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The Crystal and Molecular Structure of Tri-μ-dimethylgermanium-bis(tricarbonyliron)

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The structural elucidation by single-crystal X-ray methods of $[(CH_3)_2Ge]_3Fe_2(CO)_6$ has revealed that the molecule has the $Fe_2(CO)_9$ structure with the three bridging carbonyl groups replaced by dimethylgermanium groups. The compound crystallizes in the hexagonal space group C_{6h}^2-$P6_3/m$ with $a = 9.756 \pm 0.005$ Å, $c = 11.944 \pm 0.009$ Å, and two molecules per unit cell. The calculated density is 1.983 g cm^{-3}; the experimental density is 2.0 g cm^{-3}. The structure was solved from 304 above-background reflections collected on an automatic diffractometer and refined to conventional residuals of $R_1 = 6.9\%$ and $R_2 = 8.5\%$. The molecular symmetry required by the space group is 3/m: the two $Fe(CO)_3$ groups lie on a threefold axis and the three $Ge(CH_3)_2$ residues lie on the perpendicular mirror plane that relates the two iron atoms. Replacement of bridging carbonyl by bridging $Ge(CH_3)_2$ has lengthened the Fe–Fe distance to 2.750 ± 0.011 Å. The Fe–Ge distance is 2.398 ± 0.004 Å and the two iron atoms subtend an acute angle of $70.0 \pm 0.2°$ at the germanium atoms.

Introduction

A considerable amount of structural information has been obtained for compounds in which various ligands have replaced carbonyl groups in the iron carbonyls and substituted carbonyls. Structures based upon $Fe_2(CO)_9$ with replacement of bridging carbonyls have been observed, for example, where the replacing groups have involved sulfur or selenium: $[SFe(CO)_3]_2$,[1,2] $[C_2H_5SFe(CO)_3]_2$,[3] $[C_6H_5CSFe(CO)_3]_2$;[4] cyclic olefins: $C_8H_8Fe_2(CO)_5$,[5] $C_{10}H_8Fe_2(CO)_5$,[6] $(CH_3)_4C_8H_4Fe_2(CO)_5$;[7] acetylene and olefin complexes: $Fe_2(CO)_6(C_5H_4CH_2)$,[8] $Fe_2(CO)_6(C_2H_2)_3$,[9] $Fe_2(CO)_6(HOCC(CH_3)C(CH_3)COH)$,[10] $Fe_2(CO)_8C_2(C_6H_5)_2$;[11] and a nitrile: $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNC_6H_5)$.[12] In all of these structures the iron–iron separation, though showing considerable variation, has been short enough to imply an Fe–Fe bond. The preparation of $[(CH_3)_2Ge]_3Fe_2(CO)_6$[13] provided a novel addition to this series. Spectroscopic data suggested a highly symmetrical structure based upon diiron enneacarbonyl with bridging germanium dimethyl groups, and the crystal structure was undertaken to confirm the stereochemistry and to provide details of molecular geometry. A preliminary report of this structure has been published.[13]

Experimental Section

Crystals of tri-μ-dimethylgermanium-bis(tricarbonyliron) were yellow needles of regular habit, revealing threefold symmetry about the needle axis. The crystals used for cell parameter determination and data collection were mounted inside thin-walled glass capillaries. Preliminary photographs established that the Laue group was 6/m and the systematic absences $000l$ with $l = 2n + 1$. Two space groups are consistent with these observations: $P6_3/m$ and $P6_3$. No attempt was made to decide between these on the basis of tests for centrosymmetry. The centrosymmetric $P6_3/m$ was assumed in the initial stages of structure solution and confirmed by the successful refinement.

