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Synthesis and Carbonylation of Bis(cyclopentadienyl)methyl(triphenylgermyl)titanium(IV)

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The synthesis of bis(cyclopentadienyl)methyl(triphenylgermyl)titanium(IV), 1, by reaction of dimethyltitanocene with triphenylgermane is described. 1 reacts rapidly with CO under ambient conditions to give acetyl(triphenylgermyl)titanocene, 2. The crystal structure of 2 was determined, providing the first example of a structurally characterized germyltitanium compound. The (η^2-acetyl)titanocene fragment is almost identical with that of the previously reported acetylchlorotitanocene, and the Ti–Ge bond was found to be 2.710 (2) Å. As in the case of the Ti–Cl bond of the acetyl chloro complex, the Ti–Ge bond is unusually long (0.23 Å longer than anticipated on the basis of covalent radii). This lengthening is attributed to the fact that the four-electron η^2-acetyl ligand binds optimally in both cases, and the other ligand partially leaves to accommodate this binding.

Introduction

Compounds containing Ti(IV)–M bonds, where M = a group 14 element other than C, are still very rare. Only one such compound containing Si, $Cp_2TiCl(SiMe_3)$, is known unequivocally.[2] Some other reported compounds[3] were almost certainly the siloxyl rather than the silyl products.[4] Another compound, $[Cp_2Ti(\mu\text{-}SiH_2)]_2$, for which even a crystal structure was reported ($R = 0.09$),[5] could well be $[Cp_2Ti(SiH_3]_2$, since our studies of congeners of the latter show that a distinction between these two possible structures would not likely be possible at $R > 0.05$.[6] The Ti(III) silyl is also a more likely product of the synthetic method used.[5]

A number of complexes containing the Ti(IV)–Ge bond have been obtained by reaction of titanocene(IV) halide complexes with germyllithiums.[7] By such routes, Vishinskaya et al. were able to prepare Cp_2TiRR', where R = R′ = Ph_3Ge and R = Ph_3Ge, R′ = Cl.[7a,b] These compounds are relatively stable at room temperature. The compound R = R′ = Et_3Ge is stable at −40 °C but decomposes rapidly at room temperature to Et_6Ge_2 and titanocene decomposition products.[7b] However, reaction of the digermyl complex with a chlorocarbon yields the more stable chlorotriethylgermyl compound.[7a] Earlier attempts to prepare compounds the type $Cp_2TiMe(MR_3)$ by reaction of group 14 hydrides with Cp_2TiMe_2 were unsuccessful.[7a] In this paper we report a successful attempt to carry out this reaction with triphenylgermane. The carbonylation of the methyltriphenylgermyl complex is also described together with the crystal structure of the resulting acetyltriphenylgermyl complex. The latter is the first crystal structure reported for a compound containing a Ti–Ge bond.

Table I. Crystal Data and Parameters for Data Collection

formula	$C_{30}H_{28}GeOTi$
fw	525.02
space group	$P2_1/c$
a, A	8.410 (6)
b, A	16.938 (9)
c, A	17.822 (10)
β, deg	102.28 (5)
V, A3	2481 (3)
Z	4
D(calcd), g/cm^3	1.406
λ, Å	0.71069 (Mo Kα)
μ, mm^{-1}	1.532
max 2θ, deg	45
transmissn factors	0.709–0.790
min scan rate, deg/min	1.5
no. of reflctns measd	3268
obsd reflctns	1329 ($I > 2.5\sigma(I)$)
background time/scan time	0.5
final no. of parameters	300
R (all reflctns)	0.070
R_w (all reflctns)	0.052

Results

Synthesis of Methyl- and Acetyl(triphenylgermyl)titanocene. In contrast to the behavior of triethylgermane, described earlier by Razuvaev et al.,[7b] we find that reaction 1 proceeds essentially quantitatively.

$$Cp_2TiMe_2 + Ph_3GeH \xrightarrow[\text{hexane}]{75\ °C} \underset{1}{Cp_2TiMe(GePh_3)} + MeH \tag{1}$$

The product, being insoluble in hexane, is precipitated out as a violet microcrystalline solid. The progress of the reaction is easily followed by NMR in toluene, in which the product remains in solution.

