

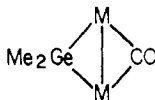
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Photochemistry of Some Bis(metal carbonyl)germanes and (Metal carbonyl)chloro-germanes. Formation of Germanium-Bridged Metal-Metal Bonds

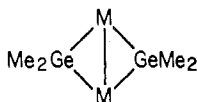
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Photolysis of Me_2GeM_2 ($\text{M} = \text{Co}(\text{CO})_4, \text{Fe}(\text{CO})_2\text{Cp}$) proceeds with loss of one carbon monoxide followed by ring closure to give complexes with the structural unit

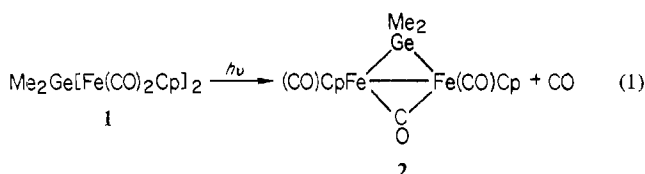


Photolysis of $\text{Me}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ gives the complex $(\text{Me}_2\text{Ge})\text{Mn}_2(\text{CO})_9$, which in solution apparently exhibits a form not containing a bridging carbonyl. Exposure of $\text{Me}_2\text{Ge}[\text{Mo}(\text{CO})_3\text{Cp}]_2$ to light cleaves the Ge-Mo bond to give $[\text{CpMo}(\text{CO})_3]_2$ or $\text{CpMo}(\text{CO})_3\text{H}$ depending on the solvent. Upon photolysis, $\text{Me}_2\text{Ge}(\text{Cl})\text{M}$ complexes ($\text{M} = \text{Mn}(\text{CO})_5, \text{Co}(\text{CO})_4, \text{Fe}(\text{CO})_2\text{Cp}, \text{Mo}(\text{CO})_3\text{Cp}, \text{Cr}(\text{CO})_3\text{Cp}$) formally lose Cl and CO and then dimerize to give compounds of the type

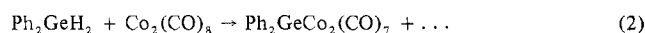


Introduction

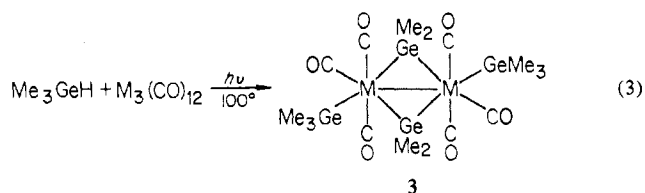
In the course of our investigations on the photolytic behavior of germanium analogs of σ -allyl complexes,¹ we observed the formation of μ -carbonyl- μ -dimethylgermylene-bis(cyclopentadienylcarbonyliron), **2**, when (dimethylvinylgermyl)cyclopentadienyliron dicarbonyl was subjected to ultraviolet light. We postulated that bis(cyclopentadienylcarbonyliron)dimethylgermane, **1**, formed initially and then decomposed according to eq 1.²



Compounds with germanium-bridged metal-metal bonds have been prepared by other methods,³⁻⁵ e.g., the reaction of a germanium dihydride with a metal carbonyl (eq 2).

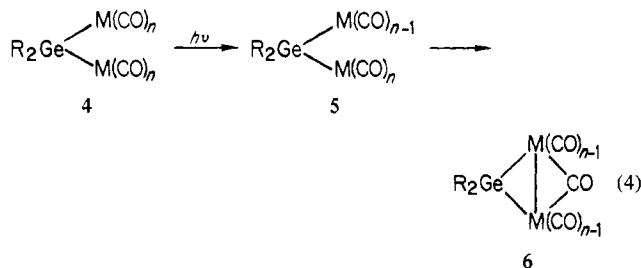


Knox and Stone⁶ have reported several complexes, e.g., **3**,



formed in the reactions of Me_3EH with $\text{M}_3(\text{CO})_{12}$ ($\text{E} = \text{Ge}, \text{Sn}; \text{M} = \text{Ru}, \text{Os}$) and by thermal decomposition of $(\text{Me}_3\text{Ge})_2\text{M}(\text{CO})_4$. The molecular structures of $(\text{Ph}_2\text{Ge})_2\text{Fe}_2(\text{CO})_7$, $(\text{Me}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$, and $(\text{Me}_2\text{Ge})_3\text{Ru}_2(\text{CO})_6$ have been reported.⁷⁻¹⁰

We have extended our investigations¹¹ of the photolytic behavior of complexes **4** since this represents a rational method for the preparation of compounds **6**. It is known that metal carbonyls lose carbon monoxide upon photolysis, forming coordinatively unsaturated metal centers.¹² The unsaturated metal in **5** becomes saturated upon formation of M-M and bridging carbonyl bonds (eq 4). During the course



of our work, Cleland, *et al.*,¹³ reported that the photolysis of $\text{Ph}_2\text{E}[\text{Fe}(\text{CO})_2\text{Cp}]_2$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$) gives the complex $(\text{Ph}_2\text{Ge})\text{Fe}_2(\text{CO})_3\text{Cp}_2$, corresponding to **6**.

We have also investigated the photolytic behavior of $\text{Me}_2\text{Ge}(\text{Cl})\text{M}(\text{CO})_n$ and have found that these complexes are precursors to compounds containing two dimethylgermylene groups.¹¹

- (1) R. C. Job and M. D. Curtis, *Inorg. Chem.*, **12**, 2510 (1973).
- (2) Abbreviations used: Me = methyl, Ph = phenyl, Cp = cyclopentadienyl, THF = tetrahydrofuran.
- (3) S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Commun.*, 1297 (1969).
- (4) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **92**, 5003 (1970).
- (5) M. J. Bennett, W. Brooks, M. Elder, W. A. G. Graham, D. Hall, and R. Kummer, *J. Amer. Chem. Soc.*, **92**, 209 (1970).
- (6) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2874 (1971), and references therein.

