Crystal Structure of Magnesium Sesquicarbide

Helmer Fjellvåg* and Pavel Karen

Department of Chemistry, University of Oslo, Blindern, N-0315, Oslo 3, Norway

Received July 19, 1991

Mg_2C_3 was prepared by reaction of Mg dust with *n*-pentane at ~680 °C. A relatively pure product (90% Mg_2C_3) was obtained with carbon and MgO as impurities. The X-ray pattern of the hydrolyzable part of the sample was indexed on an orthorhombic cell having a = 6.4108 (3) Å, b = 5.2786 (2) Å, c = 3.7283 (2) Å, and Z = 2. Since $a{:}b{:}c \approx \sqrt{3}{:}\sqrt{2}{:}1$, various derivative lattices may be found. The crystal structure solved from powder X-ray and neutron diffraction data is described in space group *Pnnm* with Mg in 4g [x = 0.2903 (3), y = 0.3901 (4)] and C in 2d and 4g [x = 0.6188 (3), y = 0.2070 (3)]. Mg_2C_3 represents the first example of a carbide structure having exclusively C_3 carbon groups. These units are linear, isoelectronic with CO_2, and their C–C distances of 1.332 (2) Å are somewhat enhanced due to the π-interaction with Mg. The bridging of the C–C bonds by Mg is reminiscent of polycenter, electron-deficient bonds.

Introduction

Unlike many carbides containing isolated carbon atoms or C_2 pairs, no carbide with solely three-membered carbon groups has to date been structurally characterized. Since Novák[1] first described the MgC_2 and Mg_2C_3 carbides, the sesquicarbide has been the most likely candidate to contain C_3 groups. Unfortunately, the Mg–C phases are thermally unstable[2,3] and highly reactive,[3,4] and that has until now prevented detailed structural studies. On the basis of hydrolysis experiments, the presence of C_3^{4-} anions was postulated,[5] with most probably a symmetrical, CO_2-related electronic structure.[4] Since no single crystal of Mg_2C_3 has yet been available, the limited crystallographic information was deduced from powder diffraction diagrams. Moreover, the powder samples were significantly contaminated by MgO. In the present study, the structural properties of Mg_2C_3 are derived from high-resolution powder X-ray and neutron diffraction data, the prerequisite of which was an improved preparation technique yielding relatively pure Mg_2C_3 samples.

Experimental Section

Preparation of Mg_2C_3. The carbide was prepared by reaction of pulverized magnesium (99.96% Mg in bulk) with *n*-pentane vapor (99.9%, Carlo Erba) dried with sodium. The magnesium dust with grain size less than 50 μm was obtained by filing the metal under dried kerosene. After the protecting liquid was filtered off under an argon atmosphere and the solid was washed with dry *n*-heptane, the still hydrocarbon-soaked powder (~9 g of Mg) was placed in an alumina boat and introduced into a tube furnace. The isothermal (±5 °C) zone of the furnace was shielded with a mixture of iron and aluminum wools, and the entire system was flushed with hydrogen, purified on Mg turnings at 650 °C in a separate furnace. After the reaction temperature 680 °C was reached, *n*-pentane was introduced into the preparation line by reducing the pressure in an evaporation vessel, kept at 15 °C. In this arrangement, the *n*-pentane flow rate was ~30 g/h. After 85 min, the reaction was complete (sample temperature ≤690 °C) and the product was cooled inside the closed furnace. All subsequent manipulations with the sample were done in argon-filled glovebags. Chemical analyses were performed on analogously prepared samples and are described in ref 4.