Unit cell dimensions were $a = 9.756 \pm 0.005$ Å and $c = 11.944 \pm 0.009$ Å obtained by accurate measurement of ω differences for axial reflections on the diffractometer.[14] Two crystals, mounted about c and a, respectively, were used for this work, and the data were refined by least squares to provide standard error estimates. Molybdenum $K\alpha_1$ radiation (λ 0.70926 Å) was used at 27°. The experimental density was 2.0 g cm^{-3}, measured by flotation in a thallous formate solution. For two molecules, molecular weight 587.8, per unit cell, the experimental density is 1.983 g cm^{-3}, in good agreement with the experimental value. Three-dimensional data were collected on a PAILRED fully automatic diffractometer equipped with a scintillation counter, using Mo $K\alpha$ radiation monochromatized from a silicon crystal. The methods of data collection and processing employed with this machine have been described in detail in a previous paper;[15] any differences will be emphasized here.

The crystal used for data collection was a needle of approximately hexagonal cross section (two sets of three faces parallel to the needle axis were almost equally developed) with a mean radius of 0.053 mm and a length of about 0.7 mm. The morphologically well-developed direction corresponded to the unique c axis and the crystal was aligned on the machine with this axis parallel to the rotation axis.

A total of 11 reciprocal lattice levels normal to c were scanned under Weissenberg geometric conditions of moving crystal and stationary counter. In each level with constant l six equivalent forms occurred for Laue group 6/m. These had indices given by the cyclic permutations of hki and $\bar{h}\bar{k}\bar{i}$. The quadrant of reciprocal space accessible to the diffractometer with the one crystal mounting contained those equivalent forms of a general reflection, $hkil$, which had both k and l either positive or zero.

Collection of data within this quadrant then provided three measurements of equivalent forms of a general reflection and four measurements in the case when one index (not l) was zero. The scan speed was 1°/min, the counter aperture was 1.5°, and the scan range varied from 1.2 min for the zero layer to 3.4 min for the eleventh. Background was measured for 0.4 min before and after each reflection scan.

Seven zero-layer reflections were measured after each layer

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[15] M. Elder and D. Hall, *ibid.*, **8**, 1273 (1969).

had been collected as a guide to crystal and counter stability. There was no systematic trend apparent in their intensities. Variations from the mean value for each of the standard reflections appeared to be random with respect to time and were in no case greater than $4\sigma_c$. Here σ_c is the counting error given by $(T + t^2B)^{1/2}$ where T is the total count, B is the total background, and t is the ratio of the scan time to the total background count time.

In the initial data processing the intensities were corrected for background, and Lorentz and polarization corrections were applied. Rejection of those data for which the corrected intensity was negative yielded 1421 observations. No absorption corrections were applied. The linear absorption coefficient for Mo Kα radiation is 61.8 cm^{-1} and $\mu R_{\text{mean}} = 0.33$. The small size of this value together with the regular cross section of the crystal used makes the errors due to neglect of absorption corrections unimportant. Equivalent forms were then combined to give a set of unique data. In general the intensities of the equivalent forms were within $4\sigma_c$ (as previously defined) of their mean value, the same range as was observed for the standard reflections. In a few cases, however, deviations from the mean of up to $6\sigma_c$ were observed, presumably indicative of absorption effects. Reflections were treated as not above background if one or more of the equivalent forms had a negative corrected intensity or if the average σ_c/I for the equivalent forms was greater than 0.4. A total of 304 above-background observations resulted. These data are limited to the range $\sin\theta < 0.48$, implying a resolution limit of 0.74 Å. The data set is not symmetrical; the resolution in the c direction is 1.0 Å.

Refinement and Structure Solution

If space group P6$_3$/m with two molecules per unit cell is assumed, then the iron atoms must lie on the positions of threefold symmetry, 4e or 4f.[16] Packing considerations rule out 4e, leaving a molecule of symmetry 3/m with the iron atoms on 4f, and the germanium dimethyl groups on the mirror plane perpendicular to the threefold axis, 6h in Wyckoff notation.