- (7) M. Elder, *Inorg. Chem.*, **8**, 2703 (1969).
- (8) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1424 (1969).
- (9) J. Howard and P. Woodward, *J. Chem. Soc. A*, 3648 (1971).
- (10) Group IV metal complexes have been the subject of review; see E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev., Sect. A*, **6**, 227 (1970).
- (11) M. D. Curtis and R. C. Job, *J. Amer. Chem. Soc.*, **94**, 2153 (1972).
- (12) W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964).
- (13) A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *J. Organometal. Chem.*, **32**, C15 (1971).

Experimental Section

A nitrogen atmosphere was maintained by Schlenk-tube techniques.¹⁴ Metal carbonyl anions were prepared by sodium amalgam reductions of the corresponding dimers in THF solution.¹⁵ Melting points were obtained in evacuated capillaries and are uncorrected. Nmr spectra were obtained in C_6D_6 solvent on a Varian T-60 at ambient temperature. The residual proton signal from C_6D_6 was used as an internal standard. Chemical shifts vs. TMS were obtained from the relation $\delta(\text{TMS}) = \delta(C_6D_6) + 428$ (δ upfield from C_6D_6 negative). Ir spectra of the carbonyl region were taken on a Perkin-Elmer 457. Unless otherwise specified, cyclohexane was used as solvent. Mass spectra were recorded on an AEI MS902 spectrometer using the direct-inlet system; the conditions given in parentheses are source temperature and ionizing energy. The m/e numbers are those of the most intense peak of the isotope pattern and the intensities are relative to the most intense peak ($I = 100$). The observed isotope distribution patterns were within experimental error of calculated distributions. Raman spectra were obtained using a Spex Ramalog laser unit (4880-Å line of Ar⁺) coupled to a Spex 1401 monochromator. Photolyses were performed with a Hanovia 450-W mercury lamp equipped with a fused silica immersion well. Ligroin refers to reagent grade petroleum ether (bp 30–60°).

Bis(cyclopentadienyldicarbonyliron)dimethylgermane, 1. CpFe(CO)₂Na (12 mmol) was dissolved in diethyl ether and cooled in an ice-salt bath. Dimethyldichlorogermane (1.0 g, 6 mmol) dissolved in 5 ml of ether was then added and the mixture stirred at -10° for 5 min. The ether was then pumped off under vacuum, and the residue was taken up in methylene chloride and filtered. The filtrate was concentrated and then rapidly filtered with suction through a 7-cm layer of Florisil. The filtrate was evaporated to dryness giving 0.6 g (22%) of thermally unstable product. *Anal.* Calcd for C₁₆H₁₆Fe₂GeO₄: C, 42.08; H, 3.54; Fe, 24.46; Ge, 15.90. Found: C, 45.70; H, 4.50; Fe, 22.2; Ge, 14.9. The extreme instability of this compound precluded adequate purification. Upon standing in the dark, the complex rapidly decomposes to give [CpFe(CO)₂]₂. The area ratio of the Cp and Me resonances was 10:6. In addition to these peaks, weak absorptions in the paraffinic region, possibly due to stopcock grease, were noted. The mass spectrum (45°, 35 eV) gave peaks at 458, 430, 402, 374, and 346 (Me₂GeFe₂(CO)_nCp₂, $n = 4, 3, 2, 1, 0$).

Photolysis of 1. A 0.3-g sample of 1 was dissolved in 200 ml of ligroin and photolyzed. Strong peaks at 1980, 1940, and 1782 cm⁻¹ grew in the ir spectrum while starting material peaks vanished. After 20 min, no starting material remained. The solvent was then removed under vacuum, and approximately half of the deep red residue was chromatographed over Florisil using methylene chloride as eluent. The first fraction (7 mg) was identified as Cp₂Fe₂(CO)₄ by its ir spectrum. The second, red fraction (ether eluent) was identified by ir and nmr as the previously obtained¹ (Me₂Ge)Fe₂(CO)₃Cp₂, 2. The nmr indicated a 4:1 mixture of cis and trans isomers as previously obtained.^{1,11}

Bis(pentacarbonylmanganese)dimethylgermane, 7. Dimethyldichlorogermane (0.9 g, 5 mmol) was added to a solution of 10 mmol of NaMn(CO)₅ in 40 ml of THF at 0°; after stirring for 2 hr, the THF was pumped off and the residue was taken up in ligroin and filtered. Following concentration, the solution was chromatographed over Florisil (ligroin eluent) to give a yellow band from which was obtained yellow crystals. After recrystallization from ligroin, 0.7 g (28%) of product was obtained. *Anal.* Calcd for C₁₂H₆GeMn₂O₁₀: C, 29.25; H, 2.05. Found: C, 29.32; H, 2.28. The mass spectrum (100°, 50 eV) gave a parent molecule ion at m/e 494 ($I = 0.5$) and peaks corresponding to consecutive loss of ten carbonyls. The most intense peak ($I = 100$) occurred at m/e 299 corresponding to Me₂GeMn(CO)₅⁺.

Photolysis of 7. A 0.5-g sample of 7 in 50 ml of ligroin was subjected to photolysis. After 1 hr, essentially all starting material had been consumed. The solution was filtered, and the filtrate was concentrated and cooled to -10° to give bright orange crystals. After recrystallization from ligroin, 0.3 g (60%) of product, 8, was obtained. *Anal.* Calcd for C₁₁H₆GeMn₂O₉: C, 29.43; H, 1.30. Found: C, 28.48; H, 1.40. The mass spectrum (135°, 20 eV) gave the parent molecule ion ($I = 100$) at m/e 466 followed by loss of nine carbonyls. Me₂GeMn(CO)₅⁺ ($I = 100$) was also observed.

