Journal of Organometallic Chemistry, **144 (1978) 389–397**
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Transition-metal Carbonyl Derivatives of the Germanes. Part VIII.* The Synthesis and Characterization of Bis(trimethylgermyl)tetracarbonyliron

By Alan Bonny and Kenneth M. MacKay, School of Science,
University of Waikato, Hamilton, New Zealand.

(Received August Ist 1977)

SUMMARY

Bis(trimethylgermyl)tetracarbonyliron (I) has been synthesized by reaction of Me_3GeCl with $Na_2Fe(CO)_4$. Vibrational, ^1H NMR and mass spectra for I are compared with hydride and methyl substituted analogues, and are best interpreted in terms of a predominance of the *cis* isomer. I rearranges *in vacuo*, eliminating $(Me_3Ge)_2O$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

We have elsewhere[1,2] reported the syntheses and spectroscopic characterizations of the complexes $(Me_xGeH_{3-x})Fe(CO)_4$ when x = 1 and 2. A recent ^{13}C NMR study[3] which included data for the complex when x = 3, bis(trimethylgermyl)tetracarbonyliron(I), has prompted this paper concerning our independent investigation of the complex. We were interested to examine whether I could be synthesized *via* the well-established alkali metal-halide elimination route (a route which did not yield the silyl analogue[4]), and to compare spectroscopic properties with the mixed hydride and methyl substituted derivatives.

---

*Part VII is ref. 1.

Experimental

Manipulations and NMR, mass and IR measurements were made as described earlier.[2] The Raman spectrum of I (enclosed in a thin-walled capiliary) was recorded using a JASCO R300 spectrometer operating at 488 nm with 21 mW power.

Synthesis of I. In one reaction,of 21.2 mmol of Me_3GeCl was allowed to react with a pentane slurry of the anion prepared[5] from 17.4 mmol of Na and 2.86 mmol of $Fe_3(CO)_{12}$. After 4 min. at room temperature, volatiles were fractionated yielding 0.07 mmol of gas which was incondensable at $-196^{\circ}C$, unreacted Me_3GeCl with $(Me_3Ge)_2O$, Me_3GeH and $Fe(CO)_5$ at $-196^{\circ}C$ (all identified by mass spectrometry and IR), and colourless $(Me_3Ge)_2Fe(CO)_4$ (I) contaminated with traces of $(Me_3Ge)_2O$ and $Me_3Ge(H)Fe(CO)_4$ at $-15^{\circ}C$. Further I was sublimed from the reaction vessel using a cold finger. The total yield was ca. 400 mg (ca. 1 mmol, 9% yield based on Me_3GeCl taken initially). I was characterized by mass, vibrational and ^1H NMR spectroscopy. The mass spectrum was obtained using a solid insertion probe and the infra-red spectrum recorded at ca. $-196^{\circ}C$ using a cold cell, since with gaseous sampling only spectra of the decomposition products $Fe(CO)_5$[6] and $(Me_3Ge)_2O$[7] were obtained*. For I, the molecular ion family was found at m/e = 396-410 $\{[C_{10}H_{18}O_4{}^{198-208}(Ge_2Fe)]^+ = 396\text{-}410\}$. Consistent with a cis configuration for I, the solution infra-red spectrum exhibits four carbonyl stretching absorptions with the one at highest energy matched by a polarized Raman mode (νCO_{axial}, a_1). One Raman mode with a degree of polarization was found at 200 cm^{-1} ($\nu GeFe$, $a_1 + b_1$). Freshly sublimed I exhibited a single ^1H NMR resonance at 9.39 tau in CS_2 solution measured from TMS internal reference. However, after standing at room temperature for several weeks in a sealed tube, a new singlet was observed at 9.74 tau which was assigned to $(Me_3Ge)_2O$ {cf. 9.74 tau measured independently}. Freshly sublimed colourless crystals of I were found to darken rapidly during glovebox handling in an exothermic reaction which produced $Fe(CO)_5$,

---

* when the IR cold cell was warmed to room temperature only the absorptions due to $Fe(CO)_5$ and $(Me_3Ge)_2O$ were observed.

