This species then would undergo rapid decomposition to give $(CH_3)_2B(H)O_2$ and BH_3, then B_2H_6. It has been suggested that both symmetrical and unsymmetrical cleavage of diboranes by nucleophiles proceeds *via* an initial step involving displacement of one bridge hydrogen to form a singly bridged species.[26]

The proposed mechanisms both involve the coordination of oxygen by a borane moiety analogous to that originally proposed by Johnson and Van Campen[27] and confirmed more recently by Davies and his coworkers.[2] The results indicate that reactivity toward oxygen under the gas-phase conditions is indicated by the series $BH_3 < (CH_3)_2BH << B(CH_3)_3$. Preliminary results indicate that CH_3BH_2 fits into the above series in the expected place.[23] This trend, although the reverse of Lewis acid strengths toward amines, can presumably be accounted for in terms of the relative stabilities of the boranes as dimers. Thus $B(CH_3)_3$ always has an empty p orbital whereas the ~36 kcal[28] involved in the reaction $B_2H_6 \rightleftharpoons 2BH_3$ increases the thermodynamic stability of the dimer. McCoy and Bauer[26] have shown that the bridge-breaking energy in substituted diboranes decreases with the number of substituents. However, the stability of the resultant peroxides, if indeed they are formed in all three cases, increases with increased substitution at boron and also with the size of the substituent on boron. Thus the peroxide is not observed as a intermediate in the oxidation of BH_3CO, although previous work undoubtedly suggests a reaction mechanism involving initial peroxide formation.[9] The stability of dimethylboryl methyl peroxide, however, is much higher, the half-life for rearrangement to the ester being about 60 days. The stability of the hydroperoxide formed in this study is apparently between the two above peroxides. The stability of these peroxides appears to be inversely related to their ease of condensation to form the trioxadiborolane as opposed to the rearrangement to form the dialkoxyborane species. Qualitative observations indicate that $(CH_3)_2B_2O_3$ is thermally more stable than $H_2B_2O_3$. Both species may be stored for periods of time without significant decomposition. Condensation to the solid at $-190°$ results in the deposition of a film of B_2O_3; warming and recooling to complete recondensation are not possible, indicating decomposition and the production of hydrogen and hydrocarbon respectively from $H_2B_2O_3$ and $(CH_3)_2B_2O_3$. This facile heterogeneous mode of decomposition is comparable to that of boroxine itself which completely disproportionates to boron oxide and borane when condensed. The oxidations of BH_3CO, BH_3PF, B_4H_{10}, and B_5H_9 all proceed heterogeneously.

[26] H. D. Johnson, II, and S. G. Shore, *Fortschr. Chem. Forsch.*, 15, 88 (1971), and references therein.

[27] J. R. Johnson and M. G. Van Campen, *J. Amer. Chem. Soc.*, 60, 121 (1938).

[28] T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, 73, 873 (1969).

Registry No. O_2, 7782-44-7; 1,1-$(CH_3)_2B_2H_4$, 12070-96-1; $(CH_3)_2BOOH$, 41557-63-5.

Contribution from the Department of Chemistry, University
of Michigan, Ann Arbor, Michigan 48104

Photochemistry of Vinyl-Substituted Germanium Derivatives of Transition Metal Carbonyls