Characterization and Diffraction Studies. Powder X-ray diffraction (PXD) data were collected at liquid nitrogen temperature with a Guinier Simon camera (Enraf-Nonius) with monochromatic Mo Kα_1 radiation (λ = 0.709 26 Å). The samples were sealed into Lindemann glass capillaries of 0.3-mm diameter. Silicon was used as an external standard.[6] Position and intensity measurements of Bragg reflections were carried out using a Nicolet L18 film scanner controlled by the SCANPI[7] program system. Trial and error indexing of the diffraction pattern was done with the help of the TREOR[8] program. Unit cell parameters were obtained by least-squares refinements with the CELLKANT[9] program. Calculation of Patterson and Fourier maps and least-squares refinements for data based on integrated intensities read from the Guinier films were performed with the GX program system.[10]

Powder neutron diffraction (PND) data were collected on the D2B high-resolution powder diffractometer at the Institute Laue-Langevin, Grenoble, France, with monochromatized neutrons of wavelength 1.5938 Å. The sample was kept in a sealed cylindrical Al container, and diffraction data were collected at room temperature for scattering angles up to 150° in steps of 0.025° (in 2θ). The parts of the diffraction diagram containing reflections due to Al were excluded from calculations, and Rietveld refinements were performed with the XRS82 program system and the programs ALLHKL and EDINP.[11] The scattering lengths, b_{Mg} = 5.375 and b_C = 6.648 fm, were taken from ref 12.

Results

Synthesis. Magnesium sesquicarbide was obtained as a porous sintered rod of gray color. The sample was found to contain ≤10% soot and ~5% MgO as impurities, on the basis of comparisons of its PXD diagram with those of samples previously analyzed[4] by chemical means.

Unit Cell Determination. The PXD pattern of pure Mg_2C_3 was obtained as the difference between the patterns of the sample and of its product of hydrolysis in air. No new reflections emerged after the hydrolysis, since the $Mg(OH)_2$ produced was amorphous and hence only MgO lines and a broadened (001) line from graphite were detected. The trial and error indexing of the diagram suggested that the unit cell is orthorhombic, 4 times

---

[1] Novák, J. *Z. Phys. Chem. Stoechiom. Verwandschaftsl.* **1910,** *73,* 513.

[2] Hájek, B.; Karen, P.; Brožek, V. *Collect. Czech. Chem. Commun.* **1983,** *48,* 1963.

[3] Rueggeberg, W. H. C. *J. Am. Chem. Soc.* **1943,** *65,* 602.

[4] Hájek, B.; Karen, P.; Brožek, V. *Collect. Czech. Chem. Commun.* **1980,** *45,* 3408.

[5] (a) Schmidt, J. *Z. Elektrochem. Angew. Phys. Chem.* **1934,** *40,* 170. (b) Irmann, F. *Helv. Chim. Acta* **1948,** *31,* 1584. (c) Cordes, J. F.; Wintersberger, K. *Z. Naturforsch., B* **1957,** *12,* 136.

[6] Deslatters, R. D.; Henins, A. *Phys. Rev. Lett.* **1973,** *31,* 972.

[7] Werner, P. E. *Program SCANPI*; Institute of Inorganic Chemistry, University of Stockholm: Stockholm, Sweden, 1981.

[8] Werner, P. E. *Program TREOR-5*; Institute of Inorganic Chemistry, University of Stockholm: Stockholm, Sweden, 1988 (see also *Z. Kristallogr.* **1964,** *120,* 375).

[9] Ersson, N. O. *Program CELLKANT*; Chemical Institute, Uppsala University: Uppsala, Sweden, 1981.

[10] Mallinson, P.; Muir, K. W. *J. Appl. Crystallogr.* **1984,** *18,* 51.

[11] (a) Baerlocher, C. *Proc. Int. Zeolite Conf.* 1984, *6.* (b) Baerlocher, C. *The X-ray Rietveld System*; Institut für Kristallographie und Petrographie: ETH, Zürich, 1982. (c) Pawley, G. S. *J. Appl. Crystallogr.* **1980,** *13,* 630. (d) Pawley, G. S. Personal communication, 1982.

[12] Sears, W. F. Thermal-Neutron Scattering Lengths and Cross Sections for Condensed Matter Research. Report AECL 8490; Chalk River Nuclear Laboratories: Ontario, Canada, 1984.