$(Me_3Ge)_2O$ and $Fe_3(CO)_{12}$ (all identified by mass and IR spectroscopy).

Traces of a complex considerably more volatile than I (collected at -15°C during a short fractionation) were identified tentatively as $Me_3Ge(H)Fe(CO)_4$ on the basis of volatility and of the following infra-red spectrum (ca. -196°C, cm^{-1}): 3000 w, 2950 w br, 2900 w, 2850 vw (νCH), 2098 m (νCO_{axial}, a'), 2066 vw, 2059 w, 2037 w sh, 2032 m, 2023 vs (νCO, 2a' + 2a"), 1990 w br ($\nu^{13}CO$), 1405 vw, 1245 vw, 1210 vw br, 1130 mw br (δCH_3), ca. 935 w br, 890 w, 832 w, 807 vw, 759 w (ρCH_3), 726 mw (δFeH), 647 mw, 624 mw (δFeCO), 594 w, 562 w (νGeC).

Discussion

From the route:

$$2Me_3GeCl + Na_2Fe(CO)_4 \rightarrow (Me_3Ge)_2Fe(CO)_4 + 2NaCl$$

we have isolated and characterized bis(trimethylgermyl)tetracarbonyliron(I). The relatively low yield is best explained by the particularly air-sensitive nature of I; transfers of residues containing the bulk of I were made in a glovebox to sublimation vessels, and we have shown that I is degraded rapidly under these conditions. These observations for I are matched by the earlier report that $(Et_3Ge)_2Fe(CO)_4$ {synthesized by reaction of Et_3GeH with $Fe(CO)_5$}, is 'extremely unstable'.[8] This synthesis of I *via* the well-established alkali metal-halide elimination route is in contrast to the reports that the reaction $Me_3SiX + Na_2Fe(CO)_4$* will not produce the silyl analogue, $(Me_3Si)_2Fe(CO)_4$[4].

The pattern of νCO vibrations, relative volatility, and an IR band at 726 cm^{-1} (cf. vibrations attributed to δFeH were found in this region for the complexes $H_3M'(H)Fe(CO)_4$, M'=Si[9] and Ge[10]) are preliminary evidence for $Me_3Ge(H)Fe(CO)_4$ as a by-product with I.

---

*THF was used as solvent in these reactions and it is worth noting that $(Me_3Si)_2Fe(CO)_4$, synthesized *via* a mercurial exchange route, does react rapidly with this ether.[16]

Table 1 Principal Fragments in the Mass Spectrum of I[a]

	$C_{16}H_{18}Ge_2Fe(CO)_n^+$	$C_5H_{15}Ge_2Fe(CO)_n^+$	$C_2H_xGeFe(CO)_n^+$	x = 7	6	5	4
n=4	396 - 410 mw	381 - 395 s	266 - 274 vvs	0	10	0	0
3	370 - 380 vvw[b]	353 - 367 ms	238 - 246 vs	0	10	0	0
2	342 - 352 w[b]	325 - 339 ms	210 - 218 s[c]	0	10	0	0
1	314 - 326 m	299 - 311 ms	182 - 191 ms	3	10	0	0
0	284 - 298 s-vs	271 - 281 m[b]	152 - 163 vs	0.4	10	0.3	0.4

	$C_yH_xGe_2Fe^+$ [b]		$C_yH_xGe^+$		$C_yH_xGeFe(CO)_n^+$		
y=4	255 - 265 mw	x=11	126 - 133 ms	x=8, 9 as 3:1	n=4, y=1	251 - 259 m	x=3
3			115 - 122 vvs	x-9, 10 as 32:1			
2	225 - 235 n	x=5	100 - 107 m	x=6, 7 as 1:1	n=1, y=1	166 - 177 ms	x=2-5 as 4:2:11:5
1	208 - 220 m	x=0-2	85 - 91 ms	x=3, 4, 6 as 10:1:1	n=0, y=1	136 - 147 x-vs	x=0, 2, 3 as 1:14:3
0	196 - 206 ms	x=0	70 - 77 mw	x=0-2 as 5:9:4			

Other ions observed were: Fe_2^+ [or $Fe(CO)_2^+$] 112 m; $Fe(CO)^+$ 84 m; CH_xFe^+ 69-71 m with x=0-3 as 1:1:1:10; Fe^+ 56 ms; CO^+ 28 vvs.