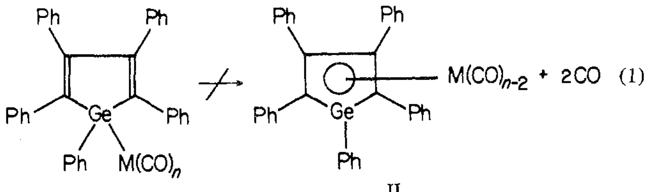
ROBERT C. JOB and M. DAVID CURTIS*

Received December 19, 1972

The preparation of vinyl-substituted germanium derivatives of transition metal carbonyls is reported. These compounds, $(CH_3)_2(C_2H_3)GeM$ ($M = Mn(CO)_5$, $Mo(CO)_3(\pi\text{-}C_5H_5)$, $Co(CO)_4$, $Fe(CO)_3NO$, $Co(CO)_2(NO)(CN)$, $Fe(CO)_2(\pi\text{-}C_5H_5)$, $Mn(CO)_4PPh_3$, $Co(CO)_3PPh_3$), are formally analogous to the corresponding σ-allyl compounds, $(\sigma\text{-}C_3H_5)M$. Photolysis proceeds with rupture of the germanium–metal bond to give complex mixtures from which compounds such as $Cp_2Mo_2(CO)_4$ (V), $Mn_2(CO)_{10}$, and μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienylcarbonyliron) (VII) may be isolated. The nmr parameters of the compounds are reported and correlated with the nucleophilicities of the metal anion, M^-.

Transition metal carbonyl groups appear to stabilize delocalized π systems. For example, π-allyl,[1] cyclobutadiene,[2] and trimethylenemethyl[3] complexes of transition metal carbonyls each contain a π system which is not stable as a free ligand. No compounds containing p_π-p_π bonds between carbon and its congeners have ever been isolated.[4] It is of interest to determine if a π system containing silicon, germanium, or tin might be sufficiently stablized by coordination to a transition metal carbonyl group to allow its isolation.

Curtis[5] found that σ-cyclopentadienyl analogs (I) did not form π-germacyclopentadienyl complexes (II) upon photolysis or heating. However, the presence of the substituent



(1)

I II

phenyl groups may have seriously hindered the desired rearrangement.[6]

[1] M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, 2, 325 (1964).

[2] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Petit, *J. Amer. Chem. Soc.*, 87, 3254 (1965).

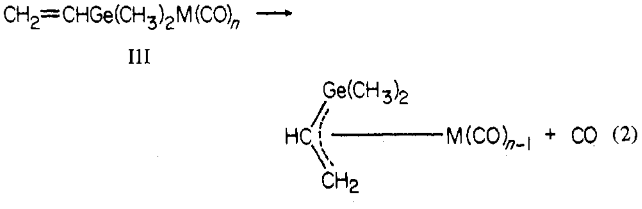
[3] G. F. Emerson, K. Erlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 88, 3172 (1966).

[4] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 113 f.

[5] M. D. Curtis, *J. Amer. Chem. Soc.*, 91, 6011 (1969).

[6] B. F. Hallam and P. C. Pauson, *J. Chem. Soc.*, 3030 (1956); S. McVey and P. C. Pauson, *ibid.*, 4312 (1965).

In this paper, we report the results of an investigation of vinyl-substituted germanium derivatives of metal carbonyls which are *formal* analogs of σ-allyl complexes of transition metal carbonyls. Of particular interest was the possibility of their rearrangement to π-allyl analogs (IV) upon photolysis or pyrolysis in a manner similar to that of σ-allyl complexes.[7-11]


III

IV

(2)

Experimental Section

All manipulations of metal carbonyl derivatives were routinely performed under a nitrogen atmosphere using standard Schlenk-ware techniques as described by Shriver.[12] The metal carbonyl anions, $CpMo(CO)_3^-$, $Mn(CO)_5^-$, $Mn(CO)_4(PPh_3)^-$, $CpFe(CO)_2^-$, $Co(CO)_4^-$, and $Co(CO)_3(PPh_3)^-$, were prepared by sodium amalgam reduction of the corresponding metal carbonyl dimer in tetrahydrofuran (THF).[13] $NaFe(CO)_3NO$ was prepared essentially according to Hieber and Beutner.[14] We found that the crude salt must be thoroughly dried under high vacuum for several hours in order for the ensuing crystallization to give high yields of clean product.

