

Multiple Bonds Between Main Group Elements and Transition Metals, III¹⁾**Synthesis, X-Ray Crystal and Molecular Structure of μ -Germanium-bis[dicarbonyl(η^5 -pentamethylcyclopentadienyl)-manganese], μ -Ge-[(η^5 -C₅Me₅)Mn(CO)₂]₂**James D. Korp^a, Ivan Bernal^a, Rolf Hörlein^b, Ricardo Serrano^b, and Wolfgang A. Herrmann^{*b}Department of Chemistry, University of Houston^a,
Houston, Texas 77004 (USA), andInstitut für Anorganische Chemie der Universität Frankfurt^b,
Niederurseler Hang, D-6000 Frankfurt am Main 50

Received January 9, 1984

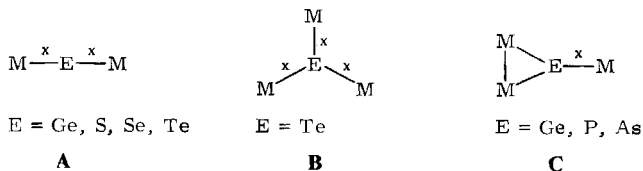
The title compound **3** has been synthesized along the hydride route by treatment of the solvent complex $(\eta^5\text{-C}_5\text{Me}_5\text{Mn}(\text{CO})_2(\text{THF}))$ (THF = tetrahydrofuran) with monogermane, GeH₄, in the presence of sulfuric acid. A single-crystal X-Ray structural analysis revealed two conformers of **3** being present in the solid state in a 1 : 1 ratio (C 2/c, monoclinic). Pairs of carbonyl groups almost eclipse each other, while the remaining two CO ligands exhibit an *anti*-conformation relative to the strictly linear Mn–Ge–Mn framework. Both enantiomeric conformers are geometrically related by a 180°-rotation of a (C₅Me₅)Mn(CO)₂ fragment around the Mn, Ge, Mn vector. The manganese–germanium bond lengths average 2.18(2) Å and thus correspond to considerable multiple bonding between these atoms.

Mehrfachbindungen zwischen Hauptgruppenelementen und Übergangsmetallen, III¹⁾**Synthese, Einkristall- und Molekülstruktur von μ -Germanium-bis[dicarbonyl(η^5 -pentamethylcyclopentadienyl)mangan], μ -Ge-[(η^5 -C₅Me₅)Mn(CO)₂]₂**

Die Titelverbindung **3** wurde nach der Hydrid-Methode durch Behandlung des Solvens-Komplexes $(\eta^5\text{-C}_5\text{Me}_5\text{Mn}(\text{CO})_2(\text{THF}))$ (THF = Tetrahydrofuran) mit Monogerman, GeH₄, in Gegenwart von Schwefelsäure synthetisiert. Eine Röntgenstrukturanalyse weist das Vorliegen zweier konformationsisomerer Moleküle im Kristall nach (C 2/c, monoklin). Bezüglich des streng linearen Mn–Ge–Mn-Gerüsts stehen zwei Carbonyl-Gruppen annähernd auf Deckung, während die anderen beiden *anti*-Konformation besitzen. Die äquimolar in der Elementarzelle vorliegenden enantiomeren Konformer leiten sich geometrisch voneinander durch 180°-Drehung einer $(\eta^5\text{-C}_5\text{Me}_5\text{Mn}(\text{CO})_2)$ -Baugruppe um den Mn, Ge, Mn-Vektor ab. Die Mangan–Germanium-Bindungslängen betragen 2.18(2) Å (Mittelwert) und weisen damit erheblichen Mehrfachbindungscharakter auf.