Bis(cyclopentadienylnickel)tricarboxylmolybdenum)dimethylgermane, 9. Dimethyldichlorogermane (1.4 g, 8 mmol) dissolved in 5 ml of THF was added to a stirred solution of NaMo(CO)₃Cp (18 mmol) in

18 ml of THF at -78°. An ice-salt bath was then placed around the mixture which was stirred for 20 min. The solvent was then pumped off, and the residue was taken up in methylene chloride and filtered. Upon removal of solvent under vacuum, 2.0 g (42%) of yellow powder was obtained. *Anal.* Calcd for C₁₈H₁₆GeMo₂O₆: C, 36.47; H, 2.73; Ge, 12.25; Mo, 32.37. Found: C, 35.9; H, 2.73; Ge, 12.08; Mo, 32.59. The mass spectrum (180°, 20 eV) shows the parent molecule ion (m/e 594, $I = 0.6$). The most intense peak occurs at m/e 349 (Me₂GeMo(CO)₃Cp⁺).

Photolysis of 9. A 0.3-g sample of 9 in 150 ml of cyclohexane gave a deep red solution when stirred in sunlight for 2 hr or when subjected to photolysis for 15 min. After removal of solvent, the residue was chromatographed over Florisil with methylene chloride as eluent. Solvent was removed from the first fraction (red) and the residue was placed in a sublimation apparatus at room temperature. White crystals (0.2 g) collected on the ice-cooled probe. These crystals were exceedingly air sensitive (turning dark red immediately) and exhibited ir bands at 2042 (s), 2005 (w), 1945 (vs), and 1912 (w) cm⁻¹. The mass spectrum (40°, 20 eV) identified this material as CpMo(CO)₃H: m/e 248, 220, 192, 164 (CpMo(CO)_xH, $x = 3, 2, 1, 0$) and 219, 191, 163 (CpMo(CO)_x, $x = 2, 1, 0$). A second band gave less than 0.1 g of [CpMo(CO)₃]₂. Carrying out the photolysis in benzene solution gave a 90% yield of [CpMo(CO)₃]₂ and only trace amounts of CpMo(CO)₃H.

Photolysis of Bis(tetracarbonylcobalt)dimethylgermane, 10. Photolysis of this compound, prepared by the method of Patmore and Graham,¹⁶ in ligroin proceeded over a period of 22 hr to give prominent new bands at 2085 and 1842 cm⁻¹. Concentration of the solution gave 0.3 g of black solid identical in all respects with authentic Co₄(CO)₁₂.¹⁷ The dark brown filtrate was chromatographed with ligroin through a Florisil column. Following an initial yellow fraction (starting material), a brown band was collected and cooled to -78° to give 0.3 g of brown crystals. The cold solvent was removed with a syringe and the crystals were dried *in vacuo* at -78°. *Anal.* Calcd for C₈H₆Co₂GeO₇: C, 25.95; H, 1.45; Ge, 16.43; Co, 28.27. Found: C, 26.20; H, 1.55; Ge, 17.78; Co, 28.55. The product, μ -carbonyl- μ -dimethylgermylene-bis(tricarboxylcobalt) (11), is air sensitive and thermally unstable, rapidly decomposing at 25° to deposit Co₄(CO)₁₂. The mass spectrum of 11 (55°, 50 eV) shows the parent molecule ion at m/e 418 (12) and stepwise loss of all seven carbonyls (most intense peak = P⁺ - 5CO). No peak at m/e 275 (Me₂GeCo(CO)₄⁺) was observed. The mass spectrum of 10 does not give a parent molecule ion, the highest observed m/e 418 corresponding to loss of carbonyl. However, the peak due to Me₂-GeCo(CO)₄⁺ at m/e 275 (21) is observed.

(Dimethylchlorogermyl)cyclopentadienylchromium Tricarbonyl, 12. Dimethyldichlorogermane (1.7 g, 10 mmol) was added to 20 mmol of NaCr(CO)₃Cp¹⁸ slurried in 20 ml of ether, and the mixture was stirred for 10 min. After pumping off the ether, the resulting tar was triturated with ten 30-ml portions of ligroin. The combined extracts were concentrated to a volume of ca. 50 ml and then cooled in an ice-salt bath to yield 0.6 g (18%) of pale green crystals. *Anal.* Calcd for C₁₀H₁₁ClCrGeO₃: C, 35.40; H, 3.27; Cl, 10.45. Found: C, 35.57; H, 3.53; Cl, 10.26. The mass spectrum (65°, 20 eV) shows relatively strong peaks at m/e 340 (33), 312 (4), 284 (15), and 256 (100) from Me₂Ge(Cl)CrCp(CO)_n⁺ ($n = 3, 2, 1, 0$) and m/e 305 (7) and 152 (60) corresponding to P⁺ - Cl and CpCrCl⁺, respectively.

Photolysis of 12. The above product, in 100 ml of ligroin, was subjected to photolysis for 35 min after which time the starting material was about three-fourths consumed and new bands had appeared at 1933, 1890, and 1840 cm⁻¹ in the ir spectrum. The solution was concentrated and allowed to stand overnight during which time a bright blue powder was deposited. The supernate was chromatographed over Florisil (CH₂Cl₂ eluent) to give several fractions. The only fraction identified was the first, which gave a trace amount of brown crystals whose spectral properties are consistent with their formulation μ , μ -bis(dimethylgermylene)-bis(cyclopentadienyldicarbonylchromium), 13. The mass spectrum (165°, 20 eV) shows a parent molecule ion at m/e 552 ($I = 25$) and stepwise loss of four carbonyls. The most intense peak is the P⁺ - 3CO followed by P⁺ - 4CO ($I = 92$). Insufficient sample was obtained for elemental analysis. The blue powder, which was not identified, does not contain carbonyl groups.

(Dimethylchlorogermyl)manganese Pentacarbonyl, 14. This com-

(14) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1968.

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

(16) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 6, 981 (1967).

(17) R. Ercoli, P. Chini, and M. Massi-Mauri, *Chim. Ind. (Milan)*, 41, 132 (1959).

