5 that has been detected in the reaction mixture by means of mass spectrometry. However, the breaking of the unsymmetrical Fe···Mn bond in 4 (eq 5, reaction b) would lead to the observed symmetrization.

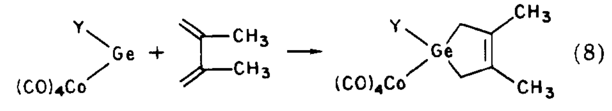
Insertion into M^{4B}–Transition-Metal Bond. Extension of this study to insertion reactions of germylenes into the M^{4B}–transition-metal bonds has been undertaken. We have studied the insertion of difluorogermylene into the silicon–cobalt bond of $Ph_3SiCo(CO)_4$, 6,[11] which leads to a polymetalated derivative, 7, of low stability. The rapid decomposition of 7, via α-elimination, gave the first halogermylene with a germanium–transition-metal bond. Such α-elimination reactions in polymetalated derivatives of group 4B elements that have silicon–germanium–halogen or germanium–germanium–halogen chains have been studied already and are one of the main preparative entries to various divalent species of germanium.[1,2]



When an excess of $Ph_3SiCo(CO)_4$ (6) was used, successive insertion and α-elimination reactions gave novel germylenes with two germanium–transition-metal bonds (eq 7).

$$\underset{6}{GeF_2 + 2Ph_3SiCo(CO)_4} \rightarrow 2Ph_3SiF + \underset{9}{[(CO)_4Co]_2Ge:} \quad (7)$$

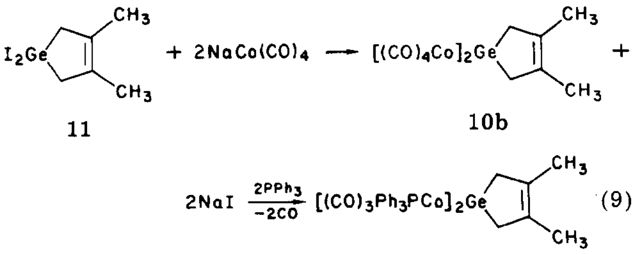
These hitherto unknown germylenes presently are being investigated. For example, some characteristic reactions of divalent species of germanium have already been observed: cycloadducts with 2,3-dimethylbutadiene have been isolated (eq 8).

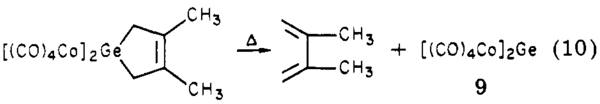


8, 9

10a, Y = F
b, Y = $(CO)_4Co$

The germacyclopentenes thus formed in these reactions also can be synthesized, using substitution reactions, from 3,4-dimethyl-1,1-diodogermacyclopent-3-ene. Crystalline products were obtained by substitution of a carbonyl ligand by triphenylphosphine (eq 9). We have noted that such metal carbonyl accumulation on germanium lowers the stability of the Ge heterocycle. Such substituted germacyclopentenes decompose readily when heated with evolution of the diene to give the original germylene (eq 10).





10b

Thus the reactions shown in eq 9 and 10 could provide a general route to germylenes with germanium–transition-metal bonds starting from dihalogermacyclopentenes and transition-metal anions. Such a thermal decomposition process has not yet been described within the germacyclopentenes series. This is very unusual since numerous and various substituted germacyclopentenes (alkyl, aryl, halogen, etc.) have been isolated.[1] However, in the case of 1,1-dichloro-1-germacyclopent-3-ene, an exchange reaction of the diene component with an external diene or triene has been reported by Nefedov.[12]

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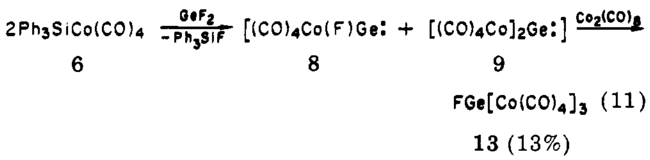
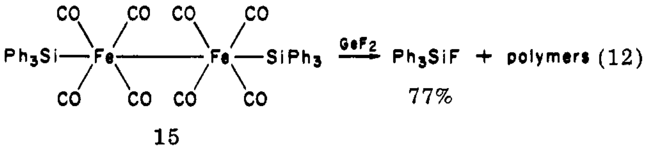
Such a germylene with a germanium–transition-metal bond has also been characterized in the insertion reaction into octacarbonyldicobalt (eq 11).