Multiple bonds between transition metals and “naked” main group elements have rarely been encountered in organometallic chemistry. The few examples belonging to this class of compounds exhibit germanium^{1b,2,3)}, phosphorus⁴⁾, arsenic⁴⁾, sulfur^{5–7)}, and tellurium^{1a,8)} as central structural units E attached to organomanganese, -chromium,

-iron, and -vanadium fragments *M* *via* double or triple bonds, thus producing linear or trigonal-planar arrangements **A** and **B**, **C**, respectively. While several X-ray diffraction studies^{2,4-7}) as well as theoretical calculations⁹) have clearly revealed multiple bond

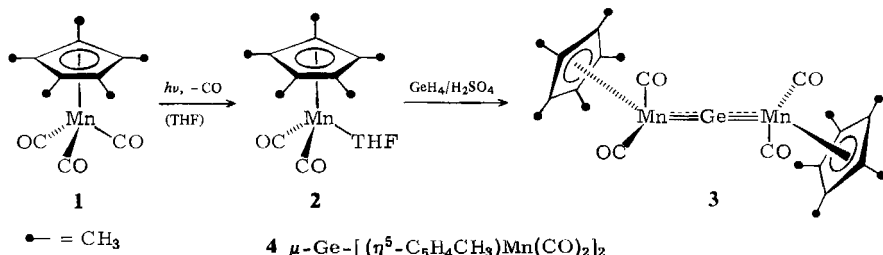


character ($1 < x < 3$), only little basic information is available about the reactivity of such structures^{1a,b}). Beyond that, most compounds came along by serendipity. General synthetic strategies appear to unfold now, but nevertheless have to await broad scopes of applicability. It is these two main objectives that made us enter a project with the aim of exploring multiple bonds between transition metals and bare main group elements in a general context. In addition, we want to find out similarities and principal differences with the well-investigated chemistry of metal–metal bonds¹⁰). In the present paper, we report on the synthesis and crystal structure of a new type-**A** compound having a linear manganese – germanium – manganese framework.

Synthesis

In a previous communication, it was shown that binary germanium hydrides as they result from acidolysis of magnesium germanide, Mg_2Ge , are useful precursors of germanium complexes such as $\mu\text{-Ge}[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$ (type **A**) and $\mu_3\text{-Ge}[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_3$ (type **C**)^{1a}). The methylcyclopentadienyl derivatives of these compounds had originally been prepared and structurally characterized during the pioneering work of *Weiss* et al. who used potassium germyl as a less easily accessible starting compound²). Both methods invariably yielded the di- and trinuclear complexes, although the ratio of products was different. Since increasing steric bulk of ancillary ligands promised to selectively form only the less crowded derivative, we chose to synthesize the hitherto unknown germanium complex $\mu\text{-Ge}[(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2]_2$ (**3**) by reacting germane with the solvens-stabilized organomanganese fragment $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2$, which cleanly forms upon photolysis of the parent compound $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_3$ (**1**) in tetrahydrofuran¹¹).

Scheme 1



The reaction sequence successfully employed for the synthesis of **3** is outlined in Scheme 1. Only compound **3**, an orange-coloured, slightly air-sensitive, crystalline

material, is formed in 40% yield, and there is no indication of the possible trinuclear derivative of composition $\mu_3\text{-Ge}[(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2]_3$ to be present at any stage of this preparation. It thus appears that the sterically demanding pentamethylcyclopentadienyl ligands prevent addition of a further $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2$ entity to **3**, provided this is the correct mechanism leading to type-C compounds; a detailed mechanistic study to elucidate the stepwise formation of such compounds is necessary.

With regard to the synthesis of **3**, an obviously important preparative detail warrants mention: if pure monogermane is generated from $\text{GeCl}_4/\text{NaBH}_4$, small amounts of conc. sulfuric acid are necessary for promoting formation of **3**; otherwise, practically no germanium-containing product is observed. Compound **3** is also formed when **2** is treated with mixtures of various germanes ($\text{Ge}_n\text{H}_{2n+2}$) as they result from decomposition of Mg_2Ge by aqueous hydrochloric acid; in this case, traces of the acid inevitably contaminate the reaction mixture when the gases are transferred into the solution of $(\eta^5\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2(\text{THF})$ (**2**) in a vacuum system¹²). Reproducible yields of the desired compound **3** were achieved with the $\text{GeCl}_4/\text{NaBH}_4/\text{H}_2\text{SO}_4$ system.