Dimethylvinylbromogermane and dimethylvinyliodogermane were prepared as described elsewhere.[15] Vinyltrichlorogermane was prepared by the method of Brinkman and Stone.[16]

Ultraviolet photolyses were performed with a 450-W medium-pressure mercury lamp (Hanovia No. 679A36). The extent of the photolytic reactions was monitored by periodically taking the ir spectrum of the carbonyl stretching region. The complex mixtures resulting from some of the photolytic reactions were chromatographed on Florisil columns prepared entirely under nitrogen using deaerated solvents. The Florisil was subjected to high vacuum for at least 1 hr before use.

Infrared spectra were obtained on either Beckman IR-10 or Perkin-Elmer 457 instruments. Proton nmr spectra were recorded on Varian A-60 or T-60 instruments. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All melting points were obtained in sealed, evacuated capillaries.

(Dimethylvinylgermyl)cyclopentadienylmolybdenum Tricarbonyl. Ten millimoles of cyclopentadienylmolybdenum tricarbonyl anion in 40 ml of THF was added with stirring to 2.1 g (10 mmol) of dimethylvinylbromogermane in 40 ml of THF. After 0.5 hr, the THF was pumped off and the residue treated with petroleum ether (bp 30–60°). After filtration, the solution was cooled in a Dry Ice bath to give pink crystals, mp 47–48°; yield 2.6 g (70%). *Anal.* Calcd for $C_{12}H_{14}GeMoO_3$: C, 38.4; H, 3.8. Found: C, 38.9; H, 3.6.

One gram of this compound was photolyzed in 600 ml of petroleum ether (bp 30–60°) for 1 hr, after which time the ir spectrum no longer exhibited peaks due to starting material. The solvent was removed and the residue chromatographed with methylene chloride eluent to give (1) starting material, (2) dicyclopentadienyltetracarbonyldimolybdenum, (3) dicyclopentadienylhexacarbonyldimolybdenum, and two other fractions which could not be characterized. The tetracarbonyl fraction (2) was obtained in small, erratic amounts (it appears to decompose on the column) and was characterized by its ir, nmr, and mass spectra (see Discussion).

(Dimethylvinylgermyl)manganese Pentacarbonyl. This compound was prepared from dimethylvinyliodogermane (10.3 g, 40 mmol) and 40 mmol of $NaMn(CO)_5$ in THF. Removal of most of the solvent, followed by filtration and vacuum distillation, gave 10.0 g (76%) of yellow oil, bp 63° (0.2 Torr). *Anal.* Calcd for $C_9H_9GeMnO_5$: C, 33.3; H, 2.8; Mn, 16.9. Found: C, 33.7; H, 3.0; Mn, 16.4.

Following photolysis, the only compound which could be isolated in a pure state was $Mn_2(CO)_{10}$.

(Dimethylvinylgermyl)cyclopentadienyliron Dicarbonyl. This complex was prepared analogously to the manganese pentacarbonyl derivative from 10.0 g of dimethylvinylbromogermane and 47 mmol of $CpFe(CO)_2Na$. Distillation gave an orange oil, bp 87° (0.2 Torr); yield 9.1 g (62%); density 1.42 g/ml. *Anal.* Calcd for $C_{11}H_{14}GeFeO_2$: C, 43.1; H, 4.6; Fe, 18.2. Found: C, 43.2; H, 4.6; Fe, 18.1.

When heated to 100–120°, the compound decomposes to give $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$. After photolysis in petroleum ether, only ferrocene, starting material, and $Cp_2Fe_2(CO)_4$ could be isolated.