Metastable ions at m/e = 333 and 307 indicate the steps when n = 4→3 and 3→2 for $C_5H_{15}Ge_2Fe(CO)_n^+$ species losing CO, and at 218 for $C_2H_6GeFe(CO)_4^+$ losing CO. Loss of Me_4Ge from $C_6H_{18}Ge_2Fe(CO)_n^+$ is metastable supported for n=4 ($m^* = 182$) and n=0 ($m^* = 87$).

---

[a] Spectrum recorded at 20°C; unless otherwise indicated, envelopes are described for the $^{194-208}Ge_2Fe$, $^{124-132}GeFe$, or $^{70-76}Ge$ combinations.

[b] In these cases only the stronger $^{140-150}Ge_2$ or $^{70-76}Ge_1$ combinations are observed.

Spectroscopic Properties of I

Mass Spectrum. Table 1 lists the principal ions observed for I. As found for the complexes $(Me_xGeH_{3-x})Fe(CO)_4$; x=0[10], 1[1], and various halide derivatives thereof[11], for $(R_3Sn)_2Fe(CO)_4$, R=Me[12], Et[13], and for $(Cl_3Ge)_2Fe(CO)_4$[14], the parent molecular ion of I is weak. The bulk of the ion current is carried by the even electron fragments $Me_5Ge_2Fe(CO)_n{}^+$, n=4-0, and by the ions $C_2H_6GeFe(CO)_n{}^+$, n=4-0. These first two observations are to those made for the complexes $(Me_3Sn)_2Fe(CO)_4$[13] {for which the only ions reported were P^+ (weak)[12]; $[P-Me-n(CO)]^+$, n=0-4; Me_nSn^+, n=0-3; and Sn_2Ru^+}, and $(Et_3Sn)_2Ru(CO)_4$ where 'after a weak molecular ion there follows loss of the 4 CO groups and the organic groups to ... leave the Sn_2Ru^+ ion'[13].

The ion $Me_2GeFe(CO)_4{}^{+\cdot}$, is one of the strongest in the spectrum of I and is metastable supported to arise from:

$$(Me_3Ge)_2Fe(CO)_4{}^{+\cdot} \rightarrow Me_2GeFe(CO)_4{}^{+\cdot} + Me_4Ge$$

No ions of the type $MeGeH_xFe(CO)_4{}^+$ nor $GeH_xFe(CO)_4{}^+$ were observed for the complexes $(Me_xGeH_{3-x})_2Fe(CO)_4$, when x=0[10] and 1[1], but the only ion found for $(Me_2GeH)_2Fe(CO)_4$ was $Me_2GeFe(CO)_4{}^{+\cdot}$ [2].

Vibrational Spectrum. The pattern of νCO modes (see Table 2) makes this spectrum best interpreted in terms of a predominance of the cisoid isomer, where the expected four νCO vibrations $(2a_1 + b_1 + b_2)$ are active in both the Raman and infra-red {cf. trans isomers will have Raman/IR exclusion for the activities of these vibrations; $2a_g + a_u + b_u$ for a C_{2h} molecule, $a_{1g} + b_{1g} + e_u$ for the D_{4h} case}. Assignment of the highest energy νCO mode to the axial (a_1) vibration is firm[15]. The lowest solution infra-red absorption is attributable to $\nu CO_{eq}(b_1)$ since it has been established that $k_{ax} > k_{eq}$ for several $(R_3M')_2M(CO)_4$ complexes[16]. Of the two remaining infra-red carbonyl absorptions, the more intense (at 2005 cm^{-1}) is tentatively assigned to the b_2 vibration[8]. As found for $(Me_2GeH)_2Fe(CO)_4$[2], the low temperature solid spectrum of I is complex in the carbonyl stretching region.

