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**The Preparation and Structure of a Germanium-Bridged Iron Carbonyl Complex,  $[(\text{CH}_3)_2\text{Ge}]_3\text{Fe}_2(\text{CO})_6$**

Sir:

Although the reaction of silanes with metal carbonyls has been shown to be rather general in scope,<sup>1</sup> related reactions of germanes and stannanes have been little studied. Germane was observed to react with manganese carbonyl at 140° to form small amounts of  $\text{H}_2\text{Ge}[\text{Mn}(\text{CO})_5]_2$ ,<sup>2</sup> while more recently methylstannanes have been found to react with iron pentacarbonyl to afford polynuclear tin-iron compounds.<sup>3</sup> As part of a general investigation of compounds between transition metals and main group metals and metalloids,<sup>4</sup> we are currently examining reactions of this type in detail. One such reaction has given rise to a novel germanium-iron cluster compound, which occasions this preliminary report.

Excess dimethylgermane reacted with triiron dodecacarbonyl during 5 hr at 65° forming a dark red mixture. From hexane extracts of the reaction products, a red crystalline compound was isolated, and it is currently under investigation. Subsequent extraction of the reaction products with dichloromethane afforded yellow needles of a compound having the empirical formula  $(\text{CH}_3)_6\text{Ge}_3\text{Fe}_2(\text{CO})_6$ .<sup>5</sup> The nmr showed a single sharp resonance at  $\tau$  8.72, and the infrared spectrum showed only two strong carbonyl stretching bands at 2007 and 1968  $\text{cm}^{-1}$  (cyclohexane solution). A highly symmetric structure was thus indicated, and the spectroscopic data were consistent with a molecule derived from diiron enneacarbonyl by replacing the bridging carbonyls with dimethylgermanium groups.

X-Ray crystallographic data confirm that the molecule has  $3/m$  symmetry. The details of the structural solution will be presented later; we wish to include here the more important features of the molecular structure, taken from an advanced stage in the structure refinement.

Crystal data are  $a = 9.764 \pm 0.006 \text{ \AA}$ ,  $c = 11.90 \pm 0.02 \text{ \AA}$ , for space group  $\text{P6}_3/\text{m}$  with two molecules per unit cell. Intensity data were collected on a PAILRED automated diffractometer using crystal monochromatized Mo  $\text{K}\alpha$  radiation. A total of 304 unique reflections from 11 reciprocal lattice layers perpendicular to  $c$  were measured as significantly above background.

(1) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).  
 (2) A. G. Massey, A. J. Park, and F. G. A. Stone, *ibid.*, **85**, 2021 (1963).

(3) J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc.*, **A**, 264 (1967).

(4) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **7**, 771 (1968), and earlier papers cited therein.

(5) The formula was established mass spectrometrically from a consideration of the isotope pattern and by determination of the exact mass of the molecular ion. Satisfactory microanalytical data were also obtained.

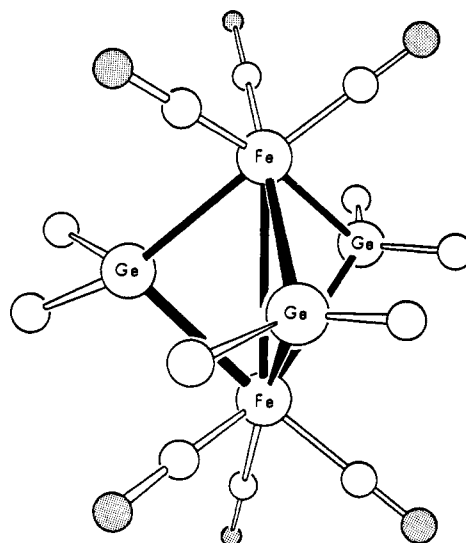


Figure 1. The molecular structure of  $[(\text{CH}_3)_2\text{Ge}]_3\text{Fe}_2(\text{CO})_6$ . Important bond lengths, with standard deviations, are Fe-Ge =  $2.398 \pm 0.005 \text{ \AA}$ ; Fe-Fe =  $2.74 \pm 0.01 \text{ \AA}$ ; Ge-CH<sub>3</sub> (mean) =  $2.02 \pm 0.03 \text{ \AA}$ ; Fe-CO =  $1.77 \pm 0.02 \text{ \AA}$ ; Fe-C-O =  $1.15 \pm 0.02 \text{ \AA}$ ; nonbonding Ge-Ge =  $3.41 \pm 0.01 \text{ \AA}$ . Some bond angles are Fe-Ge-Fe,  $69.8 \pm 0.2^\circ$ ; Fe-Fe-Ge,  $55.1 \pm 0.2^\circ$ ; Ge-Fe-CO,  $86.1 \pm 0.7^\circ$ ; CH<sub>3</sub>-Ge-CH<sub>3</sub>,  $105.4 \pm 1.0^\circ$ ; CH<sub>3</sub>-Ge-Fe,  $121.2 \pm 0.6^\circ$ .