The sharpened Patterson function computed from all of the above-background data provided the positional parameters of the heavy atoms not determined by the space group and also confirmed the presence of the horizontal mirror plane, at least as far as the heavy atoms were concerned. A series of heavy-atom-phased F_o syntheses produced a satisfactory set of light-atom positions, after one false solution had been tried and discarded. This model, with individual isotropic thermal parameters for each atom and an over-all scale factor, was refined by full-matrix methods.[17]

Atomic scattering factors for neutral atoms were taken from Cromer's compilation[18] with the real part of the anomalous dispersion correction for Mo Kα radiation[19] applied to the iron and germanium curves. A weighting scheme of the form $w = a^2/[a^2 + (|F_o| - b)^2]$ was used, with $a = 37$ and $b = 49$ on the absolute scale, chosen to minimize the dependency of $\Sigma w(|F_o| - |F_c|)^2$ upon $|F_o|$ calculated for small ranges of increasing $|F_o|$. The refinement converged at discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 9.8\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2]^{1/2} = 12.8\%$. Refinement was continued with individual anisotropic temperature parameters for each atom, reducing the discrepancy factor R_1 to 6.8%. Inspection of the anisotropic thermal parameters for the mirror plane methyl groups, however, revealed that these were unrealistic and not supported by the standard deviations. Continued refinement with the methyl carbon atoms isotropic and the other atoms anisotropic gave final residuals of $R_1 = 6.9\%$ and $R_2 = 8.5\%$. The increased agreement over the model with all atoms isotropic is significant by Hamilton's criteria.[20] A final difference map was computed and showed residual electron density in the range 1.2 e$^-$/Å^2, about one-fifth the height of a methyl carbon atom on the same scale. No attempt was made to interpret the residual density for hydrogen atom positions.

Final positional and thermal parameters are listed in Table I. The standard error estimates are those obtained from the inverse normal equations matrix. The vibration amplitudes of the anisotropic ellipsoids and their orientations are indicated in Figure 1. Table II lists the important parameters of the molecular geometry. The values were calculated using the program ORFFE;[17] the error estimates come from the variance–covariance matrix of structure parameter errors and include an allowance for the error in measurement of the cell parameters. The shortest intermolecular contacts of their type are given in this table. None is abnormally short for a van der Waals contact, indicating that individual molecules are well isolated and that intermolecular interactions can have little effect upon molecular geometry. Observed and calculated structure factors are listed in Table III; there is no evidence of the need for a secondary extinction correction.

Discussion

The structure consists of isolated molecular units of $[\mathrm{Ge(CH_3)_2}]_3\mathrm{Fe_2(CO)_6}$, each possessing 3/m crystallographic symmetry. The successful refinement of the structural model provides the main evidence for the choice of the space group P6$_3$/m. The alternative space group P6$_3$ would involve removing the horizontal mirror plane, with molecular symmetry 3 resulting. Small deviations from 3/m symmetry cannot be ruled out but the evidence of the final difference map confirms that there are no major deviations. The orientations of the vibration ellipsoids are essentially reasonable. The larger vibration amplitudes in the direction of the unique axis we attribute to the effects of the anisotropy in the data set, rather than to any physically meaningful factor. Comparison of this structure with $\mathrm{Fe_2(CO)_9}$[21] reveals major differences in the length of the Fe–Fe bond and in the geometry of the bridging atoms. In iron enneacarbonyl an Fe–Fe bond of 2.46 (5) Å is bridged symmetrically by three carbonyl groups, sub-

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[16] "International Tables for X-Ray Crystallography" Vol. I, The Kynoch Press, Birmingham, England, 1962.

[17] Programs for the IBM 360/67 were of local origin, together with Ahmed's crystallographic program system, the Busing and Levy full-matrix refinement program, ORFLS, and molecular geometry program, ORFFE, and Johnson's ORTEP thermal ellipsoid plotter.