(18) R. B. King and F. G. A. Stone, *Inorg. Syn.*, 7, 105 (1963).

pound was prepared by adding a solution of 10 mmol of $\text{NaMn}(\text{CO})_5$ in THF to 1.7 g (10 mmol) of dimethyldichlorogermane in 30 ml of THF at 0° . After 5 min, the solution was allowed to warm to room temperature, and the THF was then pumped off. The residue was extracted with ligroin and filtered, and the filtrate was cooled to 0° to give white needles. After two recrystallizations, 1.9 g (57%) of pure product was obtained. *Anal.* Calcd for $\text{C}_7\text{H}_6\text{ClGeMnO}_3$: C, 25.24; H, 1.82. Found: C, 25.07; H, 1.69.

Photolysis of 14. A 1.8-g sample of 14 in 200 ml of ligroin was photolyzed for 4.5 hr after which the solution was deep red and exhibited new ir bands at 2090, 2035, 2000, 1970, and 1960 cm^{-1} . The mixture was filtered, and the solvent was removed from the filtrate. The red, oily residue was chromatographed (Florisil-ligroin), and the first fraction yielded 0.5 g of bright yellow crystals identified as μ,μ -bis(dimethylgermylene)-bis(tetracarbonylmanganese), 15. *Anal.* Calcd for $\text{C}_{12}\text{H}_{12}\text{Ge}_2\text{Mn}_2\text{O}_8$: C, 26.72; H, 2.25. Found: C, 26.55; H, 2.30. The mass spectrum (135° , 20 eV) showed a very intense parent molecule ion ($I = 100$) at m/e 540 and sequential loss of five carbonyls. An intense peak ($I = 90$, m/e 373) was observed for $(\text{Me}_2\text{Ge})_2\text{Mn}(\text{CO})_4^+$.

Photolysis of (Dimethylchlorogermyl)cobalt Tetracarbonyl, 16. A 1.0-g sample of compound 16, prepared by the method of Patmore and Graham,¹⁶ was dissolved in 100 ml of ligroin and subjected to photolysis for 18 hr. Following filtration, the solvent was removed and the residue chromatographed (Florisil-ligroin). The first fraction yielded 0.1 g of bright yellow μ,μ -bis(dimethylgermylene)-bis(tricarbonylcobalt), 17. *Anal.* Calcd for $\text{C}_{10}\text{H}_{12}\text{Co}_2\text{Ge}_2\text{O}_6$: C, 24.45; H, 2.45. Found: C, 24.21; H, 2.77. The mass spectrum (75° , 50 eV) shows a parent molecule ion peak ($I = 47$) at m/e 497. Loss of six carbonyls was observed with the $\text{P}^+ - 4\text{CO}$ peak most intense ($I = 100$). The peak at m/e 264 (Ge_2Co_2^+) had an intensity of 87.

(Dimethylchlorogermyl)cyclopentadienyliron Dicarboxyl, 18. To 1.7 g (10 mmol) of dimethyldichlorogermane in 30 ml of THF at -78° was slowly added 10 mmol of $\text{NaFe}(\text{CO})_2\text{Cp}$ in 25 ml of THF. After standing overnight at -78° , the mixture was warmed to room temperature, and the THF pumped off. The remaining sludge was taken up in ligroin. Filtration gave a red solution which deposited a red oil upon cooling to -10° . Scratching caused the oil to solidify, and the solid was recrystallized three times from ligroin to give 2.2 g (70%) of product. *Anal.* Calcd for $\text{C}_8\text{H}_{11}\text{ClFeGeO}_2$: C, 34.31; H, 3.52. Found: C, 34.17; H, 3.43. The mass spectrum (75° , 20 eV) gave the following peaks, m/e (I): 316 (8), 288 (55), 260 (100) corresponding to $\text{Me}_2\text{GeClFe}(\text{CO})_2\text{Cp}^+$ ($n = 2, 1, 0$) and 281 (6) corresponding to $\text{Me}_2\text{GeFe}(\text{CO})_2\text{Cp}^+$.

Photolysis of 18. A 2.2-g sample of 18 in 100 ml of ligroin was subjected to photolysis for 4 hr during which time a dark red solid (0.2 g) deposited on the walls of the container. Concentration of the ligroin gave an additional 0.4 g of the red solid which was shown by ir and nmr analysis to be primarily 2. From the mother liquor traces of ferrocene and $\text{Me}_3\text{GeFe}(\text{CO})_2\text{Cp}$ were recovered by sublimation and chromatography, respectively. Chromatography of the red solid gave, with methylene chloride eluent, an orange-brown fraction which yielded a very small amount of reddish brown solid after removal of solvent. This product was identified as *cis*- μ,μ -bis(dimethylgermylene)-bis(cyclopentadienylcarbonyliron), 19, by its ir, nmr, and mass spectra. The last (180° , 20 eV) displays a parent molecule ion at m/e 504 ($I = 45$) followed by consecutive loss of two carbonyls and then two methyl groups, m/e (I): 476 (100), 448 (73), 433 (9), 418 (3).

(Dimethylchlorogermyl)cyclopentadienylmolybdenum Tricarbonyl, 20. To 10 mmol of $\text{NaMo}(\text{CO})_3\text{Cp}$ slurred in 20 ml of ether at -5° was rapidly added 1.7 g (10 mmol) of dimethyldichlorogermane in 10 ml of ether. The mixture was stirred at 0° for 5 min, allowed to warm to room temperature, and then filtered. Petroleum ether (bp 90 – 100°) was added and the ether pumped off under vacuum causing yellow crystals to precipitate. These were recrystallized several times from petroleum ether–methylene chloride to give 1.3 g (46%) of pale salmon product. *Anal.* Calcd for $\text{C}_{10}\text{H}_{11}\text{ClGeMoO}_3$: C, 31.34; H, 2.89. Found: C, 31.52; H, 2.79. The mass spectrum gives a parent molecule ion at m/e 384 (20) and stepwise loss of three carbonyls, m/e 365 (100), 328 (46), and 285 (76). Loss of Cl gives a weak peak at m/e 349 (<8).