Treatment of a solution of 1 in a 2:1 ether/hexane solution with CO results in rapid formation of acetyl(triphenylgermyl)titanocene, 2, which crystallizes out essentially quantitatively as black prisms (in intense transmitted light the crystals are purple). Following the reaction by ^1H NMR, its progress is evident from the disappearance of the methyl resonance of the reactant (−0.42 ppm) and the appearance of the acetyl resonance (2.08 ppm). Solutions of 2, freshly prepared in toluene under a CO atmosphere, are stable and show no evidence of 1. Solutions made up in the absence of excess CO show variable

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Table II. Positional Parameters ($\times 10^4$) with Their Esd's and Temperature Factors [$U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* \bar{a}_i \bullet \bar{a}_j$ ($\times 10^3$)]

atom	x	y	z	U_{eq}, Å^2
Ge	33 (1)	710 (1)	6816 (1)	49
Ti	1026 (2)	7619 (1)	5552 (1)	55
C(1)	2580 (19)	8591 (9)	5869 (7)	138
C(2)	3816 (29)	9267 (13)	5727 (11)	277
O	2383 (11)	8421 (5)	6450 (5)	133
C(11)	1373 (12)	6401 (7)	4990 (6)	76
C(12)	2025 (13)	6300 (6)	5785 (5)	66
C(13)	3401 (12)	6786 (7)	5956 (6)	79
C(14)	3556 (12)	7199 (8)	5295 (6)	81
C(15)	2314 (12)	6954 (8)	4706 (5)	84
C(21)	−1495 (12)	7598 (7)	4654 (6)	81
C(22)	−536 (15)	8115 (8)	4345 (5)	107
C(23)	−241 (15)	8729 (8)	4859 (6)	97
C(24)	−1055 (14)	8616 (6)	5438 (6)	91
C(25)	−1806 (12)	7875 (7)	5326 (5)	72
C(31)	−947 (10)	7925 (6)	7326 (5)	43
C(32)	−2629 (11)	7970 (6)	7310 (5)	60
C(33)	−3278 (12)	8588 (6)	7656 (6)	71
C(34)	−2308 (13)	9181 (6)	8045 (6)	65
C(35)	−680 (12)	9171 (6)	8043 (5)	59
C(36)	−35 (11)	8550 (6)	7714 (5)	52
C(41)	1854 (11)	6713 (6)	7652 (4)	46
C(42)	3228 (11)	7145 (7)	7897 (5)	64
C(43)	4509 (11)	6893 (6)	8446 (6)	73
C(44)	4492 (13)	6155 (7)	8757 (6)	84
C(45)	3095 (14)	5702 (7)	8503 (6)	83
C(46)	1795 (12)	5969 (6)	7963 (5)	64
C(51)	−1598 (12)	6232 (6)	6649 (5)	53
C(52)	−2371 (13)	5952 (6)	7234 (6)	71
C(53)	−3399 (13)	5328 (7)	7135 (6)	76
C(54)	−3785 (12)	4975 (6)	6424 (6)	71
C(55)	−3163 (12)	5232 (6)	5834 (6)	69
C(56)	−2103 (12)	5862 (6)	5936 (5)	54