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Table I

Positional and Thermal[a] Parameters for $[Ge(CH_3)_2]_3Fe_2(CO)_6$

Atom	x	y	z	B, Å^2
Ge	0.5167 (3)[b]	0.8822 (3)	$^1/_4$	
Fe	$^1/_3$	$^2/_3$	0.3651 (5)	
C_1	0.4993 (24)	0.6907 (25)	0.4387 (24)	
O_1	0.6103 (19)	0.7072 (20)	0.4877 (16)	
C_2	0.5055 (36)	1.0892 (36)	$^1/_4$	3.2 (0.6)
C_3	0.7456 (42)	0.9503 (43)	$^1/_4$	4.9 (0.8)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge	0.00508 (37)	0.00434 (37)	0.00549 (28)	0.00192 (30)	0.0	0.0
Fe	0.00553 (37)	0.00553	0.00466 (44)	0.00276	0.0	0.0
C_1	0.0108 (32)	0.0122 (32)	0.0095 (29)	0.0069 (28)	−0.0034 (24)	−0.0025 (24)
O_1	0.0154 (27)	0.0215 (33)	0.0112 (20)	0.0114 (26)	−0.0053 (18)	−0.0002 (20)

[a] The form of the anisotropic ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Values in parentheses are the estimated standard deviations in the least significant figures.

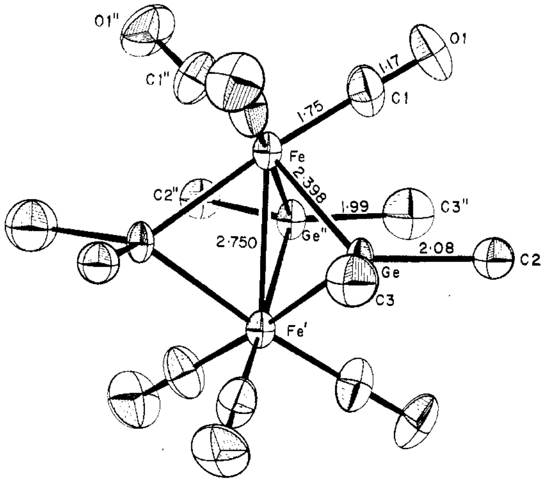

Figure 1.—The molecule of $[Ge(CH_3)_2]_3Fe_2(CO)_6$. The three $Ge(CH_3)_2$ groups lie on a horizontal mirror plane perpendicular to the threefold axis passing through the iron atoms.

Table II

Bond Lengths and Angles in $[Ge(CH_3)_2]_3Fe_2(CO)_6$[a]

Intramolecular Distances, Å

Bonding		Nonbonding	
Ge–Fe	2.398 (4)	Ge···Ge	3.403 (5)
Fe–Fe′	2.750 (11)	$C_2 \cdots C_3$	3.24 (4)
Ge–C_2	2.08 (3)	$C_2 \cdots C_3''$	3.90 (5)
Ge–C_3	1.99 (4)	$C_1 \cdots C_1''$	2.62 (4)
Fe–C_1	1.75 (2)	Ge···C_1	2.88 (3)
C_1–O_1	1.17 (2)	Ge···C_1''	2.87 (3)

Intramolecular Distances, Å

Ge···O	3.71	O···C	3.54
O···O	3.44	O···CH_3	3.54

Angles, deg

Fe–Ge–Fe′	70.0 (2)	C_1–Fe–Fe′	120.2 (9)
Ge–Fe–Fe′	55.0 (1)	Ge–Fe–Ge″	90.3 (2)
Fe–C_1–O_1	179.3 (23)	C_2–Ge–C_3	105.3 (11)
C_1–Fe–C_1''	97.0 (12)	Fe–Ge–C_2	121.2 (7)
C_1–Fe–Ge	86.3 (8)	Fe–Ge–C_3	118.4 (5)
C_1–Fe–Ge″	86.2 (7)		

[a] Atom labels are those of Figure 1. Superscripts denote atoms related by the mirror plane (single prime) and by the threefold axis (double prime).