When the compound was irradiated in the absence of solvent for 10 hr, a tar was formed which gave four fractions upon chromatography using a 3:1 mixture of methylene chloride–petroleum ether eluent: (1) starting material, (2) $Cp_2Fe_2(CO)_4$, (3) a red crystalline solid, (4) $[CpFe(CO)]_4$ which elutes with a 9:1 mixture of methylene chloride–petroleum ether. On the basis of its ir, nmr, and mass spectra and elemental analyses, fraction (3) was identified as μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienylcarbonyliron)(*Fe-Fe*). The mass spectrum exhibits the parent ion pattern characteristic of Ge_1Fe_2 at *m/e* 430 and intense patterns at *m/e* 402, 374, and 346 representing $(CH_3)_2GeFe_2(C_5H_5)_2(CO)_n$ (n = 2, 1, 0). Other intense patterns occur at *m/e* 281, 253, and 225 corresponding to $(CH_3)_2GeFe(C_5H_5)(CO)_n$ (n = 2, 1, 0). The compound shrinks at 213° and then melts at 218–220°. *Anal.* Calcd for $C_{15}H_{16}Fe_2GeO_3$: C, 42.04; H, 3.76. Found: C, 41.99; H, 3.78.

(Dimethylvinylgermyl)nitrosyliron Tricarbonyl. Sodium tricarbonylnitrosylferrate[14] (8.0 g, 40 mmol), slurried in 40 ml of ether, was added to a solution of dimethylvinyliodogermane in 10 ml of ether at −10°. After the mixture was stirred at −10° for 0.5 hr, the ether was pumped off and the residue sublimed from the ice–salt bath onto a liquid nitrogen cooled probe. The product, which decomposed rapidly at room temperature, was a yellow-orange oil. The compound was too unstable for elemental analysis, but spectral data support its formulation.

Upon photolysis, the compound gives a mixture of $Fe(CO)_5$, $Fe(CO)_2(NO)_2$, $Fe_2(CO)_9$, and black solid which is incompletely characterized at present.

(Dimethylvinylgermyl)cobalt Tetracarbonyl. This compound prepared in 60% yield from sodium tetracarbonylcobaltate (10 mmol) and dimethylvinylbromogermane (10 mmol) was worked up in the same manner as described for (dimethylvinylgermyl)cyclopentadienyliron dicarbonyl. The product was a brown oil, bp 70° (110 Torr). *Anal.* Calcd for $C_8H_9CoGeO_4$: C, 32.0; H, 3.0; Co, 19.6. Found: C, 32.0; H, 3.1; Co, 19.3. This compound is thermally unstable.

(Dimethylvinylgermyl)triphenylphosphinecobalt Tricarbonyl. Triphenylphosphinecobalt tricarbonyl anion (4 mmol) and dimethylvinylbromogermane (4 mmol) were allowed to react for 0.5 hr. Work-up from methylene chloride–ethanol gave pale yellow crystals, mp 150° with decomposition; yield 1.7 g (81%). The product was recovered unchanged after refluxing for 16 hr in benzene. The compound was identified by its ir and nmr spectra (the latter showing the proper integration ratio, 15:3:6, for the phenyl, vinyl, and methyl protons, respectively).

(Dimethylvinylgermyl)nitrosylcyanocobalt Dicarbonyl. Potassium cyanonitrosyldicarbonylcobaltate (1−)[17] (5 mmol) was dissolved in 25 ml of THF at −10°. Dimethylvinyliodogermane (1.3 g, 5 mmol) was added dropwise with stirring. After 10 min, the solvent was pumped off and the residue extracted with cold petroleum ether (bp 30–60°). The cold extract was concentrated under vacuum and cooled to −78° to yield rust brown crystals which melt below 0° and begin to decompose noticeably near 10°. The substance was too unstable for elemental analysis, but the ir and nmr spectra, obtained in fresh, cold solutions, support the formulation given.

Results and Discussion

All of the compounds were readily prepared by treating the vinylgermanium halide with the appropriate transition

---

(7) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(8) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Horok, *J. Amer. Chem. Soc.*, 83, 1601 (1961).

(10) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 82, 4438 (1960).

(11) G. R. Knox and P. L. Pauson, *Z. Naturforsch. B*, 20, 73 (1965).

(12) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

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

(14) W. Hieber and H. Beutner, *Z. Anorg. Allg. Chem.*, 320, 101 (1963).

(15) R. C. Job and M. D. Curtis, *Inorg. Nucl. Chem. Lett.*, 8, 251 (1972).