X-Ray and Crystal Structure

In order to confirm the expected "cumulene-type" bonding geometry of the Mn_2Ge core, compound **3** was subjected a single crystal X-ray diffraction study (Figures 1 and 2). Atomic coordinates and thermal motion parameters are listed in Table 1, while the data collection and processing parameters are summarized in Table 3. The average values of the bond lengths and angles, shown in Table 2, are not far from the expected values, possibly due to having three independent determinations of each resulting from the unusual contents of the crystallographic unit cell. The average Mn – Ge distance of

Table 1. Atomic Coordinates and Thermal Parameters ($\times 100$) of **3**

Atom	x/a	y/b	z/c	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ge (1)	.2737 (6)	.0631 (8)	.2505 (6)	5 (1)	4 (1)	6 (2)	0 (1)	3 (1)	-1 (1)
Ge (2)	.0000 (0)	.2871 (9)	.2500 (0)	5 (1)	6 (2)	4 (2)	0 (0)	3 (1)	0 (0)
Ge (3)	.5000 (0)	.3350 (10)	.2500 (0)	3 (1)	6 (2)	7 (2)	0 (0)	1 (1)	0 (0)
Mn (1)	.2992 (9)	.0844 (9)	.3511 (10)	4 (1)	3 (2)	8 (2)	0 (1)	1 (1)	-1 (1)
Mn (2)	.2503 (8)	.0422 (8)	.1511 (9)	5 (1)	5 (2)	7 (2)	1 (1)	3 (1)	-1 (1)
Mn (3)	.0043 (8)	.2873 (8)	.3501 (10)	2 (1)	4 (2)	10 (2)	1 (1)	2 (1)	0 (1)
Mn (4)	.4528 (8)	.3345 (9)	.1491 (9)	2 (1)	4 (2)	7 (2)	-1 (1)	1 (1)	0 (1)
O (1)	.164 (4)	.092 (3)	.347 (4)	12 (3)					
O (2)	.312 (4)	-.038 (4)	.378 (4)	14 (4)					
O (3)	.242 (3)	-.175 (4)	.126 (3)	8 (3)					
O (4)	-.114 (4)	.025 (4)	.146 (4)	11 (3)					
O (25)	-.011 (4)	.417 (5)	.341 (5)	17 (4)					
O (26)	.149 (4)	.298 (4)	.388 (4)	12 (4)					
O (37)	.454 (4)	.201 (4)	.149 (4)	12 (3)					
O (38)	.567 (4)	.334 (4)	.122 (4)	13 (4)					
C (1)	.220 (4)	.081 (6)	.348 (6)	9 (0)	C (27)	-.081 (2)	.266 (2)	.381 (2)	8 (2)
C (2)	.289 (6)	.017 (5)	.353 (6)	11 (5)	C (28)	-.068 (2)	.217 (2)	.343 (2)	8 (2)
C (3)	.239 (6)	-.120 (4)	.145 (7)	12 (5)	C (29)	-.009 (2)	.191 (2)	.375 (2)	8 (2)
C (4)	.166 (4)	.046 (6)	.148 (7)	10 (0)	C (30)	.014 (2)	-.224 (2)	.432 (2)	8 (2)
C (5)	.365 (2)	-.112 (2)	.439 (2)	6 (2)	C (31)	-.030 (2)	.270 (2)	.436 (2)	8 (2)
C (6)	.319 (2)	-.159 (2)	.427 (2)	6 (2)	C (32)	-.139 (2)	.307 (2)	.364 (2)	11 (2)
C (7)	.319 (2)	.186 (2)	.368 (2)	6 (2)	C (33)	-.109 (2)	.196 (2)	.281 (2)	11 (2)
C (8)	.365 (2)	.155 (2)	.344 (2)	6 (2)	C (34)	.023 (2)	.138 (2)	.353 (2)	11 (2)
C (9)	.394 (2)	-.110 (2)	.388 (2)	6 (2)	C (35)	.075 (2)	.212 (2)	.481 (2)	11 (2)
C (10)	.381 (2)	-.071 (2)	.497 (2)	7 (2)	C (36)	-.025 (2)	.316 (2)	.468 (2)	11 (2)
C (11)	.277 (2)	-.177 (2)	.469 (2)	7 (2)	C (37)	.436 (6)	.252 (4)	.140 (7)	9 (0)
C (12)	.277 (2)	.237 (2)	.336 (2)	7 (2)	C (38)	.516 (5)	.348 (6)	.137 (6)	9 (0)
C (13)	.381 (2)	-.169 (2)	.282 (2)	7 (2)	C (39)	.357 (2)	.359 (2)	.142 (2)	10 (2)
C (14)	.445 (2)	.066 (2)	.381 (2)	7 (2)	C (40)	.361 (2)	.340 (2)	.081 (2)	10 (2)
C (15)	.305 (2)	-.043 (2)	.158 (2)	9 (2)	C (41)	.402 (2)	.379 (2)	.060 (2)	10 (2)
C (16)	.253 (2)	-.046 (2)	.104 (2)	9 (2)	C (42)	.425 (2)	.423 (2)	.108 (2)	10 (2)
C (17)	.259 (2)	.001 (2)	.062 (2)	9 (2)	C (43)	.397 (2)	.411 (2)	.158 (2)	10 (2)
C (18)	.315 (2)	-.034 (2)	.090 (2)	9 (2)	C (44)	.318 (2)	.330 (2)	.182 (2)	12 (2)
C (19)	.344 (2)	.007 (2)	.149 (2)	9 (2)	C (45)	.326 (2)	.286 (2)	.045 (2)	12 (2)
C (20)	.317 (2)	-.085 (2)	.214 (2)	13 (2)	C (46)	.420 (2)	.375 (2)	-.002 (2)	12 (2)
C (21)	.200 (2)	-.092 (2)	.093 (2)	13 (2)	C (47)	.471 (2)	.474 (2)	-.105 (2)	12 (2)
C (22)	.214 (2)	.014 (2)	-.001 (2)	13 (2)	C (48)	.408 (2)	.447 (2)	.219 (2)	12 (2)