Three equivalent forms of each of these reflections were measured and averaged.

Structural solution by Patterson and Fourier methods established the space group  $\text{P6}_3/\text{m}$  in preference to  $\text{P6}_322$ , as was the case for  $\text{Fe}_2(\text{CO})_9$ ,<sup>6</sup> to which this structure bears a close resemblance. The Fe atoms lie on positions of threefold symmetry (4f in  $\text{P6}_3/\text{m}$ ) and the Ge(CH<sub>3</sub>)<sub>2</sub> groups on the perpendicular mirror plane (6h). The carbonyl groups lie on the general positions (12i). At the present stage of refinement by full-matrix least-squares methods, the conventional  $R$  factor is 0.067 for all atoms vibrating anisotropically. We have no evidence that the space group is  $\text{P6}_3$  (the third possibility from the systematic absences); analysis of the anisotropic motion of the atoms does not suggest that the molecular mirror plane is pseudo only. The structure is shown in Figure 1. The most striking feature is the Fe-Ge-Fe angle of  $69.8^\circ$ , a distortion that is clearly necessary to bring the iron atoms sufficiently close for bond formation. The Fe-Fe distance of  $2.744 \text{ \AA}$  is near the longer limit of measured iron-iron distances,<sup>7</sup> and very considerably longer than the  $2.46 \text{ \AA}$  found in  $\text{Fe}_2(\text{CO})_9$ .<sup>6</sup> It is, of course, the larger size of the germanium atom (Fe-Ge =  $2.398 \text{ \AA}$ ) relative to carbon (Fe-bridging CO =  $1.8 \text{ \AA}$  in  $\text{Fe}_2(\text{CO})_9$ )<sup>6</sup> that accounts for the longer Fe-Fe bond. This distortion of bond angles by metal-metal bond formation is reminiscent of the acute Fe-S-Fe angles observed in  $[\text{SFe}(\text{CO})_3]_2$  and  $[\text{C}_2\text{H}_5\text{SFe}(\text{CO})_3]_2$ ,<sup>8</sup> and quite similar to that reported<sup>9</sup> for  $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ .

Among the products isolated from the reaction of diphenylgermane with triiron dodecacarbonyl is yellow, crystalline  $(\text{C}_6\text{H}_5)_2\text{GeFe}_2(\text{CO})_8$ ,<sup>5</sup> which shows seven

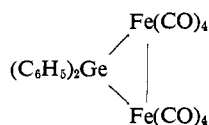
(6) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

(7) A convenient summary has been given by M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

(8) C. H. Wei and L. F. Dahl, *ibid.*, **4**, 1 (1965).

(9) P. F. Lindley and P. Woodward, *J. Chem. Soc.*, **A**, 382 (1967).

infrared-active carbonyl bands in cyclohexane. The compound may be formulated with some confidence as the  $C_{2v}$  structure



It is evident that the ability of  $R_2M$  ( $M = \text{Si, Ge, and Sn}$ ) groups to bridge transition metals is more general than suggested by examples known heretofore, and that reactions of  $R_2MH_2$  compounds with metal carbonyls offer a promising synthetic route.

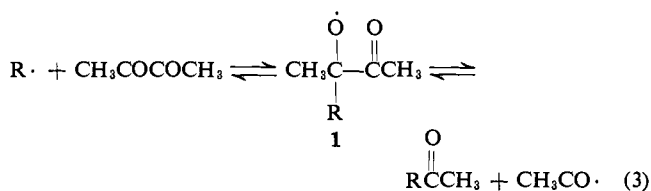
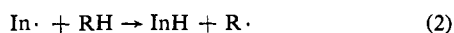
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## A Free-Radical Acylation

Sir:

We wish to report a free-radical reaction sequence which leads ultimately to acetylation products. When benzoyl peroxide (BPO) is decomposed thermally in deoxygenated dioxane or cyclohexane (RH) to which biacetyl has been added, reasonable yields of acetyl products are formed, as recorded in Table I. The most likely sequence of reactions to rationalize these products is given by eq 1-3. We believe reaction sequence 3



to be one of fundamental importance which has not been well recognized and, to our knowledge, not previously reported in solution.<sup>1</sup> Beyond the novelty of the processes suggested, these reactions are of interest in relation to the question of the direction of radical attack on the carbonyl group and, viewed as a free-radical acetylation sequence, may also have synthetic applications.

