Table I. Abstraction Yields from Recoil Tritium Reactions with Propylene in Excess Perfluorocyclobutene

	Parent molecule					Approx average
	$CH_3CH{=}CH_2$	$CH_3CD{=}CD_2$		$CD_3CH{=}CD_2$	$CD_3CD{=}CD_2$	
Relative yields[a]						
Total molecule						
HT	9300	6490	6170	1200	. . .	
DT	. . .	1880	1870	5630	7200	
Per bond						
CH_3	1550 (av)	2160	2060	. . .	. . .	2100
CD_3	. . .	. . .	. . .	1130 (av)	1200 (av)	
CH	(av)	. . .	. . .	1200	. . .	1200
CD	. . .	(av)	(av)	. . .	(av)	
CH_2	(av)	. . .	. . .	. . .	. . .	800
CD_2	. . .	630 (av)	620 (av)	(av)	(av)	

[a] HT from CH_4 = 2500; per C–H = 625.

ments in C–C bond distances would be roughly comparable to the period of a C–C stretching vibration ($\sim$1200 cm^{-1} or 3×10^{-14} sec), the time scale for the typical abstraction reaction is indicated as not longer than about 2–5 $\times 10^{-14}$ sec. For comparison of the times and distances involved, one can recall that tritium atoms of 1 and 50 eV have velocities of 8×10^{13} Å/sec and 6×10^{14} Å/sec, respectively, corresponding to translational motions of 2 and 20 Å in a period of 3×10^{-14} sec.

The additional question can be asked whether there is sufficient time for *any* appreciable relaxation of the geometrical structure of C_3H_5 toward that of the allyl radical during reaction 1; for example, a stripping mechanism[4] involving hydrogen-atom transfer during the grazing passage of a 50-eV tritium atom would require a time scale of about 2×10^{-15} sec. The correlation of bond dissociation energies with HT yield has, of course, been established through study of the recoil abstraction reaction, presumably on the same time scale, with a number of other molecules, each of which may *also* require some geometrical adjustments of the residual radical during or after the hydrogen atom transfer step, *e.g.*, planar CH_3 from $T^* + CH_4$. The success of the correlation indicates that these factors are either negligible, or cancel out, in these other cases for which the possible residual excitation energies are so much smaller.[3,5] We suggest that the higher abstraction yields found from CH_3 in propylene *vs.* that from CH_3 in ethane, propane, or neopentane indicate that some adjustment in geometrical structure has already occurred in the C–C bond distances at the time of reaction, and partially reflect the extra stability of the residual radical left after completion of the reaction. By inference, we conclude that the time scale of the abstraction reaction is usually $\gtrsim 10^{-14}$ sec, and place the median energy of the hot abstraction reaction in the low electron volt range, and not in the range of either tenths or tens of electron volts.

The recoil tritium reactions were carried out with a variety of isotopic propylene molecules as targets and utilized radio gas chromatographic analysis of the separated HT and DT peaks to identify the yields from particular positions, including that of the CH_3 group. These data are summarized in Table I, and can be compared with the following values for relative HT yields under equivalent conditions:[5,6,10] CH_4, 625, 104.0 kcal/mole;[11] *neo*-C_5H_{12}, 966, 99.3 kcal/mole; C_2H_6, 1150, 98.0 kcal/mole; *c*-C_5H_{10}, 2130, 92.9 kcal/mole; CH_2Br_2, 2350; $CHCl_3$, 9100. The various isotopic propylene molecules give consistent results, and the relative HT yield from CH_3 in propylene is approximately equal to that for C–H in cyclopentane, nominally corresponding to a bond dissociation energy of $\sim$93 kcal/mole.

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(10) Perfluorocyclobutene was used extensively in ref 5 as the major component required to establish equivalent conditions of tritium flux for different RH molecules; comparable results were also obtained for these additional systems: perfluorobutadiene, argon, nitrogen, C_2D_4.

(11) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(12) This research was supported by A.E.C. Contract No. AT-(11-1)-34, Agreement No. 126.