Table 2. Selected Structural Data of Compound 3^{a)}

Bond Lengths (Å)			
Mn–Ge	2.18(2)	C–O	1.25(8)
Mn–C(O)	1.71(9)	C–C	1.42
Mn–C(Cp)	2.20(4)	C–Me	1.51
Mn–Cent	1.82(4)		
Bond Angles (deg)			
Mn–Ge–Mn	179(1)	C(O)–Mn–C(O)	88(7)
Ge–Mn–Cent	127(1)	C(O)–Mn–Cent	124(5)
Ge–Mn–C(O)	89(5)		
Torsions Angles (deg)			
C–Mn···Mn–C	15(5)		
C–Mn···Mn–C	165(5)		
Cent–Mn···Mn–Cent	83(3)		

a) All values are averages over the three independent molecules in the asymmetric unit. All parameters of the pentamethylcyclopentadienyl rings were fixed. Cent = Center of the π -bonded C_5Me_5 ligands.

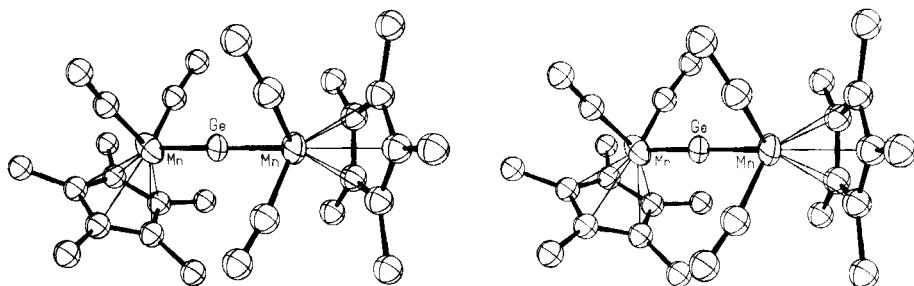


Figure 1. Stereoscopic View of a Single Molecule of Compound 3. The Mn and Ge Atoms are Shown as 50% Equiprobability Ellipsoids and the Remaining Atoms as Spheres of Arbitrary Diameter. The Hydrogen Atoms Could not be Located