0020-1669/92/1331-3260$03.00/0 © 1992 American Chemical Society

smaller than the hexagonal cell originally proposed by Irmann,[5b] who included one MgO line in the indexing. The room-temperature unit cell parameters were derived from the Rietveld refinements, with $a = 6.4108$ (3) Å, $b = 5.2786$ (2) Å, and $c = 3.7283$ (2) Å. From PXD, unit cell parameters at 77 K were obtained with singly indexable reflections only: $a = 6.376$ (2) Å, $b = 5.260$ (2) Å, $c = 3.711$ (2) Å. The ratios of the orthorhombic unit cell parameters are close to $\sqrt{3}$:$\sqrt{2}$:1, for which numerous derivative lattices having higher metric symmetry are found with converse transformation analysis.[13] The orthorhombic unit cell is distinctly favored by the $M(20)$ figure of merit of the PXD data indexation.[14] The PXD data are listed in Table I.

Crystal Structure Determination. In the diffraction pattern, reflections of the type $0kl$ with $k + l = 2n + 1$ and of the type $h0l$ with $h + l = 2n + 1$ were absent or could equivalently well be indexed as other hkl reflections. This suggests that the space group is *Pnnm* (No. 58). On the basis of the integrated intensities from the PXD photographs, the magnesium atoms (in 4g) could be identified from the Patterson map, whereas the positioning of the carbon atoms had to be based on the PND data. In view of the chemical information about the nature of the C_3 groups, only a few structure models were to be tested. The assumption of linear C_3 groups was fully verified by the structure refinements. The atomic coordinates and temperature factors as obtained from the Rietveld refinement are listed in Table II. The observed, calculated, and difference PND patterns are shown in Figure 1. The obtained R values from the EDINP[11c] structure refinements are $R_p = 0.069$ and $R_{wp} = 0.094$ ($R_{exp} = 0.089$; 4067 data points; 130 Bragg reflections and 22–25 refined parameters in the final Rietveld refinement). The unit cell parameters were refined initially, together with the zero point, and were fixed in the final refinement. For Mg and C(2), the introduction of anisotropic temperature factors ($B_{11}, B_{22}, B_{33}, B_{12}$) gave significantly improved fits. For C(1), no improvement in R_i was obtained, and hence C(1) was refined isotropically. For Mg and C(2), and also for C(1) if refined anisotropically, B_{22} is appreciably smaller than B_{11} and B_{33}. The choice of the temperature factor description influences only slightly the refined values for atomic coordinates, which are consistent within calculated standard deviations. Notably, a very slight extension of the C–C bond would follow if C(1) were allowed to be refined anisotropically. The atomic arrangement is shown in Figure 2.

Discussion

The carbide Mg_2C_3 contains linear three-membered carbon groups. In accordance with the site symmetry, both the C–C bonds are equivalent, with a length of 1.332 (2) Å. The distance is 0.02 Å longer than that of allene (1.31 Å[15]). This feature must be considered as rather surprising since the C–C bonds in prevailingly ionic dicarbides are shorter than the bond in acetylene. Thus, the C–C distance of 1.205 Å in C_2H_2[16] shortens to 1.19 Å in CaC_2.[17] The observed extension of the C–C bonds is most probably caused by bridging of the bonds by Mg.

CNDO/2 calculations (using a standard set of coefficients[18] and assuming core–core repulsions for point charges) support the stability of the linear, symmetrical arrangement of the C_3^{4-} molecular ion. A C–C distance of 1.36 Å is obtained, independent of the chosen starting geometry (with an exception of a local minimum of the overall energy occurring when a triangular model is adopted). Analogous calculations give a C–C distance of 1.25 Å for the C_2^{2-} molecular ion.