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Magnetic and Spectral Properties of $[Fe(en)_3]Cl_3$

Sir:

Relatively little information is available on the d–d spectra of low-spin Fe(III) complexes. This is due primarily to the fact that complexes of ligands strong enough to cause spin pairing such as CN^-, phen, bipy, and terpy have relatively intense charge transfer and/or ligand bands in the visible which obscure the d–d bands. Naiman[1] has interpreted the spectrum of $Fe(CN)_6^{3-}$ and obtained values of $10Dq$ and the Racah parameter B of 35,000 and 720 cm^{-1}, respectively.

We have recently prepared[2] $[Fe(en)_3]Cl_3$[3] which is low-spin and is sufficiently free of charge-transfer bands to allow a reasonably quantitative interpretation of the very rich d–d spectrum. The reflectance spectra[4] at 80 and 290° are shown in Figure 1. As can be seen, the

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(1) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961).

(2) The compound was prepared by adding slowly and with stirring a stoichiometric amount of 98% en in absolute ethanol to a solution of anhydrous iron(III) chloride also dissolved in absolute ethanol. The flesh-colored solid was filtered, washed with ether, and dried in a vacuum. The preparation, filtration, and drying were carried out in a closed system under nitrogen. The dry solid is stable for months in a desiccator. *Anal.* Calcd for $FeC_6N_6H_{24}Cl_3$: C, 21.03; H, 7.08; N, 24.54. Found: C, 21.26; H, 6.79; N, 24.57.

(3) That the compound is actually as represented, that is, one having three chelated en groups, is indicated by several lines of evidence. The X-ray powder pattern is essentially identical with that of $[Cr(en)_3]Cl_3$ which in turn was characterized by its absorption spectrum. Further, molar conductivity measurements in absolute methanol give values of 163 compared to 187 for $Cr(NO_3)_3 \cdot 9H_2O$.

(4) Spectra were also obtained in methanol solution and as mulls in Kel-F grease. From the solution spectra it can be concluded that the maximum value of the molar extinction coefficient for any of the bands assigned is 50. The precise values cannot be determined because of overlapping of the bands. Resolution in these media was not as good as in the reflectance although there seems to be general agreement of the more intense bands.

Table I. Spectral Data

Transition	Diagonal element	Calcd energy[a]	Obsd energy
${}^2T_{2g} \rightarrow {}^2E_g$	$\Delta + 16B + 2C$	31,500	31,500
$\rightarrow {}^2A_{1g}$	$\Delta + 17B - C$	26,000	27,500
$\rightarrow {}^2T_{2g}, {}^2T_{1g}$	$\Delta + 12B - C$	23,500	. . .
$\rightarrow {}^2E_g$	$\Delta + 7B - C$	21,000	21,500
$\rightarrow {}^2T_{2g}$	$\Delta + 2B - C$	18,500	18,750
$\rightarrow {}^2A_{2g}$	$\Delta - 3B - C$	16,000	16,250
$\rightarrow {}^2T_{1g}$	$\Delta - 2B - C$	16,500	
$\rightarrow {}^4T_{2g}$	$\Delta + 3B - 4C$	13,000	13,000
$\rightarrow {}^4T_{1g}$	$\Delta - 5B - 4C$	9,000	9,000

[a] Calculated using $\Delta = 19{,}500$, $B = 500$, and $C = 2000$ cm^{-1}.

Table II. Magnetic Data

T, °K	285.4	265.8	241.0	221.6	199.9	183.0
$\chi_M' \times 10^6$	2640	2714	2915	3070	3350	3585
μ_{eff}	2.45	2.40	2.37	2.33	2.31	2.29
T, °K	164.5	147.0	138.8	127.0	113.4	80
$\chi_M' \times 10^6$	3955	4260	4490	4880	5290	7360
μ_{eff}	2.28	2.24	2.23	2.23	2.19	2.17

spectrum at 80° is not only better resolved but the two low-energy bands are not observable in the 290° spectrum. We do not understand why these bands show the observed temperature dependence, but repeated measurements give the same spectra, both at room temperature and 80°. It is worth noting that only the two low-energy bands show this effect and both are assigned to spin-forbidden transitions.