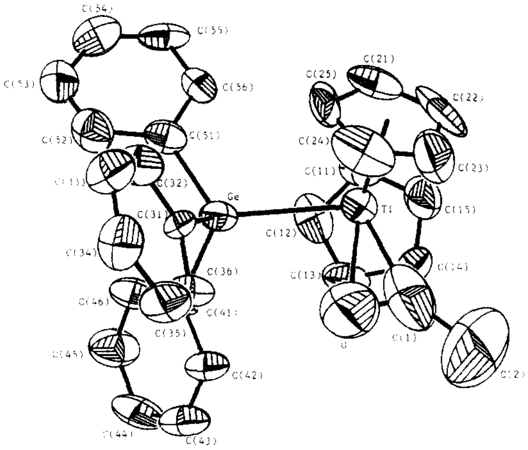

Figure 1. A view of the molecular structure of acetyl(triphenylgermyl)titanocene. The ellipsoids correspond to 50% probability.

amounts of 1 due to facile loss of CO. Purging solutions of 2 with an inert gas, or even hydrogen, pushes the equilibrium entirely to 1, from which 2 may be regenerated by a further purge with CO.

Attempts to carry out the analogues of reaction 1 with R_3MH (R = Ph or Et; M = Si or Sn) did not lead to the successful isolation of products. NMR evidence showed clearly that the reaction of triethylsilane was leading to the analogue of 1, but the product was not very stable under conditions of its formation. The other reactions gave no evidence for the formation of analogues of 1. They all appeared to lead to reduced titanium species, some of which gave high-field hydride resonances (ca. −8 ppm) characteristic of hydride-bridged Ti(III) compounds.[6,8]

Table III. Bond Lengths (Å) and Angles (deg)

Ti–Ge	2.710 (2)	Ge–Ti–C(1)	109.0 (4)
Ti–C(1)	2.15 (2)	Ge–Ti–Cp(1)	102.7 (3)
Ti–O	2.220 (9)	Ge–Ti–Cp(2)	103.2 (4)
Ti–Cp(1)	2.06 (1)		
Ti–Cp(2)	2.08 (1)		
Ti–C(11)	2.34 (1)	C(1)–Ti–Cp(1)	102.9 (5)
Ti–C(12)	2.39 (1)	C(1)–Ti–Cp(2)	101.8 (5)
Ti–C(13)	2.43 (1)	Cp(1)–Ti–Cp(2)	135.7 (5)
Ti–C(14)	2.38 (1)	Ti–C(1)–O	78.1 (9)
Ti–C(15)	2.33 (1)	Ti–C(1)–C(2)	155 (1)
Ti–C(21)	2.37 (1)	O–C(1)–C(2)	126 (1)
Ti–C(22)	2.42 (1)	C(1)–Ti–O	30.5 (5)
Ti–C(23)	2.37 (1)	Ti–O–C(1)	71.4 (8)
Ti–C(24)	2.41 (1)	C(11)–C(12)–C(13)	106 (1)
Ti–C(25)	2.37 (1)	C(12)–C(13)–C(14)	109 (1)
C(1)–C(2)	1.54 (3)	C(13)–C(14)–C(15)	107 (1)