(16) F. E. Brinkman and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, 11, 24 (1959).

(17) R. Nast and N. Rohmer, *Z. Anorg. Allg. Chem.*, 285, 280 (1956).

Table I. Properties of (Dimethylvinylgermyl)metal carbonyls[a]

Compd	Color, state	Mp or bp, °C	ν(-C=C-), cm^{-1}	ν(CO), cm^{-1} (solvent)
$Me_2ViGeMoCp(CO)_3$	Pink crystals	47–48		2010 vs, 1938 s, 1915 vs (C_6H_{12})
$Me_2ViGeMn(CO)_5$	Yellow oil	63 (0.2 Torr)	1585 w	2095 m, 2044 sh, 1985 s (neat)
$Me_2ViGeMn(CO)_4(PPh_3)$	Yellow platelets	119–121	1586 w (KBr)	2057 w, 1993 w, 1955 vs, 1929 w (C_6H_{12})
$Me_2ViGeFeCp(CO)_2$	Orange oil	87 (0.2 Torr)		1996 s, 1940 s (CH_2Cl_2)
$Me_2ViGeFeNO(CO)_3$	Yellow oil		ν(NO) 1779 s	2074 s, 2000 m, 1977 vs (C_6H_{12})
$Me_2ViGeCo(CO)_4$	Pale brown oil	70 (110 Torr)		2092 s, 2030 s, 1992 vs (C_6H_{12})
$Me_2ViGeCo(CO)_3(PPh_3)$	Pale yellow crystals	155 dec	1580 w	2000 w, 1935 s
$Me_2ViGeCo(CN)(NO)(CO)_2$	Rust brown crystals	<0	1595 w	2105 m, 2038 s, 1991 s, ν(NO) 1770 s (pentane)

[a] Vi = vinyl, Cp = cyclopentadienyl, Ph = phenyl.

Table II. Chemical Shifts and Coupling Constants Determined by LAOCN3[a]

Compd	δ(CH_3)	δ(H^1)	δ(H^2)	δ(H^3)	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
$Me_2ViGeFeCp(CO)_2$	0.52	5.43	5.70	6.40	3.2	16.6	11.7
$Me_2ViGeMnPPh_3(CO)_4$	0.63	5.50	5.82	6.72	3.5	19.1	13.4
$Me_2ViGeMn(CO)_5$	0.65	5.57	5.92	6.65	3.3	18.9	13.0
$Me_2ViGeMoCp(CO)_3$	0.66	6.57	5.85	6.65	3.0	19.0	13.3
$Me_2ViGeCo(CN)(NO)(CO)_2$[b]	0.76	5.98	6.15	6.33	3	19	13
$Me_2ViGeCo(CO)_3PPh_3$	0.77						
$Me_2ViGeCo(CO)_4$	0.82	5.72	5.97	6.67	3.1	18.7	13.2
$Me_2ViGeFeNO(CO)_3$	0.87	5.72	5.98	6.68	2.9	18.7	13.0
$ViCl_3Ge$[b]		6.23	6.35	6.40	3	19	13

[a] Chemical shifts are in ppm downfield from TMS; coupling constants are in Hz. [b] Estimated values for vinyl chemical shifts and coupling constants.

metal anion. Because of the thermal instability of the products arising from the syntheses involving the nitrosyltricarbonyliron and cyanonitrosyldicarbonylcobalt anions, these reaction mixtures were kept cold. The properties of the compounds prepared for this study, summarized in Table I, are similar to other trialkylgermane derivatives of metal carbonyls.[18-22]

Because of the extreme instability of the nitrosyl derivatives, we were unable to obtain elemental analyses. However, the ir spectrum of (dimethylvinylgermyl)nitrosyliron tricarbonyl is essentially the same as that of (triphenylgermyl)nitrosyliron tricarbonyl in which the NO group is equatorial.[23] The spectrum of (dimethylvinylgermyl)nitrosylcyanocobalt dicarbonyl closely resembles those of the tricarbonylnitrosyliron derivatives, as would be expected if the NO group were equatorial and the stretching frequency of the cyano group were in the CO stretching region.