Table I. Observed and Calculated PXD Data for Mg_2C_3 at 77 K (Mo $K\alpha_1$)

d_o, Å	$(I/I_0)_o$	hkl[a]	d_c, Å	$(I/I_0)_c$
4.06	2	110	4.06	5
3.21	100	101	3.21	100
		200	3.19	29
3.03	10	011	3.03	25
2.736	10	111	2.738	23
2.429	79	120	2.431	86
2.200	73	211	2.200	82
1.971	11	310	1.971	16
1.853	47	002	1.856	37
		301	1.844	17
1.780	20	221	1.780	24
1.740	20	311	1.740	27
1.654	4	320	1.653	7
1.604[b]	6	202	1.604	9
		400	1.594	1
1.585	1	031	1.585	3
1.538	42	131	1.538	34
		230	1.536	7
		410	1.526	6
1.475	38	122	1.475	32
1.416	2	411	1.411	3
		231	1.420	2
1.364	1	420	1.363	1
1.352	7	312	1.351	8
1.314	1	040	1.315	2
1.282	9	421	1.280	11
1.272	3	331	1.271	3
1.235	2	322	1.234	5
		510	1.239	3
1.213[c]	11	240	1.216	6
		501	1.206	4
		103	1.214	3
		013	1.204	2
		402	1.209	1
1.182[c]	7	232	1.183	5
		412	1.178	4
		430	1.179	3
		113	1.183	2
1.126[c]	8	213	1.126	6
		431	1.124	4
		340	1.118	1
1.099	2	521	1.096	3
		422	1.099	2
1.072	3	341	1.071	3
		303	1.069	2
		042	1.073	1
1.057[c]	1	223	1.056	3
1.047[c]	2	313	1.048	3
		610	1.042	3
1.032[c]	1	512	1.031	2
		530	1.031	2
		150	1.038	1
1.013[c]	7	051	1.012	5
		242	1.017	5
0.9983[b]	5	133	0.9983	5
		432	0.9954	2
0.9556[c]	2	621	0.9523	3
		251	0.9647	2
		342	0.9578	1

[a] Orthorhombic cell indices; data given only if $(I/I_0)_c > 1$. [b] Line splitting indicated by some film scans, not resolved by unaided eye. [c] Line broadening seen both by densitometer scans and by eye.

The overall coordination around the C_3 group is shown in Figure 3. Two different bond qualities are seen in the carbon coordination polyhedra. The terminal and more negatively charged carbon atoms of the C_3 group coordinate the Mg atoms in a manner similar to that found in the salt-type carbides of the alkaline earth metals. However, two of these Mg atoms have almost equal bond distances to the terminal and the central carbon atom. This features a π-complex, multicentered bond situation, as previously proposed for the Li_2C_2 molecule[19] and for some related organolithium compounds.[20] The consequent elongation of the par-

---

(13) Karen, V. L.; Mighell, A. D. *J. Appl. Crystallogr.* **1991**, *24*, 1076.
(14) De Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108.
(15) Stoicheff, B. P. *Can. J. Chem.* **1955**, *33*, 811.
(16) Yearian, H. Cited in: Allen, P. W.; Sutton, L. E. *Acta Crystallogr.* **1950**, *3*, 46.
(17) Atoji, M. *J. Chem. Phys.* **1961**, *35*, 1950.
(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Table II. Positional Parameters and Temperature Factor Coefficients for Mg_2C_3 As Refined from Powder Neutron Diffraction Data by the Rietveld Method[a]

atom	Mg	C(1)	C(2)
site	4g	2d	4g
x	0.2903 (3)	$^1/_2$	0.6188 (3)
y	0.3901 (4)	0	0.2070 (3)
z	0	0	0
B_{11}, Å^2	1.28 (12)		0.60 (6)
B_{22}, Å^2	0.59 (8)		0.36 (5)
B_{33}, Å^2	1.02 (8)		1.14 (6)
B_{12}, Å^2	−0.01 (6)		−0.03 (5)
B_{iso}, Å^2	0.96 (9)	1.02 (4)	0.70 (6)

[a] Space group *Pnnm*; a = 6.4108 (3) Å, b = 5.2786 (2) Å, c = 3.7283 (2) Å. Calculated standard deviations are given in parentheses.