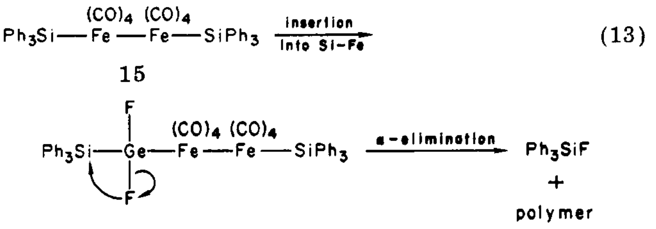
$$\underset{\mathbf{6}}{2Ph_3SiCo(CO)_4} \xrightarrow[-Ph_3SiF]{GeF_2} [\underset{\mathbf{8}}{(CO)_4Co(F)Ge\colon} + \underset{\mathbf{9}}{[(CO)_4Co]_2Ge\colon}] \xrightarrow{Co_2(CO)_8} \underset{\mathbf{13}\ (13\%)}{FGe[Co(CO)_4]_3} \quad (11)$$

In this case only the insertion product formed from the unsymmetrical germylene **8** has been isolated even when the reaction was carried out by using an excess of **6** (eq 11). The adduct corresponding to the symmetrical germylene **9** has not been detected.

The M^{4B}–Fe bond is less reactive compared to the other M^{4B}–transition-metal bonds studied above. No reaction was observed between difluorogermylene and $Ph_3SiFe(\eta\text{-}C_5H_5)(CO)_2$, **14**.[13] However, difluorogermylene reacted on gentle heating with $[Ph_3SiFe(CO)_4]_2$, **15**,[14] and leads to formation of triphenylfluorosilane and polymers that are insoluble in the usual solvents (eq 12).



This last reaction (eq 12) may be explained in terms of an initial insertion of GeF_2 into the Si–Fe bond followed by α-elimination as described above (eq 6).



A stereochemical probe of the mechanism of these insertion reactions of germylenes into transition-metal–transition-metal bonds has been attempted, using an optically active silylcobalt complex, **16**,[15,16] which is stable under the experimental conditions used. However, an optically pure sample of the fluorosilane (*S*)-(+)-1-NpPhMeSiF[17] ($[\alpha]_D$ +47°) was shown to undergo partial racemization under the experimental conditions used for the difluorogermylene insertion reaction. This, of course, makes a stereochemical interpretation of these reactions impossible at this time.

$$\underset{\mathbf{16}}{(S)\text{-}(+)\text{-}1\text{-}NpPhMeSi\text{–}Co(CO)_4} + GeF_2 \rightarrow FGeCo(CO)_4 + \underset{\mathbf{17}}{(\pm)\text{-}1\text{-}NpPhMeSiF} \quad (14)$$

These insertion reactions of germylenes into transition-metal–transition-metal and 4B metal (M^{4B})–transition-metal bonds are of great interest. First, in that they lead to previously unknown unsymmetrical and symmetrical germylenes with germanium–transition-metal bonds; second, in their formation of polymetallic compounds. The chemistry of these new species of group 4B–transition-metal compounds is under investigation.

Experimental Section

General Comments. All reactions were carried out in a standard high vacuum system. Proton NMR spectra were recorded with an EM 360A Varian spectrometer, and fluorine NMR spectra with an EM 390 Varian spectrometer. Mass spectra were obtained by using a JEOL JMS D100 mass spectrometer. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using Nujol. Elemental analyses were carried out by the "Service Central de Microanalyse du CNRS" (France). Melting points were determined with a Reichert Microscope.