tending an angle of 87 (4)°, and with an Fe–CO (bridge) distance of 1.8 Å. In the present compound the greater size of the bridging dimethylgermanium groups appears to have increased the Fe–Fe distance by about 0.3 Å, while the angle subtended at the bridging atoms is a considerably more acute 70°. The germanium–iron distance of 2.40 Å is slightly larger than the 2.357 (4) Å found in $Cl_2Ge[\pi\text{-}C_5H_5Fe(CO)_2]_2$,[22] a difference which is probably attributable to the significantly different coordination geometry of the germanium atoms in the two compounds. The germanium–methyl distances do not differ significantly; the mean value of 2.03 Å is larger than the microwave determined value of 1.945 Å for H_3GeCH_3[23] but not significantly larger than the 1.98 (3) Å distance in $Ge(CH_3)_4$.[24] While the angles about the germanium in $Cl_2Ge[\pi\text{-}C_5H_5Fe(CO)_2]_2$ could be rationalized in terms of varying s and p character in the different bonds, this approach does not seem applicable to the present compound. The acute Fe–Ge–Fe angle of 70°, which is closely comparable with the corresponding values in the sulfur-bridged iron compounds,[1–4] presumably indicates some d character in the Fe–Ge bonds.[25] The $Fe(CO)_3$ entities are in all respects normal. The lengths Fe–C and C–O of 1.75 and 1.17 Å and the angles Fe–C–O and C–Fe–C of 179 and 97° agree well with previously observed values.[26] The Fe–Fe distance of 2.75 Å is toward the upper limit of the range of distances in comparable structures[27] but short enough to imply a bonded interaction. A long Fe–Fe distance would be expected in view of the steric requirements of the germanium atom: the Fe–Ge length is about 0.6 Å greater than a bridging Fe–C distance in similar compounds. The presence of an Fe–Fe bond requires a considerable distortion in the Fe–Ge–Fe bridging angle. A similar distortion is observed in $Sn[Fe(CO)_4]_4$[26] in

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(26) A summary is given by P. F. Lindley and P. Woodward, *J. Chem. Soc., A*, 382 (1967).

(27) See ref 6 for a convenient tabulation.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS ON A SCALE OF ABSOLUTE VALUES × 10