Photolysis of 20. A 1.2-g sample of 20 in 100 ml of ligroin was photolyzed for 1.5 hr after which all carbonyl bands had disappeared from the solution. A deep red solid which had coated the walls of the vessel was taken up in methylene chloride and chromatographed to give (in order of elution) red, yellow, green, and dark red bands. The last band remains at the top of the column. The first fraction was $[\text{CpMo}(\text{CO})_3]_2$. The second fraction was again chromatographed

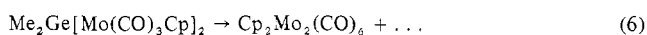
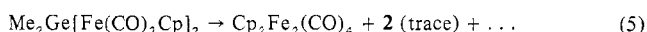
over a fresh column to give a pink fraction, followed by a bright yellow band. Removal of solvent from the yellow band gave *ca.* 10 mg of orange crystals which darken at 200 – 220° and do not melt up to 300° . These crystals were identified as μ,μ -bis(dimethylgermylene)-bis(cyclopentadienylcarbonylmolybdenum), 21. *Anal.* Calcd for $\text{C}_{18}\text{H}_{22}\text{Ge}_2\text{Mo}_2\text{O}_4$: C, 33.81; H, 3.47. Found: C, 33.91; H, 3.60. The mass spectrum (160° , 20 eV) gave a parent molecule ion at m/e 640 (100).

Results and Discussion

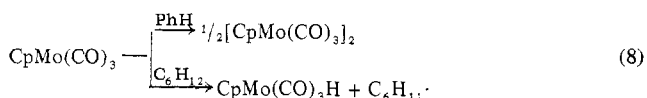
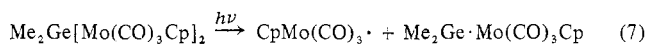
Some physical properties of the compounds prepared in this work are presented in Table I.

Bis(metal carbonyl)germanes may be prepared by the interaction of metal carbonyl anions and dihalogermanes provided certain precautions are observed. The reactions of $\text{CpFe}(\text{CO})_2^-$, $\text{CpMo}(\text{CO})_3^-$, and $\text{Mn}(\text{CO})_5^-$ with dimethyldibromogermane were erratic^{19,20} and we obtained the best results using dimethyldichlorogermane. This was rather surprising in view of the recent report²¹ that bromide is the halide of choice in the preparation of diphenylbis(metal carbonyl)germanes. However, in agreement with the conclusions of Cleland, *et al.*,²¹ we found that excess $\text{Co}(\text{CO})_4^-$ or $\text{CpCr}(\text{CO})_3^-$ gave predominantly $\text{Me}_2\text{Ge}(\text{Cl})\text{Co}(\text{CO})_4$ and $\text{Me}_2\text{Ge}(\text{Cl})\text{Cr}(\text{CO})_3\text{Cp}$, respectively, upon reaction with Me_2GeCl_2 .

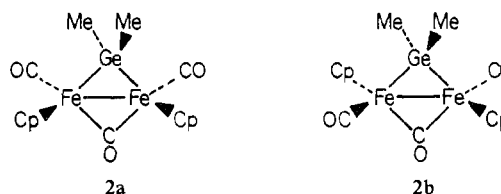
Several of the dimethylbis(metal carbonyl)germanes are thermally unstable, decomposing at room temperature to the corresponding metal carbonyl dimers



All of the bis(metal carbonyl)germanes studied decompose under ultraviolet light to give a mixture of products. The molybdenum compound, 9, decomposes upon photolysis to give $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ or $\text{CpMo}(\text{CO})_3\text{H}$ ²² in benzene or cyclohexane, respectively. Apparently, photolysis results in homolytic cleavage of the Ge–Mo bond giving $\text{CpMo}(\text{CO})_3$. As postulated previously,²⁰ these radicals may dimerize or abstract hydrogen from solvent. Dimerization is favored in benzene which has stronger C–H bonds compared to cyclohexane.



Photolysis of the iron, manganese, and cobalt complexes, 1, 7, and 10, proceeds with loss of carbon monoxide to give 2, 8, and 11, respectively. The nmr spectrum of 2 establishes that this complex exists in solution at room temperature as a 4:1 mixture of *cis* and *trans* isomers, 2a and 2b.^{1,11} The



(19) Occasionally, metal carbonyl complexes containing no germanium were obtained. These reactions were reminiscent of the anomalous reactions of Ph_3SiCl with metal carbonyl anions.²⁰

(20) M. D. Curtis, *Inorg. Chem.*, 11, 802 (1972).

(21) A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Commun.*, 155 (1971).

(22) We found pure $\text{CpMo}(\text{CO})_3\text{H}$ to be colorless. A previous report describes the compound as yellow: E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, 282, 47 (1955).

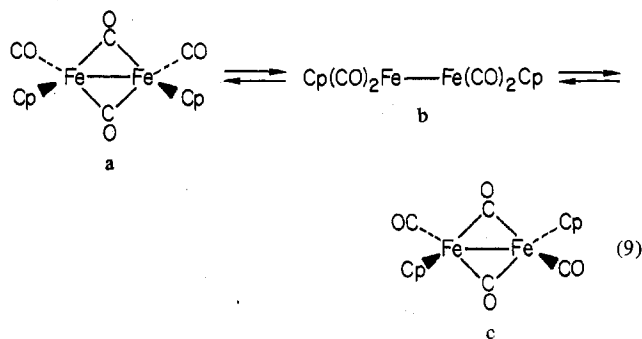
Table I. Metal Carbonyl Complexes Containing the Dimethylgermylene Group