Yields in Table I are based on moles of radicals produced in theory from complete decomposition of the peroxide. If corrected for cage effects these yields would be higher; however, the fact that they are not greater than 100% suggests that the initiation process is very inefficient, or, as seems more likely, the kinetic chain length is extremely short<sup>2</sup> if chains are involved

(1) The gas-phase reaction of methyl radicals with biacetyl has been proposed to account for the high quantum yields of acetone in the photolysis of biacetyl (D. S. Herr, M. S. Matheson, and W. D. Walters, *J. Am. Chem. Soc.*, **63**, 1464 (1941); F. E. Blacet and W. E. Bell, *Discussions Faraday Soc.*, **14**, 70 (1953)), but methyls were only reactive in this manner above 80°.

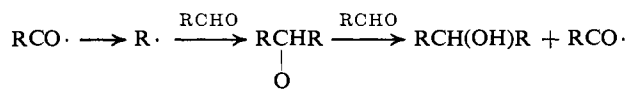
at all. Attempts to maximize the yield of acetyl product from cyclohexane by increasing the concentration of biacetyl (expt 4) were unsuccessful, in part because of the addition of phenyl radicals themselves to biacetyl. The efficient trapping of phenyls and formation of acetophenone in expt 6 should be noted. It is also significant that, whereas phenyl radicals and solvent radicals from dioxane and cyclohexane are apparently readily acetylated, reaction in toluene (not listed in Table I) gave at most traces of acetyl product, the major identified benzyl radical product being bibenzyl. In contrast, dimers (RR) were formed in less than 10% yields from dioxane and cyclohexane. These results suggest that sequence 3 is correctly represented as an equilibrium, the position of which is dependent on the relative stabilities of  $R\cdot$  and acetyl.<sup>3</sup>

Table I. Free-Radical Acetylation Reactions<sup>a</sup>

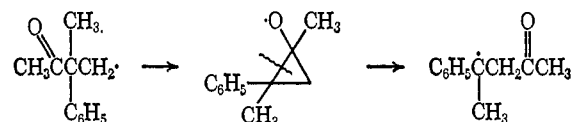
Expt.	Solvent	BPO, M	Biacetyl, M	% $\text{RCOCH}_3^b$
1	Cyclohexane	0.02	0.04	32
2	Cyclohexane	0.02	0.15	69
3	Cyclohexane	0.02	0.20	66
4	Cyclohexane	0.02	1.0	48 <sup>c</sup>
5	Dioxane	0.02	0.20	70
6	Biacetyl	0.02		62 <sup>d</sup>

<sup>a</sup> Deoxygenated solutions at reflux (77-80°) for 21-29 hr. <sup>b</sup> Based on the assumed formation of 2 moles of radicals per mole of BPO decomposed. <sup>c</sup> Acetophenone also formed. <sup>d</sup>  $\text{R} = \text{C}_6\text{H}_5$ .

Considerable precedent may be found for the individual reaction steps postulated in sequence 3. Radical additions to *carbonyl carbon* have been proposed previously: (a) to explain the formation of secondary alcohols in low yields during the decarbonylation of aldehydes;<sup>4</sup> (b) in the recently reported addition of



propyl radicals to hexafluoroacetone to give 1,1,1-trifluoro-2-(trifluoromethyl)-2-pentanol;<sup>5</sup> (c) as the first step in the facile 1,2-acetyl shift very recently noted,<sup>6</sup>



and quite likely are involved in the 1,2-carboethoxy migration observed<sup>7</sup> in the thermolysis of substituted carboethoxy bicyclo[2.1.0]pentanes. That acetyl radicals

(2) Acetyl radicals would likely not abstract hydrogens readily, and decarbonylation to give chain-carrying methyls probably does not compete efficiently with other processes at these temperatures.

(3) The extremely facile elimination of benzyl *via*  $\beta$  cleavage of alkoxy radicals generated from the corresponding hypochlorite is well documented (C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963)).

(4) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *ibid.*, **70**, 4253 (1948).

(5) W. H. Urry, A. Nishihara, and J. H. Y. Niu, *J. Org. Chem.*, **32**, 347 (1967).

(6) W. Reusch and C. L. Karl, Abstracts of the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P-79.

(7) M. J. Jorgenson and T. J. Clark, *J. Am. Chem. Soc.*, **90**, 2188 (1968).