Difluorobis[(η-cyclopentadienyl)dicarbonyliron]germanium, 2a. A mixture of (0.45 g, 4.1 mmol) of germanium difluoride[18] and 1.45 g (4.1 mmol) of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ was heated in refluxing tetrahydrofuran (20 mL) for 15 h. The solution was filtered while hot and allowed to cool. Subsequent filtration and recrystallization from THF gave 0.89 g (47%) of yellow product, **2a**: mp 196–198 °C dec as in ref 6; IR ν(CO) 2015 (w), 2005 (s), 1950 (vs) cm^{-1}; mass spectrum, *m/z* 466 (M^+). Other significant fragment ions were $[F_2GeFe_2Cp_2(CO)_3]^+$ (*m/z* 438), $[F_2GeFeCp_2(CO)_2]^+$ (*m/z* 410), and $[Fe_2Cp_2(CO)_2]^+$ (*m/z* 298). Anal. Calcd for $C_{14}H_{10}F_2O_4Fe_2Ge$: C, 36.20; H, 2.15; F, 8.18. Found: C, 36.37; H, 2.20; F, 8.25.

Difluorobis(tetracarbonylcobalt)germanium, 2b. $Co_2(CO)_8$ (1.07 g, 3.1 mmol) was added to a diethyl ether (20 mL) suspension of 0.34 g (3.1 mmol) of difluorogermylene. Evolution of CO was observed. After 12 h at 20 °C, the mixture was filtered, reduced in volume to 5 mL, and then allowed to cool. The solvent was removed, and the black residue was sublimed at 40–60 °C (10^{-3} mmHg), giving 0.25 g (18%) of yellow crystals, **2b**: IR ν(CO) 2100 (s), 2060 (m), 2045 (s), 2025 (m) cm^{-1}; mass spectrum, *m/z* 454 (M^+). Ions corresponding to successive loss of eight carbonyl groups also were observed. Anal. Calcd for $C_8F_2O_8Co_2Ge$: C, 21.21; F, 8.39. Found: C, 20.71; F, 8.45. Black crystals of $Co_4(CO)_{12}$ (0.11 g, 7%) also were obtained.

Difluorobis[(triphenylphosphine)tricarbonylcobalt]germanium, 2c. Difluorogermylene (0.22 g, 2.0 mmol) and 1.60 g (2.0 mmol) of $[Ph_3P(CO)_3Co]_2$ were heated in refluxing THF (20 mL) for 60 h. The mixture was filtered while hot, and the filtered extract was evaporated under vacuum. The recrystallization of the residue from toluene gave 0.83 g (45%) of orange-yellow crystals, **2c**: mp 205–208 °C dec; IR ν(CO) 2045 (w), 2020 (w), 1980 (vs) cm^{-1}; ^{19}F NMR (CH_2Cl_2) δ_F 60.00 (t, ^3J(PF) = 16.7 Hz) (internal reference $CFCl_3$). Anal. Calcd for $C_{42}H_{30}F_2O_6P_2Co_2Ge$: C, 54.77; H, 3.28. Found: C, 55.28; H, 3.59.

Difluorobis[(triphenyl phosphite)tricarbonylcobalt]germanium, 2d. Difluorogermylene (0.15 g, 1.4 mmol) and 0.90 g (1.36 mmol) of $[(PhO)_3P(CO)_3Co]_2$ were heated in refluxing dioxane (10 mL) for 12 h. The solvent was evaporated under vacuum, and the residue was extracted with 10 mL of toluene. The extracts were reduced to 2 mL and allowed to cool. The yellow-orange crystals thus obtained were recrystallized twice from toluene to give 0.32 g (32%) of **2d**: mp 155 °C dec; IR ν(CO) 2015 (s), 1985 (vs) cm^{-1}. Anal. Calcd for $C_{42}H_{30}F_2P_2O_{12}Co_2Ge$: C, 39.05; H, 2.03; F, 5.15. Found: C, 40.12; H, 2.25; F, 4.90.

Difluorobis(pentacarbonylmanganese)germanium, 2e. $Mn_2(CO)_{10}$ (1.41 g, 3.6 mmol) was added to a xylene suspension (20 mL) of 0.40 g (3.6 mmol) of difluorogermylene, and the mixture was heated at reflux for 48 h. The mixture then was filtered while hot and the filtrate concentrated under vacuum. Subsequent filtration and recrystallization from petroleum ether and THF gave 0.15 g of yellow powder, **2e**: mp 166 °C; IR ν(CO) 2118 (s), 2037 (vs), 2025 (s) cm^{-1}; mass spectrum, *m/z* 502 (M^+). Other significant fragment ions were $[(CO)_5MnGeF_2Mn]^+$ (*m/z* 362), $[(CO)_5MnGeF_2]^+$ (*m/z* 307), and $[MnGeF_2Mn]^+$ (*m/z* 222). Anal. Calcd for $C_{10}F_2O_{10}GeMn_2$: C, 23.99; F, 7.59; Mn, 21.95. Found: C, 23.93; F, 7.65; Mn, 21.98.