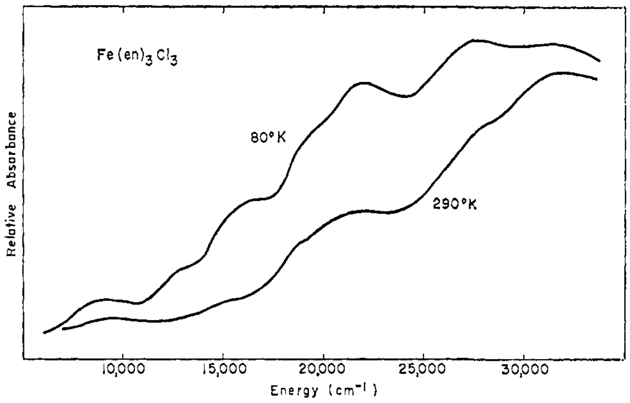

Figure 1. Reflectance spectra of [Fe(en)$_3$]Cl$_3$ at 80 and 290°K.

Table I shows the band assignments and a comparison of the calculated and observed energies. The agreement between the observed and calculated energies is generally good, except for the predicted band at 23,500 cm^{-1} which is not observable. The complexity of the spectra in this region, however, is such that it is quite possible that the band is present but simply not resolved. The calculated values of 10Dq, B, and C are also reasonable. The condition for spin pairing of a d^5 system,[5] $10Dq > 7.5B + 5C$, is clearly met with the assigned values. If we accept the free-ion B value of 1015 cm^{-1} as given by Tanabe and Sugano,[6] then the reduction of B amounts to ~50% which compares favorably with a 47% reduction[7] of B in Co(en)$_3{}^{3+}$. The C/B ratio of 4.0 is also a reasonable value.[6] The 10Dq value of 19,500 cm^{-1} is harder to assess, since little data are available for comparison, but it is not unreasonable considering the values of 23,200 and 21,900 cm^{-1} for Co(en)$_3{}^{3+}$ and Cr(en)$_3{}^{3+}$, respectively.

Something should be said about the use of diagonal elements for the calculated energies. Obviously off-diagonal elements should be considered, but because of the very large number of states,[8] the difficulty in doing so is prohibitive. We have considered configuration interaction between only those states arising from the same $t_{2g}e_g$ configuration. The best fit of the data using calculated energies obtained by this method gives a slightly larger value of 10Dq, but the agreement with the observed spectrum is much poorer. It is questionable whether or not a limited consideration of off-diagonal terms is worthwhile.

Magnetic data for [Fe(en)$_3$]Cl$_3$ are given in Table II. It is obvious that the formulation of the complex as a spin-paired d^5 system is justified. The data can be more precisely treated using the theory of Figgis[9] for ${}^2T_{2g}$ systems in axially distorted cubic fields. The observed moments agree well with those predicted assuming a spin-orbit coupling constant of −400 cm^{-1}, the delocalization constant of 1.0, and the axial distortion to be near zero. Actually, a distortion of anywhere between +400 and −400 cm^{-1} gives a reasonable fit of the observed data. The small value may be compared with values of 600 cm^{-1} found[10] for Fe(phen)$_3{}^{3+}$ and Fe(bipy)$_3{}^{3+}$ and about 1200 cm^{-1} found[11] for Fe(terpy)$_2{}^{3+}$.

Mössbauer data for [Fe(en)$_3$]Cl$_3$ are in accord with the magnetic data. The spectrum consists of a quadrupole split doublet with an isomer shift and a quadrupole splitting[12] at 290° of 0.14 and 1.09 mm/sec. At 77° the corresponding values are 0.23 and 1.36 mm/sec. The quadrupole splitting is in agreement with the magnetic data in predicting a low distortion from cubic symmetry. The analogous values for Fe(phen)$_3{}^{3+}$ and Fe(terpy)$_2{}^{3+}$ are 1.67[13] and 3.09[10] mm/sec, respectively. Thus both the magnetic and Mössbauer data predict the degree of distortion to be terpy > phen > en.

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[5] J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 229 (1956).

[6] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

[7] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 110.

[8] For example, there are ten states of ${}^2T_{2g}$ symmetry within the d^5 manifold.

[9] B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).

[10] B. N. Figgis, *ibid.*, **57**, 204 (1961).

[11] W. M. Reiff, W. A. Baker, Jr., and N. E. Erickson, unpublished results.