The nmr spectra of several of the complexes were analyzed by computer[24] (Table II). No simple relationship between the coupling constants or the chemical shifts of the vinylic protons and the substituent metal is apparent. However, the chemical shifts of the methyl protons increase monotonically with decreasing nucleophilicity[25] of the metal carbonyl group. The chemical shifts do not parallel the group electronegativities[26] of the metal carbonyls. From the relation between the chemical shift and nucleophilicity, it is predicted that tricarbonylnitrosylferrate(1−) should be slightly less nucleophilic and that dicarbonylcyanonitrosylcobaltate(1−) slightly more nucleophilic than tetracarbonylcobaltate(1−).

While σ-allyl complexes are extremely unstable with respect to loss of carbonyl and rearrangement to π-allyl complexes,[1] the vinylgermyl complexes show no tendency to undergo such rearrangement. Instead, transition metal carbonyl dimers, formed by scission of the germanium-metal bond, are the most common products formed when these complexes are subjected to photolysis or pyrolysis.

Thus photolysis of $(CH_3)_2(C_2H_3)GeMo(CO)_3Cp$ gave low yields of cyclopentadienylmolybdenum dicarbonyl dimer (V) and cyclopentadienylmolybdenum tricarbonyl dimer. The mode of formation of V is not known.

$$(\pi\text{-}C_5H_5)(CO)_2Mo{\equiv}Mo(CO)_2(\pi\text{-}C_5H_5)$$

V

The tetracarbonyl exhibits only a single peak for the cyclopentadienyl ligand at δ 4.7 ppm in the nmr spectrum, and the mass spectrum has Mo_2 isotope patterns at *m/e* 434 (21), 406 (10), 378 (4), 350 (2), and 322 (100) representing $Cp_2{}^{96}Mo_2(CO)_n$ (n = 4, 3, 2, 1, 0), respectively (relative intensity in parentheses). The ir spectrum shows two peaks, 1898 and 1841 cm^{-1}, in the CO stretching region. These properties are to be compared with those of $(C_5Me_5)_2Mo_2(CO)_4$, the analogous pentamethylcyclopentadienyl compound reported by King, *et al.*,[27,28] and formulated with a Mo≡Mo triple bond. The pentamethyl derivative absorbed in the ir spectrum at 1874 and 1846 cm^{-1} and shows essentially the same relative intensities for the mass spectrum peaks corresponding to loss of CO. The tetracarbonyl V is thus formulated with a Mo≡Mo triple bond.

Dimanganese decacarbonyl was the only isolable product from the photolysis of (dimethylvinylgermyl)manganese pentacarbonyl. The $Mn_2(CO)_{10}$ may arise from recombination of $Mn(CO)_5$ radicals formed by scission of the Ge-Mn bond (eq 3, 4).

$$(CH_3)_2(C_2H_3)GeMn(CO)_5 \xrightarrow{h\nu} (CH_3)_2(C_2H_3)Ge\cdot + Mn(CO)_5 \qquad (3)$$

$$2Mn(CO)_5 \longrightarrow Mn_2(CO)_{10} \qquad (4)$$

---

(18) W. Jetz, P. Simons, J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 5, 2217 (1966).

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

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

(21) R. E. J. Bichler, M. R. Booth, H. C. Clark, and B. K. Hunder, *Inorg. Syn.*, 12, 60 (1970).

(22) M. D. Curtis, *Inorg. Chem.*, 11, 801 (1972).

(23) A. J. Cleland, S. A. Fieldhouse, B. H. Freedland, C. D. M. Mann, and R. J. O'Brien, *J. Chem. Soc. A*, 736 (1971).

(24) A. A. Bothner-By and S. Costellano, LAOCN3, Mellon Institute.