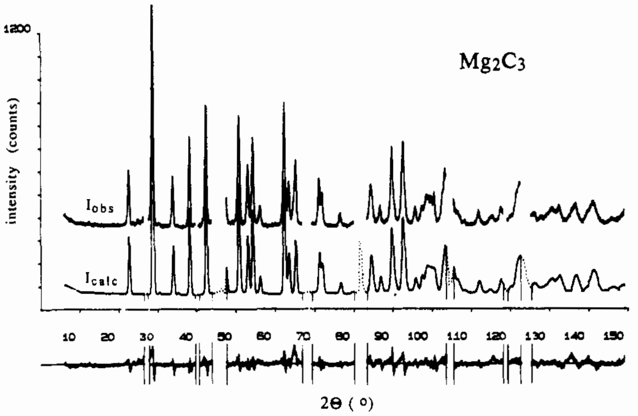

Figure 1. Observed, calculated, and difference powder neutron diffraction patterns for Mg_2C_3. Excluded regions are omitted on I_o; calculated intensities in excluded regions are shown by dotted lines. Extent of excluded regions is shown by vertical thin lines.

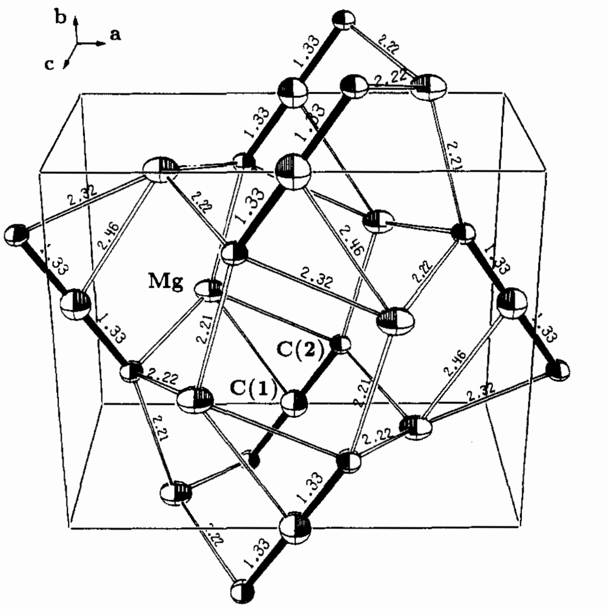

Figure 2. ORTEP-II plot of the atomic arrangement of Mg_2C_3. Thermal vibration ellipsoids are drawn at 75% probability, C–C bonds are full thick lines, and C–Mg bonds appear as empty double lines. Calculated standard deviations for interatomic distances do not exceed ±0.006 Å. Note, for full coordination around Mg, see Figure 4.

ticipating bonds, i.e., both the C–C and the bridging Mg–C, supports this view (Figure 3).

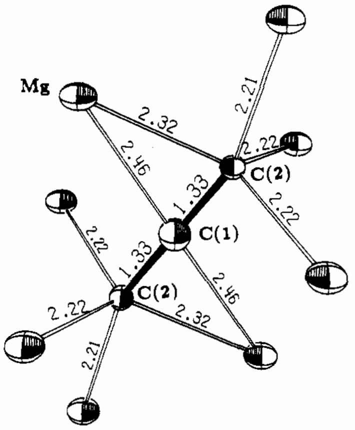

Figure 3. Coordination around the C_3 group in Mg_2C_3. For other notes, see the caption to Figure 2.

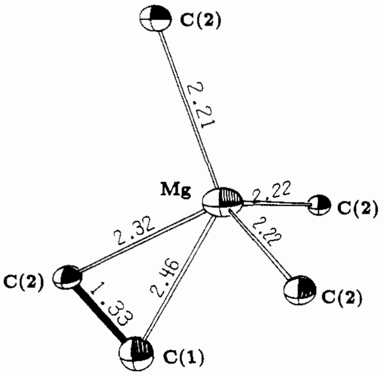

Figure 4. Magnesium coordination in Mg_2C_3. For other notes, see the caption to Figure 2.