H	K	FO	FC
	L = 0		
-1	2	567	516
-2	3	648	-528
-3	3	397	401
0	4	882	-834
-1	4	749	-720
-3	4	647	565
-1	5	2249	2249
-2	5	486	-457
-4	5	554	480
-5	5	1061	-1003
0	6	844	782
-1	6	827	-788
-2	6	325	-292
-3	6	194	212
-4	6	757	-757
-5	6	291	290
-1	7	296	-264
-2	7	614	620
-3	7	406	-379
-4	7	527	559
-7	7	661	-658
0	8	414	434
-1	8	295	283
-2	8	284	328
-3	8	579	-594
-4	8	232	251
-5	8	307	-348
-6	8	359	-350
-1	9	217	-283
-2	9	310	-360
-4	9	326	380
-5	9	495	-488
-6	9	869	870
-8	9	247	-271
-9	9	255	267
-1	10	444	-390
-2	10	558	621
-5	10	518	492
-6	10	469	-478
-7	10	296	-299
-9	10	351	-350
-1	11	508	501
-2	11	312	-362
-5	11	396	-392
-7	11	481	534
-8	11	284	-301
-9	11	341	375
-4	12	274	-301
-5	12	366	376
-8	12	249	-249
	L = 1		
0	2	321	-312
-1	2	721	-678
-1	3	362	308
-2	3	301	400
-3	3	420	-408
0	4	912	853
-1	4	501	-501
-2	4	912	-823
-3	4	410	421
-2	5	576	557
-3	5	160	32
-4	5	225	216
-5	5	1284	1191
0	6	220	239
-1	6	1228	1182
-2	6	931	-917
-3	6	743	699
-4	6	410	-372
-5	6	548	-527
-1	7	408	-376
-2	7	377	-360
-4	7	357	-327
-5	7	535	515
-7	7	238	212
0	8	241	-246
-2	8	304	307
-3	8	243	255
-5	8	199	139
-7	8	633	-638
-3	9	617	-614
-4	9	333	343
-5	9	537	-572
-7	9	382	369
0	10	349	337
-1	10	512	-582
-6	10	760	775
-7	10	537	-587
-2	11	505	553
-3	11	416	-367
-6	11	340	-376
-10	11	314	343
	L = 2		
0	2	740	-666
-1	3	1134	-1085
-2	3	1799	1696
-3	3	513	421
0	4	286	320
-1	4	224	207
-2	4	230	204
-3	4	961	-862
-1	5	1223	-1145
-3	5	198	-274
-4	5	198	-159
-5	5	424	397
0	6	271	-310
-1	6	475	431
-2	6	443	420
-4	6	807	696
1	7	264	232
-4	7	978	-896
-5	7	445	416
-6	7	356	-342
-7	7	427	375
0	8	616	-590
-1	8	467	414
-2	8	648	-626
-3	8	416	328
-3	9	309	277
-4	9	261	-262
-6	9	692	-650
-1	10	279	247
-2	10	479	-454
-5	10	321	-324
-6	10	334	350
-1	11	389	-323
-9	11	388	-428
-10	11	285	149
-5	12	486	-438
	L = 3		
-1	2	711	869
-2	2	449	517
0	3	485	-536
-1	3	287	362
-2	3	1067	-1289
-1	4	354	-368
-2	4	938	1018
0	5	444	407
-3	5	599	-615
-1	6	411	-397
-3	6	560	-573
-4	6	813	883
-6	6	230	257
0	7	702	754
-1	7	349	-326
-2	7	401	363
-3	7	543	500
-5	7	523	-561
-6	7	403	391
-2	8	244	269
-3	8	642	-693
-5	8	351	354
-6	8	299	-254
-7	8	503	544
-2	9	353	-429
-3	9	525	582
-5	9	241	256
-8	9	460	-493
-4	10	370	-370
-6	10	308	-436
-9	10	349	331
-5	11	336	349
	L = 4		
-1	2	917	-1091
-2	2	725	816
0	3	903	-916
-1	3	911	957
-2	4	1039	-1082
-3	4	1157	1207
-4	4	220	-203
0	5	292	-264
-1	5	755	736
-2	5	269	250
-3	5	349	353
-4	5	605	-613
-2	6	236	221
-3	6	787	-783
-5	6	702	704
-6	6	307	-310
-2	7	440	-417
-4	7	968	965
-5	7	713	-691
-6	7	450	438
-1	8	515	-457
-2	8	695	686
-4	8	528	-569
-7	8	628	-626
-8	8	712	723
0	9	258	-245
-3	9	605	-625
-4	9	580	620
-7	9	283	313
-3	10	290	265
-4	11	362	-361
	L = 5		
0	2	714	748
-1	2	337	-359
-1	3	734	-730
-2	3	1248	1269
-3	3	316	-282
-1	4	383	367
-2	4	606	-591
-3	4	567	-554
-2	5	326	-351
-3	5	869	833
-5	5	217	241
0	6	235	156
-1	6	403	333
-3	6	607	590
-4	6	1015	-992
-2	7	232	-264
-3	7	582	-566
-4	7	324	303
-5	7	391	403
-6	7	377	-380
-7	7	646	630
-3	8	742	721
-5	8	400	-363
-6	8	475	460
-7	8	591	-559
-2	9	413	426
-3	9	540	-518
-4	10	430	420
	L = 6		
-1	2	156	202
-2	2	441	-517
0	3	614	617
-1	3	750	-804
-2	3	631	669
-2	4	570	561
-3	4	627	-655
0	5	336	283
-1	5	654	-680
-3	5	471	-439
-4	5	227	173
-1	6	332	303
-3	6	280	269
-4	6	389	400
-5	6	246	-267
0	7	269	259
-4	7	722	-719
-5	7	507	510
-6	7	427	-369
-1	8	403	372
-2	8	500	-508
-4	8	343	337
-7	8	369	327
-8	8	484	-484
-3	9	370	355
-4	9	341	-322
	L = 7		
-1	2	485	558
0	3	309	-316
-1	3	190	-115
-2	3	481	-503
-2	4	564	584
-4	4	306	319
0	5	701	671
-2	5	325	-283
-1	6	694	-637
-2	6	520	440
-3	6	473	-404
-4	6	378	353
0	7	321	302
-5	7	317	-353
-3	8	321	-251
-7	8	378	378
-3	9	353	390
-5	9	388	370
	L = 8		
-1	2	206	222
0	3	250	219
-1	3	248	268
-2	3	595	-615
-1	4	458	-441
-3	4	327	418
-4	4	567	-509
0	5	453	-441
-1	5	1057	1098
-4	5	330	322
-1	6	408	-350
-4	6	450	-416
-4	7	329	393
-2	8	318	255
-6	9	542	566
	L = 9		
-1	2	196	-244
-2	2	166	211
0	3	216	225
-1	3	244	249
-2	3	220	182
-1	4	348	-370
-2	4	483	-476
-3	4	352	355
-4	4	502	-508
0	5	565	-605
-2	5	336	364
-1	6	624	573
-2	6	486	-477
-3	6	326	339
-5	6	273	-331
-1	7	292	-222
-3	9	351	-359
-5	9	365	-361
	L = 10		
-1	2	172	-176
-1	3	277	-273
-2	3	453	467
-1	4	224	162
0	5	353	299
-1	5	642	-646
-4	6	302	352
-2	7	316	-213
-4	7	350	-316