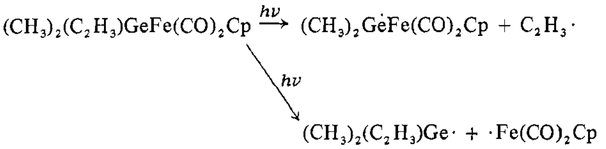
(25) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 88, 5121 (1966).

(26) R. P. Stewart and P. M. Treickel, *J. Amer. Chem. Soc.*, 92, 2711 (1970).

(27) R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, 94, 3773 (1972).

(28) R. B. King and M. Bisnette, *J. Organometal. Chem.*, 8, 287 (1967).

The primary product formed in the photolysis of $(CH_3)_2(C_2H_3)GeFe(CO)_2Cp$ is μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienylcarbonyliron)(*Fe-Fe*), VII. We postulate that this compound forms *via* the sequence of reactions 5-7. Bis(cyclopentadienyldicarbonyliron)dimethylgermane (VI) has been prepared by an independent route and shown to form VIII very rapidly and quantitatively upon photolysis.[29]

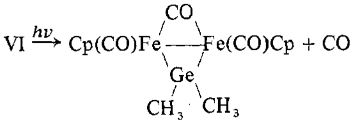


$$\mathrm{(CH_3)_2(C_2H_3)GeFe(CO)_2Cp \xrightarrow{h\nu} (CH_3)_2\dot{G}eFe(CO)_2Cp + C_2H_3\cdot} \quad (5)$$

$$\xrightarrow{h\nu} \mathrm{(CH_3)_2(C_2H_3)Ge\cdot + \cdot Fe(CO)_2Cp}$$

$$\mathrm{(CH_3)_2\dot{G}eFe(CO)_2Cp + \cdot Fe(CO)_2Cp \rightarrow (CH_3)_2Ge[Fe(CO)_2Cp]_2} \quad (6)$$

VI



$$\mathrm{VI \xrightarrow{h\nu} Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}Ge(CH_3)_2)Fe(CO)Cp + CO} \quad (7)$$

VII

The cyclopentadienyliron dicarbonyl radicals may also combine to form the tetracarbonyl dimer, which upon irradiation loses carbon monoxide to form cyclopentadienyliron carbonyl tetramer (eq 8, 9), thus accounting for all the carbonyl products isolated.

$$\mathrm{2Fe(CO)_2Cp \rightarrow [CpFe(CO)_2]_2} \quad (8)$$

$$\mathrm{[CpFe(CO)_2]_2 \xrightarrow{h\nu} [CpFe(CO)]_4 + 4CO} \quad (9)$$

Compound VII exists in two isomeric forms as evidenced by the ir and nmr spectra (Figure 1). In the trans isomer, both germanium methyl groups are in equivalent magnetic environments and give a single peak. The methyl groups are in different environments in the cis isomer, however. One is adjacent to two C_5H_5 rings, while the other is adjacent to the two terminal carbonyl groups. Thus, the two peaks at 1.50 and 1.33 ppm are assigned to the cis isomer methyl groups, while the resonance from the trans isomer methyl appears at 1.40 ppm. The cyclopentadienyl resonances appear at 4.31 (trans) and 4.12 (cis) ppm. The ratio of cis to trans isomer was determined by integration to be 4:1. The ir spectrum may also be interpreted in terms of the two isomers. A strong set of peaks at 1980 (s), 1941 (m), and 1788 (m) cm^{-1} is assigned to the cis isomer while the corresponding bands for the trans isomer are found at 1955 (w), 1946 (sh), and 1791 (sh) cm^{-1}. It is noteworthy that irradiation of pure VI also gives a 4:1 mixture of cis and trans VII.[29]