The differences in the Mg–C bond lengths give clues to the nature of the bonding. In the π-complex part of the coordination polyhedra, the Mg–C distances average to a rather high value of 2.39 Å, which is comparable with that in dicyclopentadienylmagnesium.[21] The remaining Mg–C bonds are shorter and have virtually equal lengths of ~2.22 Å. This is shorter than bonds in some hypercarbon magnesium alkyls (2.24 Å in polymeric dimethylmagnesium[22]) but longer than the s-type bonds in Grignard reagents (2.15 Å in ethylmagnesium bromide dietherate[23]).

As seen in Figure 4, Mg is coordinated by four C_3 groups within a virtually tetrahedral arrangement, three via terminal atoms of the C_3 rods and one via the C–C multiple bond. The tetrahedron departs slightly from regularity, since the normals to the multiple C–C bond and to the plane of the terminal carbons intersect at 2.3 (1)°. The six edges of the tetrahedron are 2 × 3.643 (1) Å, 3.7283 (2) Å, 2 × 3.60 (1) Å, and 3.66 (1) Å, the last three being connected with the apex at the multiple bond. The Mg bonds to the terminal carbons are slightly different [2 × 2.224 (3) Å and 2.205 (5) Å], likewise the angles [113.9 (1)° and 2 × 110.7 (3)°]. The distance of Mg from the multiple C–C bond is 2.28 (1) Å, and the normal intersects the C–C bond 0.92 (1) Å away from the central C(1) atom. Tetrahedral coordination for magnesium is well-known from, e.g., magnesium dialkyls with symmetrically bridging alkyl groups[22] and is also rather typical for some other diorganylmagnesium compounds. It is possible to show that the requirement of tetrahedral bonding of Mg to the three end carbons and to the C–C bond accounts for the special ratios of the unit cell parameters.

The crystal structure of magnesium sesquicarbide may be discussed using two available sets of Mg_2C_3 chemical analogues:

---

(19) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Jorgensen, W. L. *Tetrahedron Lett.* **1976**, *43*, 3923.

(20) (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 2848. (b) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(21) Bünder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

(22) Weiss, E. *J. Organomet. Chem.* **1964**, *2*, 314.

(23) Guggenberger, L. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 5375.

(i) Li compounds with comparable isoelectronic non-metal groups and (ii) carbides of neighboring metals.

The array of anions N_3^-, NCN^{2-}, NBN^{3-}, and C_3^{4-} comprises isoelectronic groups composed of atoms of comparable electronegativities. The stability of these groups as anions decreases rapidly throughout this array, as demonstrated by the acidity of their related hydrogen acids. In accordance with this, the structure of LiN_3 is of typical ionic nature, with Li bonded exclusively to the terminal nitrogens.[24] Considering both stoichiometry and size relations, the structure of Li_2CN_2 could well be isomorphic with that of Mg_2C_3. However, owing to a rather pronounced ionic nature of Li_2CN_2, an exclusive contact of Li to the terminal N atoms is preferred, and the anions align parallel in a very simple tetragonal structure.[25] The metal coordination to the terminal nitrogens prevails also in α- and β-Li_3BN_2.[26] In α-Li_3BN_2, the NBN groups are coordinated linearly to a portion of the Li atoms, forming chains which are interconnected by a second portion of Li atoms having tetrahedral coordination. In β-Li_3BN_2, the structure is skewed so that *all* Li atoms possess tetrahedral coordination.[26] These comparisons show that the peculiar structural features of Mg_2C_3 are a consequence of its low ionicity, which enables the electron-deficient Mg atoms to be coordinated simultaneously to both the terminal and the central atom of the C_3 group. Therefore, the C_3 groups cannot align parallel while conserving the tendency of Mg for tetrahedral coordination.