C(1)–O	1.15 (2)	C(14)–C(15)–C(11)	109 (1)
Ge–C(31)	1.94 (1)	C(15)–C(11)–C(12)	108 (1)
Ge–C(41)	2.01 (1)	C(21)–C(22)–C(23)	105 (1)
Ge–C(51)	1.99 (1)	C(22)–C(23)C(24)	110 (1)
C(31)–C(32)	1.41 (1)	C(23)–C(24)–C(25)	108 (1)
C(32)–C(33)	1.38 (1)	C(24)–C(25)–C(21)	106 (1)
C(33)–C(34)	1.39 (1)	C(25)–C(21)–C(22)	112 (1)
C(34)–C(35)	1.37 (1)	Ti–Ge–C(31)	113.1 (3)
C(35)–C(36)	1.37 (1)	Ti–Ge–C(41)	113.7 (3)
C(36)–C(31)	1.40 (1)	Ti–Ge–C(51)	116.1 (3)
C(41)–C(42)	1.36 (1)	C(31)–Ge–C(41)	102.8 (4)
C(42)–C(43)	1.36 (2)	C(31)–Ge–C(51)	104.7 (4)
C(43)–C(44)	1.37 (2)	C(41)–Ge–C(51)	105.2 (4)
C(44)–C(45)	1.40 (2)	Ge–C(31)–C(32)	123.5 (7)
C(45)–C(46)	1.37 (2)	Ge–C(31)–C(36)	122.1 (7)
C(46)–C(41)	1.38 (1)	Ge–C(41)–C(42)	121.7 (7)
C(51)–C(52)	1.42 (1)	Ge–C(41)–C(46)	120.6 (7)
C(52)–C(53)	1.35 (2)	Ge–C(51)–C(52)	123.0 (7)
C(53)–C(54)	1.38 (2)	Ge–C(51)–C(56)	122.2 (7)
C(54)–C(55)	1.34 (1)	C(31)–C(32)–C(33)	121 (1)
C(55)–C(56)	1.38 (1)	C(32)–C(33)–C(34)	122 (1)
C(56)–C(51)	1.40 (1)	C(33)–C(34)–C(35)	118 (1)
C(11)–C(12)	1.42 (1)	C(34)–C(35)–C(36)	120 (1)
C(12)–C(13)	1.40 (2)	C(35)–C(36)–C(31)	124 (1)
C(13)–C(14)	1.40 (2)	C(36)–C(31)–C(32)	114 (1)
C(14)–C(15)	1.38 (1)	C(41)–C(42)–C(43)	123 (1)
C(15)–C(11)	1.39 (2)	C(42)–C(43)–C(44)	120 (1)
C(21)–C(22)	1.38 (2)	C(43)–C(44)–C(45)	117 (1)
C(22)–C(23)	1.37 (2)	C(44)–C(45)–C(46)	123 (1)
C(23)–C(24)	1.37 (2)	C(45)–C(46)–C(41)	119 (1)
C(24)–C(25)	1.40 (2)	C(46)–C(41)–C(42)	118 (1)
C(25)–C(21)	1.36 (1)	C(51)–C(52)–C(53)	123 (1)
		C(52)C(53)–C(54)	119 (1)
		C(53)–C(54)–C(55)	122 (1)
		C(54)–C(55)–C(56)	120 (1)
		C(55)–C(56)–C(51)	122 (1)
		C(56)–C(51)–C(52)	115 (1)