The single 200 cm^{-1} band observed in the Raman spectrum of I is also

Table 2

The Vibrational Spectrum of I (cm^{-1})

IR				Raman[c]		Assignment
Solid[a]		Solution[b]				
2970	vw			2980	mw vbr	νCH
2910	w			2908	w br	
2089	w					νCO
2061	w sh					
2056	s	2067	s	2067	w p	νCO_{axial} (a_1)
2046	w sh					$\nu^{13}CO$ (in-phase)
2013.3	mw					νCO
1995.3	mw					
1980.5	w					
1971.1	mw	2005	s			νCO_{axial} (b_2)
ca. 1953	vbr sh	2000	m sh			νCO_{eq} (a_1)
1941	vs	1983	vs			νCO_{eq} (b_1)
1918	w					$\nu^{13}CO$ (out-of-phase)
1242	vw sh			1245	vw sh	δCH_3 (symmetric)
1226	w			1232	w	
832	vw sh					ρCH_3
829	mw br					
819	w sh					
755	w br					
624	w sh			627	w p	δFeCO (a_1)
615	s					δFeCO
595	w					νGeC
585	vw			587	s dp	
558	w					δFeCO
544	w					
512	w					
				445	ms p	νFeC (a_1)
				200[d]	vs	νGeFe (a_1 + b_1)
				105	vvs	δCGeFe, δCFeGe, and δGeFeGe

---

[a] Data obtained using a conventional cold cell; sample held at ca. -196°C.

[b] N-pentane solution, reference 21 (carbonyl region only).

[c] Data for a liquid sample at ambient temperature.

[d] A change was noted in the contour of this band during polarization studies consistent with the superimposition of the a_1 and b_1 νGeFe modes.

consistent with a major cis configuration; the a_1 and b_1 νGeFe vibrations appear to superimpose and thus the contour of the resonance was altered in polarization studies. {cf. 13 and 15 cm^{-1} separations were found between the a_1 and b_1 νFeGe vibrations of the complexes cis $(Me_xGeH_{3-x})_2Fe(CO)_4$, x=0[10] and 1[1].} The rest of the vibrational spectrum assignment (Table 2) follows earlier discussion for the complexes $(Me_xGeH_{3-x})_2Fe(CO)_4$, x=1[1] and 2[2].

^1H NMR. The resonance observed at 9.39 tau for I in CS_2 solution compares with data reported for $(Me_2GeH)_2Fe(CO)_4$ (9.36 tau, CS_2[2]), $(Me_3Si)_2Fe(CO)_4$ (9.53 tau, C_6D_6[17]), $(Me_3Ge)_2Ru(CO)_4$ (9.46 tau, C_6H_6[18]) and other transition metal germyls (see Table 1 of ref. 2), and again is consistent with the predominance of one isomer {cf. two ^1H NMR resonances were reported for cis and trans $(Me_3Ge)_2Os(CO)_4$ at 9.37 and 9.27 tau respectively[18]}.

We have observed $(Me_3Ge)_2O$ as a product from the decomposition of I, both in the presence of oxygen traces and in vacuo. For the latter situation our preliminary ^1H NMR evidence, together with observations during IR spectral handing, and mass and IR spectra recorded for gaseous samples taken from fresh samples of I, indicate that the oxygen in these cases arises through degradation of the iron (carbonyl) moiety itself. No evidence was found for oxide species from the complexes $(Me_xGeH_{3-x})_2$-$Fe(CO)_4$ x=0 and 1 under similar conditions. The formation of silyl-oxides is well established for silicon analogues,[1] but this type of reaction for germanium (in the exclusion of air) has been reported in only one other instance; $(Ph_2Ge)_2Fe_2(CO)_7$ completely converts to $O[GePh_2Fe(CO)_4]_2$ in a reaction where the only source of oxygen for the digermyl oxide linkage appeared to be the oxygen of a carbonyl group. As with these studies, the fate of the residual carbon atom was not established.[20]