No.	Compd	Color	Mp, °C	$\nu(\text{CO}), \text{cm}^{-1}$	$\delta(\text{Me})^a$	$\delta(\text{Cp})^a$
1	$\text{Me}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{Cp}]_2$	Yellow-brown	121-124 dec	2008 (2), 1999 (3.5), 1987 (7), 1952 (2), 1941 (7)	0.93	4.20
2	$\text{Me}_2\text{GeFe}_2(\text{CO})_3\text{Cp}_2$	Red	218-220	2005 (0.5), 1980 (4.5), 1965 (0.5), 1955 (0.5), 1945 (1.5), 1940 (1.7), 1785 (2)	1.33, 1.50 ^b 1.40 ^c	4.12 ^b 4.32 ^c
7	$\text{Me}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$	Yellow	78-79.5	2105 (2.5), 2080 (8), 2045 (2), 2010 (9.5), 2000 (9.5), 1985 (8.5), 1955 (2)	1.02	
8	$\text{Me}_2\text{GeMn}_2(\text{CO})_9$	Orange	143-144 dec	2100 (1), 2060 (4), 2010 vs, 1970 (4.5), 1835 (0.5)	1.17	
9	$\text{Me}_2\text{Ge}[\text{Mo}(\text{CO})_3\text{Cp}]_2$	Yellow	158-159 dec	2003 (1.5), 1984 (4.5), 1937 (1), 1926 (2), 1912 (2.5), 1899 (3)	1.35	4.78
10	$\text{Me}_2\text{Ge}[\text{Co}(\text{CO})_4]_2$	Yellow	43-44.5	2105 (2), 2090 (6), 2035 sh, 2025 (6.5), 2010 (7), 1995 (4.5), 1960 (0.1)	1.23	
11	$\text{Me}_2\text{GeCo}_2(\text{CO})_7$	Brown	<20	2085 (7.5), 2047 (9.5), 2024 (9.5), 2006 (9.5), 1998 sh, 1971 (1), 1844 (8)	0.63	
12	$\text{Me}_2\text{Ge}(\text{Cl})\text{Cr}(\text{CO})_3\text{Cp}$	Pale green	88-91	2005 (9), 1948 (8.5), 1930 sh, 1913 (9)	0.80	4.05
13	$(\text{Me}_2\text{Ge})_2\text{Cr}_2(\text{CO})_4\text{Cp}_2$	Brown		1932 (5.5), 1900 sh, 1890 (8.5), 1838 (4)	1.08 ^c	4.08 ^c
14	$\text{Me}_2\text{Ge}(\text{Cl})\text{Mn}(\text{CO})_5$	White	71-73	2100 (3.5), 2035 (2.5), 2005 (9), 1970 (0.5)	0.88	
15	$(\text{Me}_2\text{Ge})_2\text{Mn}_2(\text{CO})_8$	Yellow	190 dec	2035 (4), 2005 (8.5), 1995 sh, 1970 (8), 1962 (8), 1844 (0.2), 1823 (0.2)	0.83	
16	$\text{Me}_2\text{Ge}(\text{Cl})\text{Co}(\text{CO})_4$	Yellow	56-57	2110 (8), 2050 (8), 2030 (8.5), 2005 (9), 1980 (2), 1962 (1)	0.83	
17	$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$	Yellow	160-161 dec	2075 (1.5), 2035 (4), 2010 (4), 1985 (4.5)	0.87	
18	$\text{Me}_2\text{Ge}(\text{Cl})\text{Fe}(\text{CO})_2\text{Cp}$	Yellow	69.5-71.5	2000 (7.5), 1975 (2), 1962 (8.5)	0.70	3.97
19	$(\text{Me}_2\text{Ge})_2\text{Fe}_2(\text{CO})_2\text{Cp}_2$	Orange-brown		1942 (5), 1918 (2)	1.28, 1.37 ^b	3.87 ^b
20	$\text{Me}_2\text{Ge}(\text{Cl})\text{Mo}(\text{CO})_3\text{Cp}$	Salmon	73-75	2025 (8.5), 1957 (8.5), 1940 (sh), 1936 (9), 1907 (sh), 1888 (sh)	0.77	4.47
21	$(\text{Me}_2\text{Ge})_2\text{Mo}_2(\text{CO})_4\text{Cp}_2$	Orange	220 dec	1951 (3.5), 1905 (3.5), 1893 (4.5), 1838 (2.5)	0.97 ^c	4.53 ^c

^a In ppm downfield from TMS in C_6D_6 . ^b Cis isomer. ^c Trans isomer.

presence of the bridging carbonyl is shown by the intense ir band at 1785 cm^{-1} .

It has been shown that $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ exists in solution as a rapidly interconverting mixture of isomers.²³

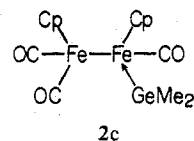


The activation energy for the $\text{a} \rightarrow \text{b}$ conversion was estimated to be $13 \pm 2 \text{ kcal/mol}$. The fact that separate, sharp resonances for **2a** and **2b** are observed at room temperature shows the rate of interconversion, P , is much lower than the separation, $\Delta\delta$, of the resonances of **2a** and **2b**.²⁴ Assuming a frequency factor of 10^{13} sec^{-1} and $P = 0.01\Delta\delta(\text{Cp}) \approx 0.1 \text{ Hz}$, the activation energy for the $\text{cis} \rightleftharpoons \text{trans}$ interconversion is estimated to be $\geq 19 \text{ kcal/mol}$. The higher activation energy presumably reflects the lower stability of the non-

(23) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

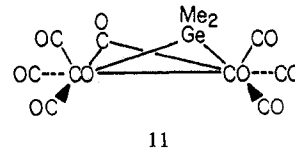
(24) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 12.

bridged form, **2c**, which contains a terminal dimethyl-



germylene group. Several complexes containing "terminal" dimethylgermylene groups have been reported, but in all cases the germanium is also bonded to a Lewis base, e.g., THF.²⁵ Preliminary results of the temperature dependence of the $\text{2a} \rightleftharpoons \text{2b}$ equilibrium suggest that the methyl group environments are averaged at a faster rate than the rate at which $\text{cis} \rightarrow \text{trans}$ isomerization occurs.