Under photochemical conditions, all reactions gave rise to reduced titanium products.

Structure of Acetyl(triphenylgermyl)titanocene. Crystal data and parameters for data collection are listed in Table I. Atom coordinates and bond lengths and angles are listed in Tables II and III, respectively. A view of the molecular structure with labeling of the atoms is shown in Figure 1. The Ti atom has a distorted tetrahedral coordination. The structure of $Ti(Cp)_2(COCH_3)GePh_3$ is very similar to the structure of $Ti(Cp)_2(COCH_3)Cl$.[9c]

The Ti–C(Cp) distances vary from 2.33 (1) to 2.43 (1) Å with an average value of 2.38 Å. The Ti–Cp(1) (centroid) and Ti–Cp(2) distances are 2.06 (1) and 2.08 (1) Å, respectively. The angles around the Ti atom are close to the tetrahedral value, except for Cp(1)–Ti–Cp(2) which is 135.7 (5)°. In the chloro analogue, the corresponding angle is

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131.6°.[9c] The two Cp rings are planar, and the Cp ring C–C distances vary from 1.36 (1) to 1.42 (1) Å with an average value of 1.39 (1) Å. The average ring angle is 108 (1)°.

The three atoms of the acetyl group, especially the methyl carbon atom C(2), are disordered as shown by the high values of the thermal factors. The bond angles associated with the acetyl group are very distorted. The Ti–C(1)–O angle is only 78.1 (9)°, while the Ti–C(1)–C(2) angle is 155 (1)° and the O–C(1)–C(2) angle is 126 (1)°. These values are identical with those found in the analogous chloro complex (78.4, 154, and 126°, respectively.[9c] The bond lengths and angles in the acetyl group may be interpreted in terms of this group acting as a bidentate four-electron ligand with a Ti–O distance of 2.220 (9) Å and an angle C(1)–Ti–O of 30.5 (5)° similar to the chloro complex. For the germyl complex, the value for Ti–C(1) is slightly larger (2.15 (2) vs. 2.07 (2) Å for the chloro analogue), but the difference is probably not significant. The C–O bond length is 1.15 (2) Å, essentially identical with the chloro analogue, and the acetyl group is coplanar with the Ti and Ge atoms.

The geometry around the Ge atom is tetrahedral as expected (angles vary from 104.7 (4) to 116.1 (3)°). The Ti–Ge bond distance is 2.710 (2) Å. The Ge–C bond distances vary from 1.943 (9) to 2.006 (9) Å. The phenyl groups are planar with an average C–C distance of 1.38 (1) Å and an average ring angle of 120 (1)°. The angles Ge–C–C are slightly larger (mean 122.7 (7)°) while the Ge bonding ring angles (C(31), C(41), and C(51)) are slightly smaller (mean 116 (1)°). The angles between the normals of the three phenyl rings are 56, 64, and 118°.

Discussion

The systematic synthesis of compounds of the type Cp_2MRR', where M is a group 4 element and RR′ is either a pair of the same, or two different, group 14 ligands, seems to be more difficult than similar syntheses involving other transition groups. This difficulty is probably due to the progressive weakening of the group 14 to transition-metal bond with decreasing transition group number. One effect of this decreasing bond strength is that the thermodynamics of halide interchange reactions become very marginal for group 4. Silyl- and germylaluminums appear to be the reagents of choice for this type of reaction[2,10] although some success has been achieved with silyl- and germyllithiums and with digermylcadmiums.[4,7c]

A number of factors recommend the reaction of $Cp_2Ti(CH_3)_2$ (**3**) with group 14 hydrides as a route to group 14-to-titanium bonds. Although **3** is easily prepared and handled, it is metastable and subject to autocatalytic decomposition in the absence of chain-terminating species such as dioxygen. This instability, combined with the fugacity and the high C–H bond energy of methane, maximizes the chances of the equilibrium 2 being displaced

$$Cp_2Ti(CH_3)_2 + R_3MH \rightleftharpoons Cp_2TiMR_3(CH_3) + CH_4 \quad (2)$$

to the right. It appears, however, that the reactions of tertiary group 14 hydrides with **3** are quite slow, and in most cases the reaction products obtained are derived from the spontaneous decomposition of **3**. This is even more the case with photochemical reactions. Earlier studies have indicated that the (triphenylgermyl)titanocenes are slightly more stable with respect to spontaneous decomposition than their trialkylgermyl analogues (e.g., $Cp_2Ti(GePh_3)_2$ is relatively stable at room temperature,[7d] but $Cp_2Ti(GeEt_3)_2$ decomposes rapidly above −40 °C.[7b] From the present work it is evident that only in the case of triphenylgermane does the combination of all of the factors outlined above allow the isolation of a product from a reaction such as (2) in good yield.

Carbonylation of Methyl(triphenylgermyl)titanocene and the Structure of the Carbonylation Product. The carbonylation of titanocene and zirconocene alkyls and aryls has been investigated in some detail.[9–11] Apart from carbon, the only other transition metal–group 14 bond reported to undergo carbonylation is the Zr–Si bond of $Cp_2ZrCl(SiMe_3)$.[12] It is of interest to know the result of competition between two different group 14 ligands for inserting carbon monoxide. In the case of methyl(triphenylgermyl)titanocene, insertion into the Ti–C bond is preferred for reasons that are not immediately obvious. In a situation where the possibility of backbonding does not exist, the Ti–C bond is expected to be stronger than the Ti–Ge bond on both bond length and polarity grounds. Thus insertion into the Ti–Ge bond is favored by the replacement of a Ti–Ge bond with a Ti–C(O) bond. Although it is conceivable that this favorable effect is overridden by the greater C–C(O) bond energy relative to Ge–C(O), we prefer the following explanation based on the structure of the acetyl complex.