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[17] Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michaël, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

[18] GeF_2 was used pure[19] and PhGeCl in benzene solution.[1]

[19] Muetterties, E. L.; Castle, J. E. *J. Inorg. Nucl. Chem.* **1961**, *18*, 148.

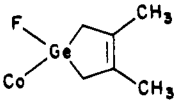
Reaction of PhGeCl with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$. A benzene solution (3 mL) of phenylchlorogermylene[18] (10 mmol) was added to 1.77 g (5 mmol) of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ in 25 mL of toluene. The mixture was refluxed for 30 h. The solvent was evaporated under vacuum and the residue recrystallized from toluene to yield 1.22 g (45%) of orange-yellow crystals of $Cl_2Ge[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$,[8] mp 194–197 °C. Anal. Calcd for $C_{14}H_{10}Cl_2O_4Fe_2Ge$: C, 33.80; H, 2.01; Cl, 14.27. Found: C, 33.67; H, 2.03; Cl, 14.00. A mixture of viscous oligomers also was obtained.

A solution of PhMgBr (0.2 mmol) in 3 mL of diethyl ether was added to 0.10 g (0.2 mmol) of **3** at −78 °C. The mixture was stirred for 30 min at −78 °C, warmed to 20 °C, and filtered in order to remove MgX_2, and the solution was allowed to cool. The yellow powder thus obtained was recrystallized from toluene (2 mL) to yield 0.04 g of the starting product **3**. However, $PhClGe[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ has not been obtained. Such results suggest a probable Ph/Cl ligand redistribution on germanium in the transient $PhClGe[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$, but attempts to isolate $Ph_2Ge[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$[6] from the residue failed in the both cases.

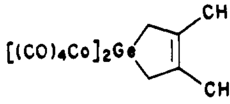
Reaction of GeF_2 with $(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}Mo(CO)_2(\eta\text{-}C_5H_5)$. $(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}Mo(CO)_3(\eta\text{-}C_5H_5)$[20] (0.61 g, 1.45 mmol) was added to 0.11 g (1.45 mmol) of difluorogermylene in 7 mL of dioxane. The mixture was stirred for 1 h and then refluxed for 20 h. After filtration, the solution was evaporated under vacuum. The residue was extracted with 10 mL of THF. The solution was evaporated and allowed to cool to yield 0.15 g (22%) of **2a**.

Reaction of GeF_2 with $(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}Mn(CO)_5$. Difluorogermylene (0.10 g, 0.9 mmol) and 0.17 g, 0.9 mmol of $(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}Mn(CO)_5$[20] were heated at reflux in dioxane (10 mL) for 12 h. The mixture was filtered and evaporated under vacuum. The solution produced yellow crystalline material (0.06 g) that was washed with 10 mL of pentane. The mass spectrum of this product showed three parent peaks corresponding to a mixture of $Mn_2(CO)_{10}$, *m/z* 390, $F_2Ge[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$, *m/z* 466, and $[(CO)_5Mn]GeF_2[Fe(CO)_2(\eta\text{-}C_5H_5)]$ (**5**), *m/z* 484. Subsequent recrystallization did not result in the isolation of **5**. Only $Mn_2(CO)_{10}$ and **2a** were separated pure in small amounts.

