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Germyl(digermanyl)tetracarbonyliron: a Route to Mixed Ligand Iron Tetracarbonyls

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While many Group IV-iron triad compounds $(R_3M')_2M(CO)_4$ [M′ = Si, Ge, Sn, Pb; M = Fe, Ru, Os] are known, species with two different R_3M' substituents are limited to (a) products of a few substitution reactions such as $(MeGeH_2)(MeGeHCl)Fe(CO)_4$ [1] from $(MeGeH_2)_2Fe(CO)_4$ and (b) compounds like $(Me_3Si)(Me_3Sn)Ru(CO)_4$ [2] derived from the $R_3M'Ru(CO)_4^-$ anion formed by cleaving the dimer. This latter route is not available for iron compounds.

In our study of the exchange of metal carbonyl moieties on germanes [3], we found that a 1:1 reaction between $Mn(CO)_5^-$ and $(GeH_3)_2Fe(CO)_4$ gave a good yield of $GeH_3Mn(CO)_5$ implying the near-quantitative formation of $(GeH_3)Fe(CO)_4^-$. This anion provides a new route to iron tetracarbonyl derivatives with two different ligands.

Experimental

$(Ge_2H_5)_2Fe(CO)_4$ [4] (165.5 mg, 0.349 mmol) was condensed onto an ether solution of anion formed from $Mn_2(CO)_{10}$ (71.8 mg, 0.184 mmol) by the action of excess sodium amalgam. After 30 minutes, fractionation yielded $Ge_2H_5Mn(CO)_5$ (96.2 mg, 0.279 mmol, 79.9%) [5]. To the residue in ether was added excess GeH_3Br, the mixture was shaken for 30 minutes and then fractionated. At −23 °C there was recovered germyl(digermanyl)tetracarbonyliron, $(GeH_3)(Ge_2H_5)Fe(CO)_4$. This is a colourless liquid, just volatile in a vacuum line, which is stable indefinitely in the dark. It slowly turns yellow in artificial light and a solution in cyclohexane was completely decomposed after 30 minutes in strong sunlight.

The compound was identified spectroscopically. The parent ion envelope in the mass spectrum spans m/e = 404–385 with $(P-H)^+$ about 20% of the intensity of P^+ ($C_4H_8O_4Fe^nGe_3$ = 408 for n = 76 and 386 for n = 70). Principal fragment families were $Ge_3H_xFe(CO)_n^+$ (carrying 36% of the ion current and with $n = 4 \ll 3 < 1 < 2 < 0$ in intensity), $Ge_2H_yFe(CO)_n^+$ (32% ion current, $n = 4 < 2 < 3 < 1 < 0$) and $GeH_zFe(CO)_n^+$ (19% ion current, $n = 4 < 2 < 1 < 3 < 0$). Minor contributors were $HFe(CO)_n^+$, $Fe(CO)_n^+$, $Ge_3H_x^+$, $Ge_2H_y^+$ and GeH_z^+ (n = 0 to 4, x = 0 to 8, y = 0 to 5, z = 0 to 3).

The ^1H n.m.r. spectrum showed strongly overlapping signals which could be analysed as a singlet ($\tau GeH_3Fe = 6.52$) superimposed on an A_3B_2 pattern ($\tau GeH_3 = 6.60$, $\tau GeH_2 = 6.55$, $^3J = 4.0$ Hz) by comparison with $(GeH_3)_2Fe(CO)_4$ ($\tau GeH_3 = 6.50$ [6]) and $(Ge_2H_5)_2Fe(CO)_4$ ($\tau GeH_3 = 6.53$, $\tau GeH_2 = 6.48$, $^3J = 4.3$ Hz [4]).

The Table shows the most important vibrations, which indicate the *cis* configuration.

TABLE. Principal Vibrations of $(GeH_3)(Ge_2H_5)Fe(CO)_4$ (cm^{-1}).*

2090 s	νCO	679 m	GeH_2 wag
2055 m	νGeH	617 s	$\delta FeCO$
2023 vs	νCO	434 s,p	νFeC
2007 vvs	νCO	268 m,p	$\nu GeGe$
870 w	asym. GeH_x bends	223 vs,p	$\nu GeFe^c$
860 w		202 s,p	$\nu GeFe^d$
813 m	$\delta GeH_3{}^a$	104 s,dp	skeletal bends
790 m	$\delta GeH_3{}^b$		

*Values above 450 cm^{-1} from infrared spectrum of cyclohexane solution: those below from Raman spectrum of neat liquid.
[a] Symmetric bend of GeH_3 group on Fe. [b] Symmetric bend of GeH_3 group on GeH_2. [c] Of $H_3Ge–Fe$, compare 229 vs,p and 216 m,dp for $(GeH_3)_2Fe(CO)_4$ [6]. [d] Of $H_5Ge_2–Fe$, compare 211 vs,p and 198 m,dp for $(Ge_2H_5)_2Fe(CO)_4$ [4].

In similar reactions, preliminary evidence was found indicating the formation of $(GeH_3)(SiH_3)Fe(CO)_4$ starting either from $(GeH_3)_2Fe(CO)_4$ or from $(SiH_3)_2Fe(CO)_4$. The silyl–germyl species was accompanied, and appeared to convert into, a second component which could not be separated but the weak parent ion envelope in the mass spectrum at m/e = 269–277 ($C_4H_6O_4SiGeFe$ = 272–280 with $(P-3H)^+$ predominating), proton resonances with $\tau SiH_3 = 6.35$, $\tau GeH_3 = 6.63$, and infrared bands at 2099 m, 2041 vs, 2019 vs (νCO), 958 w (δSiH_3) and 815 m (δGeH_3) are all compatible with $(GeH_3)(SiH_3)Fe(CO)_4$.

Discussion

Germyl(digermanyl)tetracarbonyliron is intermediate in volatility, stability, and spectroscopic properties between di(germyl)- and bis(digermanyl)-tetracarbonyliron. For example, the strong symmetric GeH_3–Fe deformation is at the average of the in- and out-of-phase symmetric deformations of

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$(GeH_3)_2Fe(CO)_4$ [6] at 835 and 809 cm^{-1}. Similarly, the GeH_2 wag at 679 cm^{-1} compares with 692 and 662 cm^{-1} found [4] for the wagging modes of $(Ge_2H_5)_2Fe(CO)_4$. The base peak in the mass spectrum is $Ge_3H_xFe^+$, compare with $Ge_2H_xFe^+$ as the base peak for $(GeH_3)_2Fe(CO)_4$ and with $Ge_4H_xFe^+$ for $(Ge_2H_5)_2Fe(CO)_4$.

The preparation of $(GeH_3)(Ge_2H_5)Fe(CO)_4$ and the indication of $(GeH_3)(SiH_3)Fe(CO)_4$ validates this route to unsymmetrically substituted tetracarbonyliron compounds. Such species will be of value in elucidating condensations to higher molecular weight species [1] such as $[R_2GeFe(CO)_4]_2$.

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