The most remarkable feature of the structure of compound **2** is the degree to which the $Cp_2TiC(O)CH_3$ fragment is identical with that of the analogous chloro complex, reported earlier by Floriani et al.[9a,b] The considerable difference between Cl and Ph_3Ge, with regard to both steric and electronic influences, seems to have no effect at all on the remainder of the molecule. A clue to why this is so is afforded by the unusually long Ti–Cl bond in the chloroacetyl compound.[9b] If we take the covalent radius of Cl to be 0.99 Å[13] and that of Ge to be 1.22 Å,[14] the difference, 0.23 Å, corresponds to the difference between the Ti–Cl bond length in the chloro acetyl compound (2.494 (6) Å) and the Ti–Ge bond length in the acetyl germyl complex **2** (2.710 (2) Å). Thus, if the Ti–Cl bond is unusually long, it can be concluded that the Ti–Ge bond is also long. A similar bond lengthening is observed for the Zr–CH_3 bond in acetylmethylzirconocene.[9d] The origin of this bond lengthening, as already suggested by Floriani et al.,[9b,d] is most likely the increase in metal electron count resulting from the η^2-coordination of the acetyl ligand. As the acetyl ligand functions as a four-electron donor, it tends to displace the other ligand as an anion. With good leaving groups, the acetyl group assumes an optimum bonding configuration and the other ligand adjusts its bond length accordingly. Carbonylation of dialkyl- and diarylzirconocenes occurs at very much higher rates than the corresponding titanium compounds.[10] This may be in part attributed to the fact that charge separation is already present in the former to a much greater extent than the latter, but the greater ease with which zirconium expands its coordination sphere is probably also important. The reluctance of titanium to assume five-coordination may be the driving force for the preferential carbonylation of the Ti–C over the Ti–Ge bond, since carbonylation of the Ti–C bond allows the molecule to benefit from η^2-bonding and the resulting steric congestion is relieved by the facile stretching of the Ti–Ge bond.

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A final question relating to **2** is, given the considerable oxophilicity of the germanium, why does it not attack the oxygen of the η^2-acetyl group to yield, for example, a methyl(triphenylgermoxy)(carbene)titanocene? Calculations have shown that the LUMO in η^2-acetyl complexes of d^0 metals resides mainly on the carbon atom of the "carbonyl" group, conferring electrophilic character at that position.[10] This orbital has little density on the oxygen. On the other hand, the oxygen atom is the main location of the HOMO (largely a nonbonding oxygen pair stabilized by coordination). Thus it is not surprising that the oxygen is not attacked by the highly nucleophilic Ph_3Ge^- moiety nor that the oxygen has no tendency to nucleophilically attack the germanium. Presumably, such attack could take place at the acetyl carbon atom if the η^2-acetyl ligand could rotate to the O-outward conformer, but this does not apparently take place easily. In the case of dibenzyltitanocene, which reacts with CO to give titanocene dicarbonyl and dibenzyl ketone,[9b] whatever acyl product is formed does not have a significant energy minimum favoring the O-inward conformer, and hence the acyl carbon becomes exposed to attack by the other benzyl ligand.

Experimental Section

Reagents. All solvents were carefully dried and deaerated before use. Dimethyltitanocene was prepared by a slight modification of the method of Bestian and Claus.[15] Triphenylgermane was purchased from Strem Chemicals Inc. and was used without further purification.