Characterization of the Germylenes $YGeCo(CO)_4$ (Y = F, $Co(CO)_4$). Reaction with 2,3-Dimethylbutadiene. (a) Difluorogermylene (0.33 g, 3 mmol) in 20 mL of dioxane and $Ph_3SiCo(CO)_4$[11] (1.29 g, 3 mmol) were introduced successively into a Schlenk tube. The mixture was allowed to react at room temperature for 5 min, and then an excess of 2,3-dimethylbutadiene (0.5 mL) was added. The reaction mixture was kept for 1.5 h at 60 °C and then was concentrated under vacuum. The triphenylfluorosilane formed in the reaction was precipitated from the mixture by addition of hexane and filtered. The residue obtained after evaporation of the filtrate under vacuum was analyzed by means of ^1H NMR (C_6D_6) spectroscopy, and the products were subsequently identified as **10a** and **10b**:



10a (10%)
δ 2.17 (s, 4 H, CH_2),
1.55 (s, 6 H, CH_3)

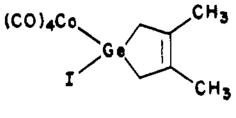


10b (5–6%)
δ 2.52 (s, 4 H, CH_2),
1.66 (s, 6 H, CH_3)

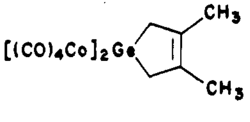
These yields have been calculated by NMR. The products have been identified by comparison with other samples prepared by a different route (see below).

(b) Using the same experimental conditions, a reaction difluorogermylene (0.33 g, 3 mmol) in 20 mL of dioxane, $Ph_3SiCo(CO)_4$ (2.50 g, 5 mmol), and an excess of 2,3-dimethylbutadiene (0.5 mL) gave, after removal of the Ph_3SiF (1.67 g, 75%), **10b**, 24% yield, identified by using NMR and a pure reference.

Synthesis of 10a. To 5.2 mmol of $NaCo(CO)_4$, prepared by reaction of octacarbonyldicobalt with Na/Hg amalgam in 50 mL of THF, was added 1,1-diodo-3,4-dimethyl-1-germacyclopent-3-ene[1] (1.00 g, 2.6 mmol). The mixture was allowed to react (15 h) at room temperature with stirring. The THF then was removed under vacuum, and hexane was added to the residue until all the NaI formed had completely precipitated. After concentration of the filtrate obtained, using a vacuum line, the isolated product analyzed by ^1H NMR (C_6D_6).



55%
δ 2.52 (s, 4 H, CH_2),
1.55 (s, 6 H, CH_3)



10b (45%)
δ 2.52 (s, 4 H, CH_2),
1.66 (s, 6 H, CH_3)

To the mixture of the above two products in approximately the same proportions was added a suspension of silver fluoride (0.15 g) in hexane. The mixture was heated 3 h at 60 °C and led after filtration and concentration of the filtrate of the mixture of **10a** (53%) and **10b** (45%) which showed the same ^1H NMR characteristics (see above). However, as before, extraction of pure compounds from the mixture failed.

Synthesis of 12. To a $NaCo(CO)_4$ (10.4 mmol) in 70 mL of THF was added **11** (1.00 g, 2.6 mmol). The mixture was allowed to react for 15 h at room temperature with stirring. It then was concentrated under vacuum, and 20 mL of hexane was added to the residue. NaI was removed by filtration. The solvent was evaporated from the filtrate to leave a yellow-brown oil that was identified by NMR as almost pure **10b** (^1H NMR see above) (about quantitative yield). The crude product was divided into two parts. Distillation of the first part was tried under 5×10^{-2} mmHg, but decomposition occurred at 60–40 °C with evolution of 2,3-dimethylbutadiene (trapped at −70 °C and identified by NMR and GLC) to produce a black polymeric residue and traces of a Ge mirror. To the second part of the solution in 20 mL of hexane was added Ph_3P (0.68 g, 2.6 mmol). The mixture was heated for 1 h at 50 °C. Concentration of the solution to 5 mL led to the precipitation of 0.2k g of Ph_3P (38%) that was separated by filtration. Further concentration of the filtrate under vacuum gave yellow crystals (0.55 g) identified as **12**: mp 58–59 °C dec; ^1H NMR (C_6D_6) δ 1.66 (s, 6 H, CH_3), 2.50 (s, 4 H, CH_2), 7.00–7.60 (m, 30 H, C_6H_5); IR ν(CO) 2030 (vs), 2100 (m), 2115 (w) cm^{-1}; mass spectrum, *m/z* 442 $[[(CO)_3Co]_2\overline{GeCH_2C(CH_3)=C(CH_3)}CH_2]^+$ 274, $[Co_2\overline{GeCH_2C(CH_3)=C(CH_3)}CH_2]^+$, 224 $[Co_2\overline{GeCH_2CH_2=CH_2}CH_2]^+$, 192 $[(Co)_2Ge]^+$, 262 $[Ph_3P]^+$. Anal. Calcd for $C_{48}H_{40}O_6P_2Co_2Ge$: C, 59.75; H, 4.15; P, 6.42. Found: C, 59.72; H, 4.28; P, 5.94.