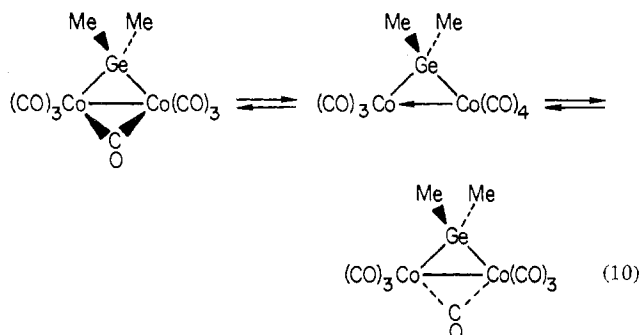
The cobalt complex, **11**, undoubtedly has the structure in



which the Me_2Ge group replaces a bridging carbonyl in $\text{Co}_2(\text{CO})_8$. This structure is indicated by the single, intense band in the bridging carbonyl region at 1844 cm^{-1} and the pattern of four strong bands in the terminal carbonyl region. In this structure, the two methyl groups are nonequivalent, so the observation of a single, sharp methyl resonance in the nmr at room temperature indicates that this molecule is fluxional.

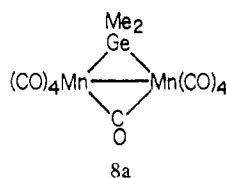
(25) T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 7090 (1971).

Adams and Cotton⁴ have shown that the bis(germylene) complex, **17**, has a temperature-dependent nmr spectrum and have discussed the mechanism. For **17**, those authors prefer a pseudorotation type of mechanism although one involving terminal germylene groups was not excluded. In addition to the above mechanisms, complex **11** may average the environments of the methyl groups *via* a terminal-bridge CO exchange in which the new Co-CO-Co bridge is formed on the opposite side of the Co-Ge-Co plane (eq 10). The

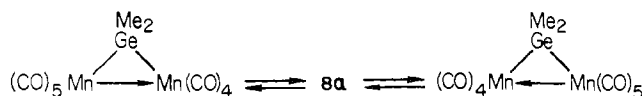


¹³C nmr should serve to establish whether or not exchange of terminal and bridging carbonyls occurs.

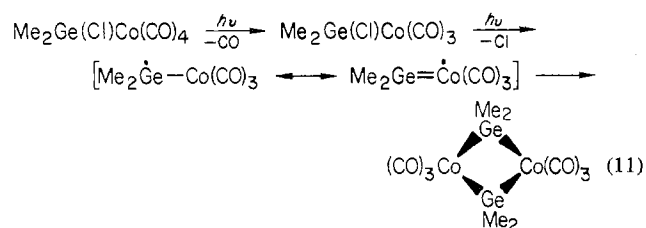
The structure of (Me₂Ge)Mn₂(CO)₉, **8**, in solution is not predominantly **8a** since the ir spectrum (Figure 1) shows only



a very weak absorption in the bridging carbonyl region. The weak peak at 1835 cm⁻¹ which slowly grows during the photolysis has the same relative intensity as observed in the final purified product. Only a single sharp resonance is observed in the proton nmr spectrum of **8**. We suggest that complex **8** exists in solution as a mixture of rapidly equilibrating isomers. The concentration of **8a** is presumably low, hence the weak 1835-cm⁻¹ peak. Compound **8** is currently the subject of an X-ray structure study.



The photolysis of chlorogermyl complexes of the type Me₂Ge(Cl)M(CO)_n leads to dinuclear compounds, (Me₂Ge)₂M₂(CO)_{2n-2}. Formally at least, the production of such compounds may be envisioned as loss of Cl· and CO to give (Me₂Ge)M(CO)_{n-1}, isoelectronic with the odd-electron species, *e.g.*, Co(CO)₄, Mn(CO)₅, etc. These odd-electron species then dimerize to give the observed products, *viz.*



Photolysis of the iron complex **18** gives mostly the mono(germylene) derivative **2** (in fact, this is the method of choice

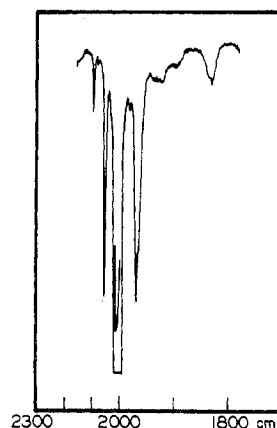
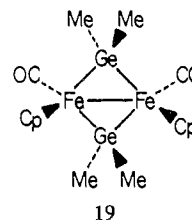


Figure 1. Infrared spectrum of Me₂GeMn₂(CO)₉, **8**, in cyclohexane.

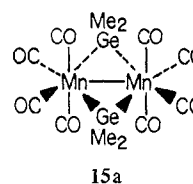
for the preparation of **2**). However, a small amount of the bis(germylene) compound, **19**, may be isolated from the reac-



tion mixture. The ir and nmr spectra (Table I) show that this compound adopts the *cis* configuration in solution at room temperature. The enhanced stability of the *cis* isomer of **19** compared to **2** is possibly related to repulsions between the cyclopentadienyl rings and the methyl groups. A slight folding (as in (Me₂Ge)₂Co₂(CO)₆) of the Fe-Ge-Fe-Ge ring about the Fe-Fe or Ge-Ge axes gives four diminished Cp-Me interactions. In the *trans* isomer, there are four undiminished Cp-Me interactions, and buckling of the ring can decrease two interactions only at the expense of increasing the remaining two. In the mono(germylene) complex, **2**, there are only two Cp-Me repulsions in the *trans* isomer and two diminished repulsions in a buckled *cis* isomer.

That rather complex rearrangements may occur during photolysis is shown by the identification of ferrocene and Me₃-GeFe(CO)₂Cp in the product mixture from the photolysis of **18**.

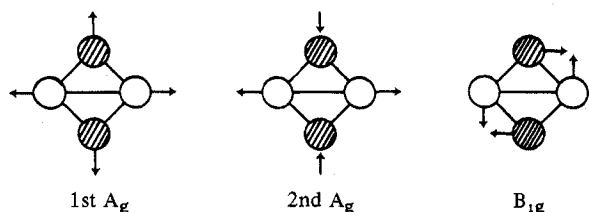
Photolysis of Me₂Ge(Cl)Mn(CO)₅ leads to high yields of the bis(germylene) complex, (Me₂Ge)₂Mn₂(CO)₈, **15**. Compound **15** exhibits one sharp methyl resonance in the nmr and four strong bands in the terminal carbonyl region. These data are consistent with the *D*_{2h} structure, **15a**, which allows



four ir-active carbonyl stretching modes (B_{1u} + 2 B_{2u} + B_{3u}).