[12] Relative to natural iron foil.

[13] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

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The Preparation and Structure of a Germanium-Bridged Iron Carbonyl Complex, $[(CH_3)_2Ge]_3Fe_2(CO)_6$

Sir:

Although the reaction of silanes with metal carbonyls has been shown to be rather general in scope,[1] 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 $H_2Ge[Mn(CO)_5]_2$,[2] while more recently methylstannanes have been found to react with iron pentacarbonyl to afford polynuclear tin-iron compounds.[3] As part of a general investigation of compounds between transition metals and main group metals and metalloids,[4] 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 $(CH_3)_6Ge_3Fe_2(CO)_6$.[5] The nmr showed a single sharp resonance at τ 8.72, and the infrared spectrum showed only two strong carbonyl stretching bands at 2007 and 1968 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 $a = 9.764 \pm 0.006$ Å, $c = 11.90 \pm 0.02$ Å, for space group $P6_3/m$ with two molecules per unit cell. Intensity data were collected on a PAILRED automated diffractometer using crystal monochromatized Mo Kα radiation. A total of 304 unique reflections from 11 reciprocal lattice layers perpendicular to c were measured as significantly above background. Three equivalent forms of each of these reflections were measured and averaged.

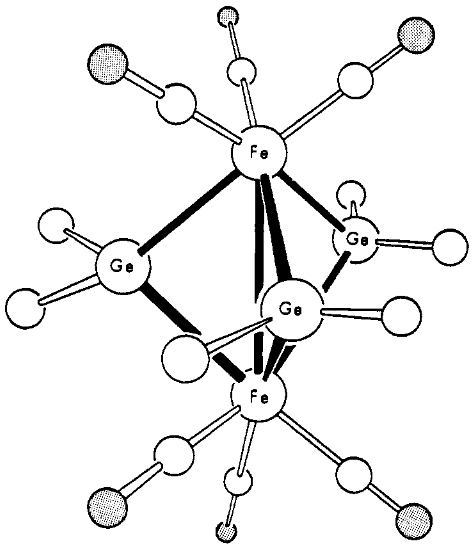

Figure 1. The molecular structure of $[(CH_3)_2Ge]_3Fe_2(CO)_6$. Important bond lengths, with standard deviations, are Fe–Ge = 2.398 ± 0.005 Å; Fe–Fe = 2.74 ± 0.01 Å; Ge–CH_3 (mean) = 2.02 ± 0.03 Å; Fe–CO = 1.77 ± 0.02 Å; FeC–O = 1.15 ± 0.02 Å; nonbonding Ge–Ge = 3.41 ± 0.01 Å. Some bond angles are Fe–Ge–Fe, 69.8 ± 0.2°; Fe–Fe–Ge, 55.1 ± 0.2°; Ge–Fe–CO, 86.1 ± 0.7°; CH_3–Ge–CH_3, 105.4 ± 1.0°; CH_3–Ge–Fe, 121.2 ± 0.6°.

Structural solution by Patterson and Fourier methods established the space group $P6_3/m$ in preference to $P6_322$, as was the case for $Fe_2(CO)_9$,[6] to which this structure bears a close resemblance. The Fe atoms lie on positions of threefold symmetry (4f in $P6_3/m$) and the $Ge(CH_3)_2$ 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 $P6_3$ (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°, a distortion that is clearly necessary to bring the iron atoms sufficiently close for bond formation. The Fe–Fe distance of 2.744 Å is near the longer limit of measured iron–iron distances,[7] and very considerably longer than the 2.46 Å found in $Fe_2(CO)_9$.[6] It is, of course, the larger size of the germanium atom (Fe–Ge = 2.398 Å) relative to carbon (Fe–bridging CO = 1.8 Å in $Fe_2(CO)_9$)[6] 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 $[SFe(CO)_3]_2$ and $[C_2H_5SFe(CO)_3]_2$,[8] and quite similar to that reported[9] for $Sn[Fe(CO)_4]_4$.

Among the products isolated from the reaction of diphenylgermane with triiron dodecacarbonyl is yellow, crystalline $(C_6H_5)_2GeFe_2(CO)_8$,[5] which shows seven

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(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.

(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).