Reaction with Octacarbonyldicobalt. To a solution of $Ph_3SiCo(CO)_4$ (1.30 g, 3 mmol) in 50 mL of ether was added the difluorogermylene (0.18 g, 1.5 mmol). The mixture was allowed to react for 3 h with stirring at room temperature. A solution of octacarbonyldicobalt (0.53 g, 1.5 mmol) in 10 mL of ether then was added. The reaction mixture was stirred for 2 h at room temperature, and the solvent then was removed under vacuum. The black residue was extracted with 40 mL of hexane. The extracts were kept for 24 h at −78 °C. A brown solid then was isolated by filtration (0.4 g), a mixture from which Ph_3SiF and traces of $Co_4(CO)_{12}$ were removed by three subsequent recrystallization in hexane. Thus $FGe[Co(CO)_4]_3$ (0.12 g, 13%) was isolated as a brown solid: mp 148–150 °C dec; IR ν(CO) 2110 (w), 2100 (w), 2080 (s), 2065 (sh), 2050 (vs), 2010 (m), 2000 (w) cm^{-1}; mass spectrum, M^+ not observed, *m/z* 578 ($M^+ - CO$), and ions corresponding to a successive loss of 11 carbonyl ligands also were observed. Anal. Calcd for $C_{12}FO_{12}Co_3Ge$: C, 23.82; F, 3.14. Found: C, 24.30; F, 3.20.

Reaction of GeF_2 with $[Ph_3Si\text{-}Fe(CO)_4]_2$. $[Ph_3Si\text{-}Fe(CO)_4]_2$[14] (0.83 g, 1 mmol) was added to a solution of 0.11 g (1 mmol) of difluorogermylene in 10 mL of dioxane. The mixture was heated at 80 °C for 12 h. The solvent was evaporated under vacuum and the residue extracted with 10 mL of hot hexane. The solution was filtered and evaporated to give 0.43 g (77%) of Ph_3SiF, mp 62 °C.

Reaction of GeF_2 with (*S*)-(+)-1-NpPhMeSiCo(CO)$_4$. By the above procedure, 0.11 g (1 mmol) of difluorogermylene was allowed to react in 10 mL of dioxane with 0.42 g (1 mmol) of (*S*)-(+)-1-NpPhMeSiCo(CO)$_4$.[15,16] Hexane extraction of residue yielded 0.17 g (65%) of racemic 1-NpPhMeSiF.[17] The optical

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stability of (*S*)-(+)-1-NpPhMeSiF under the same experimental conditions has been tested. By the above procedure, 0.11 g (1 mmol) of difluorogermylene was allowed to react in 10 mL of dioxane with 0.28 g (1 mmol) of (*S*)-(+)-1-NpPhMeSiF,[17] $[\alpha]_D$ +47°. Pentane extraction of residue yielded 0.25 g of 1-NpPhMeSiF, $[\alpha]_D$ +15.1° (in pentane, 68% racemization).

Registry No. **2a**, 86885-11-2; **2b**, 86885-12-3; **2c**, 86885-13-4; **2d**, 86885-14-5; **2e**, 21863-04-7; **3**, 12086-96-3; **5**, 86885-15-6; **6**, 14095-19-3; **10** (Y = I), 86885-18-9; **10a**, 86885-16-7; **10b**, 86885-17-8; **11**, 5764-63-6; **12**, 86885-19-0; **13**, 86885-20-3; **15**, 86885-21-4; **16**, 63976-34-1; **17**, 75247-27-7; $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, 38117-54-3; $Co_2(CO)_8$, 15226-74-1; $[Ph_3P(CO)_3Co]_2$, 24212-54-2; $[(PhO)_3P(CO)_3Co]_2$, 21118-36-5; $Mn_2(CO)_{10}$, 10170-69-1; $(\eta\text{-}C_5H_5)(CO)_2Fe\text{–}Mo(CO)_3(\eta\text{-}C_5H_5)$, 12130-13-1; $(\eta\text{-}C_5H_5)(CO)_2Fe\text{–}Mn(CO)_5$, 12088-73-2; $NaCo(CO)_4$, 14878-28-5; GeF_2, 13940-63-1; PhGeCl, 32329-21-8; PhBr, 108-86-1; Ph_3SiF, 379-50-0; (*S*)-(+)-1-NpPhMeSiF, 13132-41-7; 2,3-dimethylbutadiene, 513-81-5.