In support of structure **15a**, the Raman spectrum shows three relatively strong lines at 102 (dp?), 206 (p) and 242 (p) cm⁻¹ (p = polarized, dp = depolarized) in the metal-metal vibration region. Additional weaker bands from M-C stretching and M-C-O bending were observed at 433 (mw) (p?), 455 (w) (dp), 512 (m) (p?), 556 (w) (dp), 583 (w) (dp), and

639 (w) (dp). Considering only the metal-metal vibrations, group theory predicts three Raman-active fundamentals, $2 A_g + B_{1g}$.

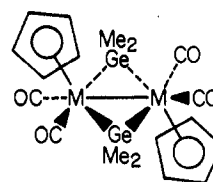


Accordingly, the two clearly polarized bands at 206 and 242 cm^{-1} are assigned to the two A_g modes and the 102- cm^{-1} band is assigned to the B_{1g} mode (overlap with the excitation line prevented accurate measurement of the depolarization ratio of this band). In the carbonyl stretching region, Raman bands were observed at 2076, 1980 (sh), 1970, and 1954 cm^{-1} . The low intensity of these bands precluded meaningful polarization studies; but the spectrum is consistent with the proposed D_{2h} structure which allows four Raman-active carbonyl stretches ($2 A_g + B_{1g} + B_{3g}$). After submission of this article, the structure of $(\text{Ph}_2\text{Si})_2\text{Mn}_2(\text{CO})_8$ was reported and conforms to approximate D_{2h} symmetry.²⁶

The chromium and molybdenum complexes $\text{CpM}(\text{CO})_3\text{Ge}(\text{Cl})\text{Me}_2$ (12 and 20) decompose extensively upon photolysis. However, low yields of the bis(germylene) complexes, 13 and 21, could be realized from the complex reaction mixtures. The spectral data for these compounds are consistent with trans-bridged structures.²⁷ It is interesting that the iron complexes 2 and 20 prefer the cis configuration while

(26) G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 783 (1973).

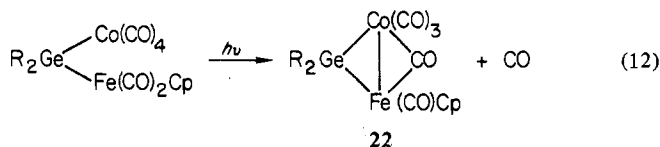
(27) The data do not exclude a rapid (nmr time scale) cis-trans isomerization involving terminal Me_2Ge groups.



13, M = Cr
21, M = Mo

the chromium and molybdenum complexes adopt the trans structure.

The methods described here for preparing germylene complexes would appear to be generally applicable to the other group IV elements, Si, Sn, and Pb.¹³ It should also be possible to prepare heterocycles, e.g., 22, by the photolysis of mixed carbonyl derivatives (eq 12). These aspects of the



photolysis reaction are currently under investigation.

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Registry No. 1, 41517-29-7; 7, 41538-92-5; 8, 12705-84-9; 9, 39382-82-6; 10, 41538-93-6; 11, 36116-50-4; 12, 41517-28-6; 13, 39382-83-7; 14, 41538-95-8; 15, 41517-08-2; 16, 41538-96-9; 17, 41550-24-7; 18, 41517-30-0; 19, 41517-31-1; 20, 41517-32-2; 21, 39382-84-8; $\text{CpFe}(\text{CO})_2\text{Na}$, 41517-33-3; $\text{NaMn}(\text{CO})_5$, 13859-41-1; $\text{NaMo}(\text{CO})_3\text{Cp}$, 12107-35-6; $\text{NaCr}(\text{CO})_3\text{Cp}$, 12203-12-2; dimethyl-dichlorogermane, 1529-48-2.

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Studies on the Pentacarbonyltechnetium Radical

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A species believed to be the $^{99\text{m}}\text{Tc}(\text{CO})_5$ radical is produced in high yield on the β decay of $^{99}\text{Mo}(\text{CO})_6$ in the solid state. This species is found to be scavenged by rapid exchange with $\text{IMn}(\text{CO})_5$ to give $\text{ITc}(\text{CO})_5$ and is destroyed by nitric oxide. It reacts slowly with photochemically produced $\cdot\text{Mn}(\text{CO})_5$ to produce a species probably $\text{TcMn}(\text{CO})_{10}$. When still trapped in the $\text{Mo}(\text{CO})_6$ lattice, it survives heating to 110°.

Introduction

The radical species $\cdot\text{Mn}(\text{CO})_5$ was first detected in neutron-irradiated $\text{Mn}_2(\text{CO})_{10}$.^{1,2} Recently, this radical has been prepared photochemically and studied more thoroughly by Hallock and Wojcicki.³ Their simple method of preparation of this radical in solution has enabled us to study further re-

(1) I. G. de Jong and D. R. Wiles, *Chem. Commun.*, 519 (1968).

(2) I. G. de Jong, S. C. Srinivasan, and D. R. Wiles, *Can. J. Chem.*, **47**, 1327 (1969).

(3) A. Wojcicki, personal communication, June 1972; S. A. Hallock and A. Wojcicki, *J. Organometal. Chem.*, in press.

actions of $\cdot\text{Mn}(\text{CO})_5$ and, in particular, to look at reactions of the homologous $\cdot\text{Tc}(\text{CO})_5$.

The compounds $\text{Tc}_2(\text{CO})_{10}$ and $\text{ITc}(\text{CO})_5$ have been prepared⁴ and characterized, but we did not have these available to us. As far as we are aware, no mention has been made of intermediate species or radicals of the type $\cdot\text{Tc}(\text{CO})_x$.

As is shown in eq 1, the starting point of our experiments is $^{99}\text{Mo}(\text{CO})_6$, carefully purified following neutron irradiation

(4) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 2953 (1961).