which two Fe–Fe distances of 2.87 (1) Å subtend angles of 68.9 (2)° at the central tin atom.

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Stereochemistry of Polynuclear Compounds of the Main Group Elements. VIII.[1] The Crystal Structure of Bis[2-dimethylaminoethyl(methyl)amino]di(methylmagnesium)[2]

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The crystal structure of bis[2-dimethylaminoethyl(methyl)amino]di(methylmagnesium), $[(CH_3)_2N(CH_2)_2NCH_3MgCH_3]_2$, has been determined by three-dimensional single-crystal X-ray diffractometer studies. A full-matrix least-squares refinement using 1812 reflections resulted in a final unweighted discrepancy factor of 4.5%. The compound crystallizes as dimers in the triclinic space group $P\bar{1}$, with two molecules in a reduced cell of dimensions a = 7.244 (2) Å, b = 10.387 (3) Å, c = 12.454 (4) Å, α = 82.10 (6)°, β = 88.61 (17)°, and γ = 80.37 (9)°, where $Z = 2$, ρ_{calcd} = 1.04 g/cm^3, and ρ_{obsd} = 1.03 g/cm^3. The dimers are located on crystallographic centers of inversion and consist of two magnesium atoms bridged by amino groups from two different 2-dimethylaminoethyl(methyl)amino ligands. An amine nitrogen of the chelate and a methyl group occupy the remaining nearly tetrahedral coordination sites on each magnesium atom. The average Mg to bridging N and Mg to terminal N distances are 2.104 ± 0.003 and 2.196 ± 0.003 Å, respectively. Within the four-membered MgNMg′N′ ring, the average MgNMg′ angle is 88.5 ± 0.1° and the NMgN′ angle is 91.5 ± 0.1°.

Introduction

Reagents formed from alkyllithium compounds and various amine derivatives have proven to be extremely useful as intermediates for a wide variety of "metalation" reactions and as catalysts in the telomerization of unsaturated hydrocarbons.[4,5] The corresponding organomagnesium reagents frequently show similar properties although they are usually less reactive and accordingly have been less extensively studied. The stereochemistries of these intermediates are almost without exception unknown, although in the case of

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[1] For Part VII and earlier references, see J. L. Atwood and G. D. Stucky, *J. Am. Chem. Soc.*, **91**, 2538 (1969).

[2] This work was supported by the Advanced Research Projects Agency under Contract SD-131 and the National Science Foundation.

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