He I and He II Photoelectron Spectra of Substituted (Cycloheptatriene)tricarbonyliron Complexes $(\eta^4\text{-}exo\text{-}7\text{-}RC_7H_7)Fe(CO)_3$ (R = H, $SiMe_3$, $GeMe_3$)

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He I and He II photoelectron spectra of $(\eta^4\text{-}RC_7H_7)Fe(CO)_3$ (R = H, $SiMe_3$, $GeMe_3$) have been studied in order to identify possible electronic factors responsible for the variation in fluxional behavior in the series. Spectral evidence indicates that there is a rupture in conjugation between the free double bond and the bound butadiene moiety and a stronger Fe–diene interaction in the substituted compounds relative to the unsubstituted molecules. These effects appear to be sufficient to cause a significant lowering of the activation energy for 1,3 iron shifts in the silyl- and germyl-substituted compounds.

Introduction

The reaction of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$, an interesting and rare example of ambident organometallic nucleophile, with Me_3SiCl and Me_3GeBr yields ring-substituted complexes $[\eta^4\text{-}exo\text{-}7\text{-}(Me_3E)C_7H_7]Fe(CO)_3$ (E = Si, **2**; E = Ge, **3**).[1] The molecules exhibit surprisingly facile fluxional motion of the $Fe(CO)_3$ moiety, the activation energy for the 1,3 iron shift being some 5 kcal/mol lower than in the unsubstituted parent compound $(\eta^4\text{-}C_7H_8)Fe(CO)_3$[1,2] (**1**). An obvious question that arises is how this behavior relates to some relevant modification in the electronic structure of the complexes upon C_7 ring substitution by the EMe_3 moieties?

To answer this question we have embarked on an investigation of both parent and ring-substituted complexes using gas-phase UV photoelectron spectroscopy (PE). The He I spectrum of $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ complex has been reported already.[3] This paper, however, includes both He I and He II spectra. The comparison of He I vs. He II relative intensity variations of bands present in the low ionization energy (IE) region has proven of crucial relevance for a critical analysis of the previous interpretation[3] and, thereore, has provided a more adequate rationale for the interpretation of PE data of present substituted complexes.

Results and Discussion

Figure 1 shows the PE spectrum of **1**. Three main features (labeled a,b, and c) can be identified in the region up to 11.5 eV. The He I spectrum is in good agreement with the previous study of Green et al.[3] (see also Table I). Notable differences in the relative spectral intensities are observed when the radiation is changed to He II. The band envelope a increases remarkably relative to all the bands that follow in the spectrum.

The spectra of the ring-substituted complexes **2** and **3** (Figures 2 and 3) are markedly different from those of **1**. The feature around 8 eV now contains only two somewhat resolved bands. The next spectral region up to 11.5 eV consists of an ill-resolved structure where four distinct ionizations are evident in the form of peaks or shoulders (see Table I). In the HeII spectra, in analogy to **1**, the onset band system a increases in relative intensity.

In the higher region (not shown in the figures) the spectra all show poorly resolved structures that are characteristic of systems containing cyclic polyolefin and carbonyl ligands. They represent ionizations from inner π and σ orbitals that are practically not involved in the metal–ligand bonding.

The assignment of present spectra can conveniently start with that of the simpler **1**. On the basis of He I data, Green et al.[3] assigned the first two peaks a and a′ to ionizations of metal 3d electrons. The following three peaks were thought to represent ionizations from ring π molecular orbitals (MO's).

Within the framework of Gelius' model[4] of PE cross sections, the present data, unfortunately, argue for a different interpretation. The identical He II vs. He I relative intensity growth of bands a, a′, and a″ points to an almost

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