Synthesis of Methyl(triphenylgermyl)titanocene. Triphenylgermane (0.15 g) was added to a solution of dimethyltitanocene (0.10 g) in hexane (5.0 mL) under argon. When the mixture was heated to 65 °C, it slowly turned bluish green with deposition of dark violet crystals. After 2 h, the supernatant solution was syphoned off and the crystals were washed carefully with several aliquots of hexane. The resulting dark prisms were dried under vacuum (yield 0.2 g, 84%). Although subject to slow oxidation in air, the crystalline material could be manipulated in the atmosphere without detectable decomposition. NMR (C_7D_8): δ 7.16–7.28 (Ph, 15), 5.80 (Cp, 10), –0.42 (Me, 3). MS [*m/e* (abundance percent)]: 433 (0.33), 305 (100), 228 (75), 151 (51). Anal. Calcd: C, 69.88; H, 5.68. Found: C, 69.79; H, 5.87.

Synthesis of Acetyl(triphenylgermyl)titanocene. Carbon monoxide was bubbled for a few minutes through a solution of **1** (0.11 g) in a 1:2 (v/v) mixture of ether/hexane, and then the solution was allowed to stand under an atmosphere of CO for a further 2 h. The mother liquor was siphoned off; the dark colored crystalline product was washed twice with aliquots of ether/hexane and then dried under vacuum (yield 0.11 g, 92%). The IR spectrum of the product was almost identical with that of **1**, with additional bands at 1600 (m) and 1118 (s) cm^{-1}. NMR (C_7D_8): δ 8.05–8.10 (Ph, 6), 7.24–7.39 (Ph, 9), 4.92 (Cp, 10), 2.08 (Me, 3). MS [*m/e* (abundance percent)]: 525 (38), 493 (100), 481 (61), 305 (75). Anal. Calcd: C, 68.63; H, 5.34. Found: C, 68.31; H, 5.64.

Crystal Structure Determination. Crystals obtained from the synthesis described above were sufficiently air-stable to allow data collection in the air. As an additional precaution the specimen was encapsulated in grease. Cell parameters were obtained by least-squares refinement from setting angles of 15 automatically centered reflectances (2θ range = 10–25°) on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo Kα radiation. Intensity data were collected from a parallel equiped with dimensions 0.23 mm (100, $\bar{1}00$), 0.25 mm (010, $0\bar{1}0$), and 0.173 mm (001, $00\bar{1}$). A total of 3268 independent reflections (h, $0 \rightarrow 9$, *k*, $0 \rightarrow 18$, *l*, $-19 \rightarrow +18$) were measured in the range $2\theta < 45°$ by the $2\theta/\theta$ scan technique. During data collection, two standard reflections (012 and $10\bar{4}$), measured after each 48 reflections, showed a rapid decrease in intensity, confirming a progressive decomposition of the crystal in air. At the end of data collection, the intensity had decreased by about one-third. All reflections were scaled on the average values of the standards.

Data were corrected for absorption, Lorentz, and polarization effects. Scattering factors and anomalous dispersion terms used in the calculations were from Cromer and Waber[16] and Cromer,[17] respectively.

A three-dimensional Patterson map indicated the positions of the Ge and Ti. Positions of all other atoms except H were obtained from structure factor and Fourier map calculations with minimization of the $\sum w(F_0 - F_c)^2$ function. Corrections were made for isotropic secondary extinction.[18] Finally, individual weights, $w = 1/\sigma^2(F)$, were applied. With the exception of CH_3, H atoms were fixed at calculated positions with isotropic B = 6.0 Å^2. Refinement of the scale factor, coordinates, and anisotropic temperature factors of all atoms converged to $R = 0.070$, $R_w = 0.052$, and $S = 1.26$. The highest residual peak was 0.4 e/Å^3 (close to Ge) and the lowest –0.2 e/Å^3 (close to Ge). The maximum Δ/σ in the final refinement cycle was <0.34.

Calculations were carried out on a Cyber 830 computer with previously described programs.[19]

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Supplementary Material Available: Table IV, anisotropic thermal parameters, Table V, weighted best planes, and Table VI, coordinates of the H atoms for compound **2** (4 pages); Table VII, observed and calculated structure factors for compound **2** (12 pages). Ordering information is given on any current masthead page.

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