2.18 Å is much shorter than the range of 2.48 to 2.60 Å observed for single bonds, and is even shorter than that found in the methylcyclopentadienyl analogue μ -Ge-[(η^5 -C₅H₄CH₃)Mn(CO)₂]₂ (**4**) (2.204 Å) which was reported as the shortest Mn–Ge contact known²⁾. The Mn–Ge–Mn skeleton is essentially linear, as found in a structurally similar triply bonded Cr₂S analogue⁵⁾. The coordination about the manganese atoms is best described as octahedral, with three facial points occupied by the symmetrically π -bonded ring ligands. The orientation of the chemically identical (η^5 -C₅Me₅)Mn(CO)₂ fragments in each molecule is such that two carbonyl groups almost eclipse each other and the remaining two are practically in an *anti*-conformation, relative to the Mn–Ge–Mn vector. The average torsion angles describing this arrangement are shown in Table 2; here, the angle involving the centroids of the C₅Me₅ ligands had to be given as an absolute value since both possible conformations, with the torsion angle positive or negative, are present simultaneously in the asymmetric unit. These two conformers are enantiomeric pairs that are expectedly present as an equimolar mixture in the crystal.

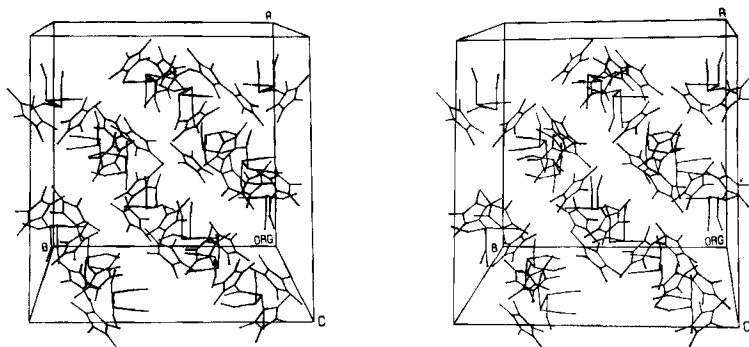
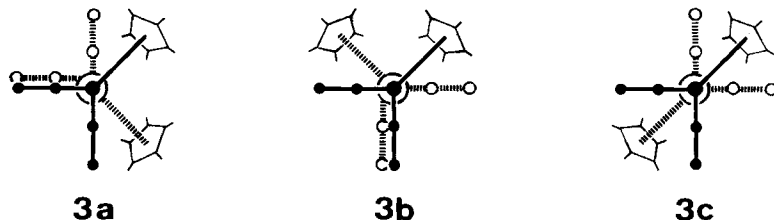


Figure 2. Stereoscopic View of the Molecular Packing in the Unit Cell, as Viewed into the c Axis

When the EAN rule is applied to the manganese atoms in this molecule, one is tempted to assign two formal double bonds to the central germanium atom, rather analogous to the situation found in allene. The shortness of the Mn – Ge bonds in both the current structure and in that of compound **4**²⁾ would seem to support this simple formalism, just as cumulated chromium – sulfur triple bonds are predicted and found for *Legzdins'* compound $\mu\text{-S}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$ ⁵⁾. Also, the linear Mn – Ge – Mn fragment is as expected for an sp -hybridized μ -germanium ligand. In a recent article, however, *Kostić and Fenske*⁹⁾ concluded that the Mn – Ge bonds in the MeCp analogue **4** are not purely double bonds as in allene, but are in reality partially triple so that internal rotation about the Mn – Ge – Mn axis is facile. They based their arguments on non-empirical molecular orbital calculations and the observed infrared spectra. An allene-like structure would be unlikely given the *anti*-conformation of this particular molecule, where the planes of symmetry of the two halves are not perpendicular and orbital overlap is not maximized. In compound **3**, however, as indicated by the above-mentioned torsion angles, orbital overlap is essentially maximized between the Ge and Mn atoms, and this would certainly explain the fact that the Mn – Ge bond lengths are somewhat shorter than in compound **4**.



The packing of the three independent molecules in the unit cell is shown in Figure 2. Unfortunately, the large number of molecules present precludes getting a “clean” view of things, but with diligence the two separate conformers can be observed in their natural habitat, keeping in mind that the ones on the crystallographic two-folds along b are of the same type. Interestingly, only the two anticlinal conformers **3a** and **b** are

observed. The bulky C_5Me_5 ligands have the same relative orientation to each other (identical absolute torsion angles). On steric grounds one would expect the antiperiplanar conformer **3c** to be the more favoured one because it contains all ligands strictly in *anti*-positions. By way of contrast, the antiperiplanar conformer is the only one found in the crystal structure of **4**²⁾.