Since it appeared that cleavage of the germanium-metal bond was the predominant reaction mode during the photolysis, triphenylphosphine derivatives, (dimethylvinylgermyl)(triphenylphosphine)manganese tetracarbonyl and (dimethylvinylgermyl)(triphenylphosphine)cobalt tricarbonyl, were synthesized in order to stabilize the germanium-metal bond. However, the triphenylphosphine derivatives were so stable that loss of carbonyl was not observed except under drastic conditions which caused total decomposition. Indeed, the metal-carbonyl bond was so stable that the normal rearrangement of σ-allyl to π-allyl complex was not observed (eq 10) (in contrast, $(\sigma\text{-}C_3H_5)Co(CO)_4$ spontaneously forms $(\pi\text{-}C_3H_5)Co(CO)_3$ at room temperature).

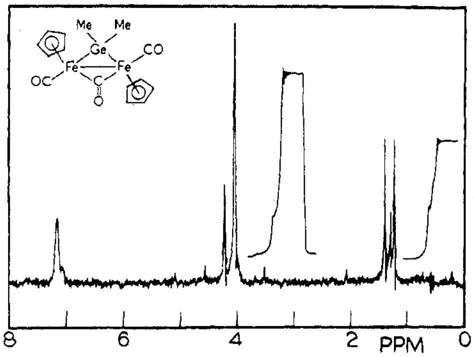


Figure 1. The 60-MHz spectrum of a 4:1 mixture of cis and trans VI in C_6D_6 solution.

$$\mathrm{(\sigma\text{-}C_3H_5)Co(CO)_3PPh_3 \xrightarrow{75^\circ} [Co(CO)_3PPh_3]_2 + \ldots} \quad (10)$$

The nitrosyl derivatives, (dimethylvinylgermyl)nitrosyliron tricarbonyl and (dimethylvinylgermyl)cyanonitrosylcobalt dicarbonyl, were then prepared with the aim of labilizing the carbonyl groups. These complexes were both extremely air sensitive. Their thermal stability was so low that each decomposed quite rapidly at room temperature to give, among other things, $Fe(CO)_5$, $Fe(CO)_2(NO)_2$, and $Co(CN)_2$.

The results presented in this paper show that the π-germaallyl analogs are not sufficiently stable to compete with alternate decomposition paths, particularly rupture of the germanium-metal bond. This is in keeping with the apparent instability of p_π-p_π bonds between carbon and its congeners.[4]

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The mass spectrometer was purchased with the aid of the National Science Foundation, Grant GP-8345.

Registry No. $(CH_3)_2(C_2H_3)GeBr$, 35935-19-4; $(CH_3)_2(C_2H_3)GeI$, 35935-18-3; $NaCpMo(CO)_3$, 12107-35-6; $NaMn(CO)_5$, 13859-41-1; $NaCpFe(CO)_2$, 41517-33-3; $NaFe(CO)_3NO$, 25875-18-7; $NaCo(CO)_4$, 14878-28-5; $NaCo(CO)_3(PPh_3)$, 33570-17-1; $KCo(CN)(NO)(CO)_2$, 15810-59-0; $Me_2ViGeMoCp(CO)_3$, 41517-37-7; $Me_2ViGeMn(CO)_5$, 41539-04-2; $Me_2ViGeMn(CO)_4(PPh_3)$, 41539-05-3; $Me_2ViGeFeCp(CO)_2$, 41517-10-6; $Me_2ViGeFeNO(CO)_3$, 41517-09-3; $Me_2ViGeCo(CO)_4$, 41539-06-4; $Me_2ViGeCo(CO)_3(PPh_3)$, 41539-07-5; $Me_2ViGeCo(CN)(NO)(CO)_2$, 41539-08-6; *cis*-μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienyliron)(*Fe-Fe*), 36180-77-5; *trans*-μ-carbonyl-μ-dimethylgermyl-bis(cyclopentadienyliron)(*Fe-Fe*), 36543-58-5.

---

(29) M. D. Curtis and R. C. Job, *J. Amer. Chem. Soc.*, **94**, 2153 (1972).