The unique character of Mg_2C_3 may be understood in terms of the chemical properties of the Mg-neighboring metals, considering that covalent carbides derived from methane are formed by the more electronegative neighbors of Mg, while ionic carbides derived from acetylene are formed by the more electropositive ones. Since the acidity of C_3H_4 lies between that of methane and acetylene, formation of carbides with C_3 groups is expected to occur for elements on the borderline between those forming carbides with methanide and acetylide groups. In agreement with this, lithium forms an acetylide,[27] but also a relatively stable carbide Li_4C_3,[28] and scandium and the most electronegative lanthanoids form a methanide M_2C_{1-x},[29] but also a carbide of the type M_3C_4,[30] which contains a portion of C_3 groups next to C_2 and C_1 units.

The chemical properties of the C_3 carbides are further demonstrated by the composition of the gaseous hydrolysis products and by the vigor of their hydrolysis.[31] In this respect, the bonding of the C_3 groups in Sc_3C_4 is very similar to that in Mg_2C_3, viz., by having an extended C–C bonding distance [1.342 (3) Å] and by showing the features of σ-donor π-acceptor behavior for Sc which bridges the C–C bonds. The same features are expected[20a] for the not yet structurally characterized solid Li_4C_3 and for other perlithiated hydrocarbons.[32]

Although the vigorous hydrolyzability of Mg_2C_3 could comply also with a preferably ionic model of bonding, the structural features point toward a significantly developed covalent nature with participation of electron-deficient, polycenter bonds. Probably the very instability of the electron-deficient interactions makes the carbide both thermally unstable and extremely vulnerable to nucleophile attacks, thereby reminiscent of several aluminum and boron compounds. Altogether, the structure of Mg_2C_3 provides not merely a new structure type but also a very interesting example of chemical bonding with mixed nature.

Acknowledgment. The opportunity for collecting PND data at the Institut Laue-Langevin, Grenoble, France, is gratefully acknowledged. Fruitful discussions and the lattice metric analysis provided by Dr. V. L. Karen and Dr. A. D. Mighell are highly appreciated.

Supplementary Material Available: A listing of observed PND intensities and a computer output listing of the final Rietveld refinement data (26 pages). Ordering information is given on any current masthead page.

---

[24] Pringle, G. E.; Noakes, D. E. *Acta Crystallogr., Sect. B* **1968**, *24*, 262.

[25] Down, M. G.; Haley, M. J.; Hubbertsey, P.; Pulham, R. J.; Thunder, A. E. *J. Chem. Soc., Dalton Trans.* **1978**, 52.

[26] (a) Yamane, H.; Kikkawa, S.; Koizumi, M. *J. Solid State Chem.* **1987**, *71*, 1. (b) Evers, J.; Münsterkötter, M.; Oehlinger, G.; Polborn, K.; Sendlinger, B. *J. Less-Common Met.* **1990**, *162*, L17.

[27] Juza, R.; Wehle, V. *Naturwissenschaften* **1965**, *52*, 537.

[28] (a) West, R.; Carney, P. A.; Mineo, I. C. *J. Am. Chem. Soc.* **1965**, *87*, 3788. (b) West, R.; Jones, P. C. *Ibid.* **1969**, *91*, 6156. (c) Shimp, L. A.; Lagow, R. J. *Ibid.* **1973**, *95*, 1343. (d) Shimp, L. A.; Morrison, J. A.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *Ibid.* **1981**, *103*, 5951.

[29] (a) Spedding, F. H.; Gschneidner, K.; Daane, A. H. *J. Am. Chem. Soc.* **1958**, *80*, 4499. (b) Krikorian, N. H.; Bowman, A. L.; Krupka, M. C.; Arnold, G. P. *High Temp. Sci.* **1969**, *1*, 360.

[30] Pöttgen, R.; Jeitschko, W. *Inorg. Chem.* **1991**, *30*, 431.

[31] Hájek, B.; Karen, P.; Brožek, V. *Rev. Inorg. Chem.* **1986**, *8*, 117.

[32] Schleyer, P. v. R. *J. Phys. Chem.* **1990**, *94*, 5560.