This work was supported by the *Deutsche Forschungsgemeinschaft*, the *Spanish Ministry of Education* (Fellowship to R. S.), the *Robert A. Welch Foundation* (grant E-594), the *Chemische Werke Huls*, and *Degussa AG*.

Experimental Part

All manipulations were carried out under exclusion of air and water (Schlenk tube technique). Tricarbonyl(η^5 -pentamethylcyclopentadienyl)manganese (**1**) was synthesized in 20–40 g-amounts according to Ref.¹³⁾ by treating decacarbonyldimanganese (Strem Chemicals Inc.) with freshly distilled pentamethylcyclopentadiene¹⁴⁾ (yields 60–70%).

1. *μ -Germanium-bis(dicarbonyl(η^5 -pentamethylcyclopentadienyl)manganese)* (**3**): A solution of 1.50 g (5.4 mmol) of **1** in ca. 200 ml of THF is irradiated in an immersion-well apparatus (Duran or Pyrex; mercury 150 Watt high-pressure lamp)¹⁵⁾. The solution of the resulting complex **2** is transferred into a water-cooled Schlenk-type reaction vessel containing a solution of one drop of conc. sulfuric acid in 20 ml of THF. This vessel is connected with a mercury pressure relief valve. A separate apparatus is used to generate monogermene and consists of the following parts: 500 ml two-necked flask with magnetic stir bar, dropping funnel, and reflux condenser. The Schlenk apparatus is connected with this assembly *via* the top of the condenser. The flask is charged with a solution of 9.0 g (236 mmol) of $NaBH_4$ in 75 ml of oxygen-free water.

The borohydride solution is kept at 0°C and treated, under vigorous stirring, with a total of 8.64 g (4.5 ml; 39 mmol) of $GeCl_4$ dissolved in 100 ml of THF for 2 h. The resulting monogermene reacts with the THF complex **2**. During the generation of GeH_4 , a slight overpressure builds up and is relieved through the Hg bubbler. After 20 h, the carmine colour of the THF complex has turned to orange indicating formation of the desired product. Further work-up is performed in the usual way (chromatography on Florisil 100–200 mesh ASTM, column dimensions 40 × 1.6 cm, +15°C). Unreacted **1** is recovered with *n*-hexane (yellow band). The product appears with toluene/hexane (3:1) as an orange band which is subsequently evaporated to dryness (oil-pump vacuum). Thus, the crystalline orange product **3** appears in 40% yield (600 mg), based upon the total amount of **1** used. – IR (ν_{CO} , cm^{-1} ; toluene): 2000 m, 1951 m, 1919 vs, 1885 s. – ¹H NMR (270 MHz, C_6D_6 , 28°C): $\delta_{CH_3} = 1.67$ [s].

$C_{24}H_{30}GeMn_2O_4$ (565.0) Calcd. C 51.02 H 5.35 Ge 12.85 Mn 19.45
Found C 51.02 H 5.10 Ge 12.3 Mn 19.4

Molecular weight 556 (mass spectrum; field desorption, solution in toluene; reference isotope ⁷⁴Ge).

2. *X-Ray Diffraction Study*¹⁶⁾: All measurements were made on a single crystal (0.03 × 0.03 × 0.02 mm), using an Enraf-Nonius CAD-4 automatic diffractometer equipped with a Mo- K_α target tube and a dense graphite crystal monochromator. Final cell constants, as well as other information pertinent to data collection and refinement, are given in Table 3. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown to be either *Cc* or *C2/c*. Intensities were measured using the Θ - 2Θ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. In reducing the data, Lorentz and polarization factors were applied, but no absorption correction was made.