ACKNOWLEDGEMENTS

We thank the N.Z.U.G.C. and the William Georgetti Trust for scholarships (A.B.) and for grants to purchase the C60-HL and P.E. 180

instruments, and Professor W.A.G. Graham for communicating the solution IR data for I after initial submission of this paper. We are grateful to Dr. P. Holland of the Ruakura Agricultural Centre, and Dr. M. J. Taylor of the University of Auckland for facilities to measure mass and Raman spectra.

REFERENCES

1. A. Bonny and K. M. MacKay, in press DAL 7/1336.
2. A. Bonny and K. M. MacKay, in press DAL 7/1131.
3. L. Vancea, R. K. Pomeroy and W.A.G. Graham, J. Amer. Chem. Soc., 98 (1976) 1407.
4. M. A. Nasta and A. G. MacDiarmid, J. Amer. Chem. Soc., 93 (1971) 2813; M. A. Nasta, A. G. MacDiarmid and F. E. Saalfield, J. Amer. Chem. Soc., 94 (1972) 2449; M. J. Bennett, W.A.G. Graham, R. A. Smith and R. P. Stewart, Jr., J. Amer. Chem. Soc., 95 (1973) 1684.
5. H. Behrens and R. Weber, Z. Anorg. Allg. Chem., 281 (1955) 190; Chem. Abstr., 50 (1956) 5441b.
6. W. F. Edgell, W. E. Wilson and R. Summitt, Spectrochim. Acta, 19 (1963) 863; R. E. Winters and R. W. Kiser, Inorg. Chem., 3 (1964) 699.
7. M. P. Brown, R. Okawara and E. G. Rochow, Spectrochim. Acta, 16 (1960) 595; F. Glockling and J.R.C. Light, J. Chem. Soc. (A), (1968) 717.
8. O. Kahn and M. Bigorgne, J. Organomet. Chem., 10 (1967) 137.
9. B. J. Aylett, J. M. Campbell and A. Walton, J. Chem. Soc. (A), (1969) 2110.
10. S. R. Stobart, J. Chem. Soc. Dalton Trans., (1972) 2442.
11. A. Bonny and K. M. MacKay, submitted for publication (J. Chem. Soc. Dalton Trans.).
12. J. D. Cotton, S.A.R. Knox and F.G.A. Stone, Chem. Comm., (1967) 965.
13. J. D. Cotton, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. (A), (1968) 2758.
14. R. Kummer and W.A.G. Graham, Inorg. Chem., 7 (1968) 1208.
15. F. A. Cotton and C. S. Kraihanzel, J. Amer. Chem. Soc., 84 (1963) 4432; L. E. Orgel, Inorg. Chem., 1 (1962) 25.

16. J. Dalton, I. Paul and F.G.A. Stone, J. Chem. Soc. (A), (1968) 1215; F. T. Delbeke, E. G. Claeys, G. P. Vander Kelen and Z. Eeckhaut, J. Organometal. Chem., 25 (1970) 213; R. K. Pomeroy, R. S. Gay, G. O. Evans and W.A.G. Graham, J. Amer. Chem. Soc., 94 (1972) 272.

17. W. Jetz and W.A.G. Graham, J. Organometal. Chem., 69 (1974) 383.

18. S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. (A), (1971) 2874.

19. B. J. Aylett and J. M. Campbell, J. Chem. Soc. (A), (1969) 1910; J. S. Allinson, B. J. Aylett and H. M. Colquhoun, J. Organometal. Chem., 112 (1976) C7.

20. D. Dong, A. S. Foust, Jr., and W.A.G. Graham, paper 184, Abstracts VIth International Organometallic Conference, Amherst, Massachusetts, August 1973.

21. W.A.G. Graham and W. Jetz, unpublished work.