Table 3. Data Collection and Processing Parameters

Space group	<i>C</i> 2/ <i>c</i> , monoclinic
Cell constants	<i>a</i> = 21.878(11) Å <i>b</i> = 21.931(10) Å <i>c</i> = 21.900(12) Å β = 104.70(5)° <i>V</i> = 10164 Å ³
Molecular formula	C ₂₄ H ₃₀ GeMn ₂ O ₄
Molecular weight	564.95 g · mol ⁻¹
Molecules per cell	<i>Z</i> = 16
Density	ρ = 1.48 g · cm ⁻³
Absorption coefficient	μ = 20.9 cm ⁻¹
Radiation (Mo- <i>K</i> _α)	λ = 0.71073 Å
Collection range	4° ≤ 2Θ ≤ 29°
Scan width	ΔΘ = (1.10 + 0.35 tan Θ)°
Maximum scan time	240 s
Scan speed range	0.4 to 4.0° min ⁻¹
Total data collected	2029
Independent data, <i>I</i> > 3σ(<i>I</i>)	728
Total variables	147
$R = \sum F_o - F_c / \sum F_o $	0.092
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.085
Weights	$w = \sigma(F)^{-2}$

Since the crystal used was so small, virtually no data could be collected beyond $2\Theta > 29^\circ$, and so data collection was stopped at that point. As shown in Table 3, only 728 observed reflections were obtained, and this, coupled with the fact that there are 16 molecules in the unit cell (2 per asymmetric unit in *C*2/*c* or 4 per asymmetric unit in *Cc*), made it mandatory to assume *C*2/*c* as the correct space group since there were nowhere near enough data to refine four independent molecules. After some difficulty, the structure was finally solved by means of the SHELX direct methods program¹⁷). The asymmetric unit was found to consist of one complete molecule plus two half-molecules, each situated on a two-fold axis passing through Ge and bisecting the Mn–Ge–Mn angle. Since there was a large number of atoms to refine and not much data, the pentamethylcyclopentadienyl rings were treated as rigid bodies having C–C (ring) distances of 1.42 Å and C–Me distances of 1.51 Å. No attempt was made to refine hydrogen positions, which in part is responsible for the somewhat large thermal parameters of the methyl carbons. Considering the small number of observed data and the lack of an absorption correction, the results of the least squares refinement seem reasonably consistent with space group *C*2/*c*, although the possibility of *Cc* cannot be completely ruled out since refinement in that space group could not be tested under the circumstances.

Final agreement factors for the full-matrix least squares are given in Table 3. Since the scale factor was highly coupled with the thermal parameters of the heavy atoms, it was held fixed during the final cycles of least squares. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions¹⁸); for hydrogen those of Stewart, Davidson, and Simpson¹⁹) were used. The anomalous dispersion coefficients of Cromer and Liberman²⁰) were used for Mn and Ge. Final positional and thermal parameters are shown in Table 1, with bond lengths and angles based on these positions given in Table 2.

- 1) ^{1a)} Part I: *W. A. Herrmann, J. Weichmann, R. Serrano, K. Blechschmitt, H. Pfisterer, and M. L. Ziegler*, *Angew. Chem.* **95**, 331 (1983); *Angew. Chem., Int. Ed. Engl.* **22**, 314 (1983); *Angew. Chem. Suppl.* **1983**, 363. — ^{1b)} Part II: *W. A. Herrmann, J. Weichmann, U. Küsthardt, A. Schäfer, R. Hörlein, Ch. Hecht, E. Voss, and R. Serrano*, *Angew. Chem.* **95**, 1019 (1983); *Angew. Chem., Int. Ed. Engl.* **22**, 979 (1983); *Angew. Chem. Suppl.* **1983**, 1543.
- 2) *W. Gäde and E. Weiss*, *J. Organomet. Chem.* **213**, 451 (1981); *D. Melzer and E. Weiss*, *ibid.* **263**, 67 (1984).
- 3) For a brief review on multiple bonds between transition metals and ligand-free main group elements see *W. A. Herrmann*, Small Hydrocarbons as Bridging Ligands in Transition Metal Chemistry: Synthesis, Structures, and Reactivity, in: *Organometallic Compounds (B. L. Shapiro, editor)*, Vol. 1, p. 383 ff., Texas A & M University Press, College Station, Texas (USA) 1983. — Bare oxygen and nitrogen atoms exhibiting multiple bonding to transition metals are hitherto confined to complexes in which the metals bear higher oxidation numbers, cf. *F. A. Cotton and G. Wilkinson*, *Advanced Inorganic Chemistry*, Fourth Edition, chapter 4, Wiley & Sons, New York 1980.
- 4) *H. Lang, L. Zsolnai, and G. Huttner*, *Angew. Chem.* **95**, 1016 (1983); *Angew. Chem., Int. Ed. Engl.* **22**, 976 (1983); *Angew. Chem. Suppl.* **1983**, 1451; *G. Huttner, B. Sigwarth, J. v. Seyerl, and L. Zsolnai*, *Chem. Ber.* **115**, 2035 (1982).
- 5) *B. W. S. Kolthammer and P. Legzdins*, *J. Am. Chem. Soc.* **100**, 2247 (1978); *T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins, and J. Trotter*, *Inorg. Chem.* **18**, 3543 (1979).
- 6) The analogous sulfur complex $\mu\text{-S}[(\eta^5\text{-C}_5\text{Me}_5)\text{Cr}(\text{CO})_2]_2$ and its μ -selenium derivative have also been prepared, cf. *W. A. Herrmann, J. Rohrmann, and A. Schäfer*, *J. Organomet. Chem.* **265**, C1 (1984); *J. Rohrmann*, Diplomarbeit, Univ. Frankfurt 1984; *W. A. Herrmann, J. Rohrmann, M. L. Ziegler, and Th. Zahn*, *J. Organomet. Chem.*, in press.
- 7) *J. Schiemann, P. Hübener, and E. Weiss*, *Angew. Chem.* **95**, 1021 (1983); *Angew. Chem., Int. Ed. Engl.* **22**, 980 (1983).
- 8) *M. Herberhold, D. Reiner, and D. Neugebauer*, *Angew. Chem.* **95**, 46 (1983); *Angew. Chem., Int. Ed. Engl.* **22**, 59 (1983); *Angew. Chem. Suppl.* **1983**, 10.
- 9) *N. M. Kostić and R. F. Fenske*, *J. Organomet. Chem.* **233**, 337 (1982).
- 10) For recent reviews see ^{10a)} *F. A. Cotton and M. H. Chisholm*, *Chem. Eng. News*, 28. Juni 1982, S. 40. — ^{10b)} *M. H. Chisholm* (editor), *Reactivity of Metal – Metal Bonds*, ACS Symposium Series, Vol. 155, American Chemical Society, Washington, D.C., 1981. — ^{10c)} *F. A. Cotton and R. A. Walton*, *Compounds With Multiple Bonds Between Metal Atoms*, J. Wiley & Sons, New York 1980.
- 11) ^{11a)} *W. A. Herrmann, R. Serrano, and J. Weichmann*, *J. Organomet. Chem.* **246**, C 57 (1983). — ^{11b)} *J. D. Korp, I. Bernal, W. A. Herrmann, and R. Serrano*, *Chem. Ber.* **117**, 434 (1984).
- 12) *J. Weichmann*, Dissertation, Univ. Frankfurt 1983.
- 13) Cf. Ref. ^{11b)}, Experimental part and footnote on page 440; *R. Hörlein*, Diplomarbeit, Univ. Frankfurt 1984.
- 14) *J. Manriquez, P. J. Fagan, L. D. Schertz, and T. J. Marks*, *Inorg. Synth.* **21**, 181 (1982).
- 15) *W. P. Fehlhammer, W. A. Herrmann, and K. Öfele*, *Metallorganische Komplexverbindungen*, in: *Handbuch der Präparativen Anorganischen Chemie (G. Brauer, editor)*, 3rd edition, Vol. III, p. 1799 ff., Enke-Verlag, Stuttgart 1981.
- 16) Further details and basic data concerning the X-Ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany) by specifying registry number CSD 50818, authors, and the reference to this publication.
- 17) *G. M. Sheldrick*, SHELX-76 Programs for Crystal Structure Determination, Cambridge University 1976.
- 18) *D. T. Cromer and J. B. Mann*, *Acta Crystallogr., Sect. A* **24**, 321 (1968).
- 19) *R. F. Stewart, E. R. Davidson, and W. T. Simpson*, *J. Chem. Phys.* **42**, 3175 (1965).
- 20) *D. T. Cromer and D. J. Liberman*, *J. Chem. Phys.* **53**, 1891 (1970).