

Reactions of the phenyl-substituted five-membered titanacyclocumulene – unusual coupling of a 1,4-disubstituted 1,3-butadiyne with two titanium atoms ¹

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Abstract

The reaction of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with equimolar amounts of $\text{PhC}\equiv\text{C-C}\equiv\text{CPh}$ gives the unstable five-membered titanacyclocumulene **1**, which is stabilized by dimerization to yield the dinuclear complex **2**. In this reaction complex **1** shows an equilibrium and also behaves as a metallacyclocumulene and a metal alkyne complex. By the coupling of the internal double bond of the cyclocumulene with a complexed triple bond of the diyne, a complex with fused titanacyclopentadiene and titanacyclopentene is formed. With acetone and water complex **1** reacts like an alkyne complex to give the titanadihydrofuran **4** and the titanoxane **5**.

Complex **2** was investigated by an X-ray structural determination. © 1997 Published by Elsevier Science S.A.

Keywords: Alkyne; Diyne; Metallocenes; Early transition metals; Titanium; Group 4; Metallacycle; Trimethylsilyl; X-ray diffraction

1. Introduction

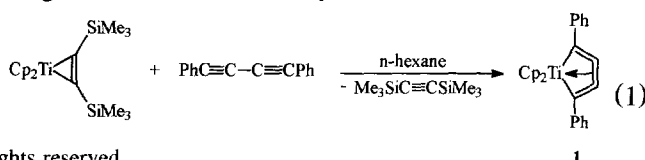
In modern acetylene chemistry [1] with Group 4 metallocene complexes, many recent investigations are directed towards diynes [2]. Recently, we found metallocene complexes of bis(trimethylsilyl)acetylene to be excellent organometallic reagents for the preparative generation of titanocene and zirconocene " Cp_2M " ($\text{M} = \text{Ti}, \text{Zr}$) [3], which gave in the reaction with 1,4-di-tertbutyl-1,3-butadiyne the novel type of five-membered metallacyclocumulenes [4,5]. X-ray diffraction studies of the obtained complexes had shown the ring system to be coplanar, containing three $\text{C}=\text{C}$ double bonds from which the central bond is internally coordinated to the metal center. Later, an alternative bonding description as a diyne–metallocene complex without a central double bond was preferred [6]. In the reaction of Ni(0)

complexed 1,4-diphenyl-1,3-butadiyne with titanocene and zirconocene sources, an external complexation of the central bond of the five-membered cyclocumulenes in heterobimetallic systems was observed [7]. These complexes are intermediates in the C–C activation and cleavage of butadiynes.

Here we report on reactions of the more reactive phenyl-substituted five-membered titanacyclocumulene which may be indicative of an equilibrium between the cyclocumulene (**1a**) and an alkyne complex (**1b**) structure (Scheme 1).

2. Results and discussion

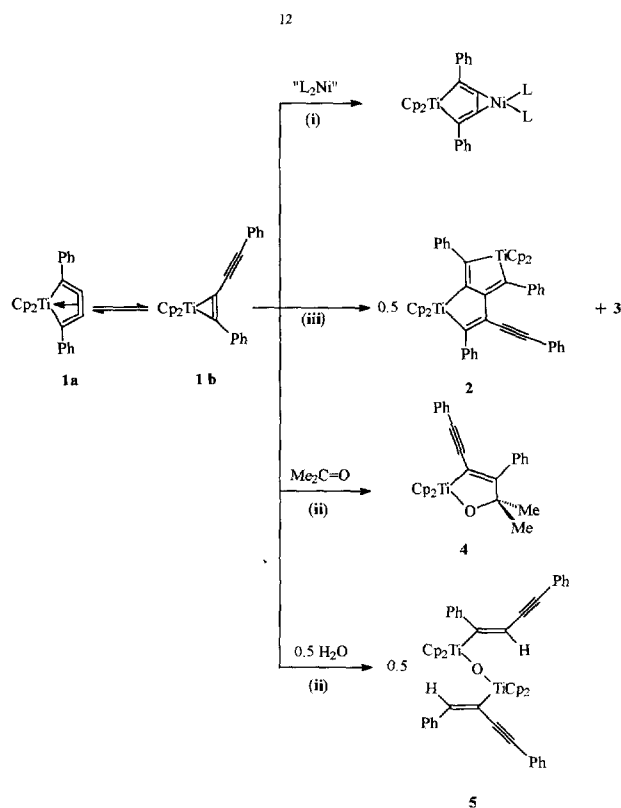
The reaction of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with equimolar amounts of $\text{PhC}\equiv\text{C-C}\equiv\text{CPh}$ in *n*-hexane at room temperature gives an air- and moisture-sensitive orange–brown material which contains 80% of the titanacyclocumulene **1** (Eq. (1)) soiled with small amounts of green and red–brown crystals (see below).



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The spectroscopic behavior of complex **1** is very close to that of the analogous five-membered titanacyclocumulene with ^tBu substituents, e.g. the ¹³C NMR signals of the titanacyclocumulene ring in **1** (C_α 176.8; C_β 103.1 ppm) and the ^tBu-substituted complex (C_α 181.9; C_β 94.7 ppm) [5].

Complex **1** is unstable in toluene solution and forms, after three days, green crystals of the dinuclear complex **2** in 46% yield together with a small amount (18%) of an until yet not fully characterized red-brown by-product **3** with an identical elemental composition (Scheme 1). Complex **3** is a symmetrical binuclear isomer of **2** which consists of two titanacyclopentadiene ring systems, fused with the β and β' carbon atoms together, yielding a radialene-like molecule [8]. The molecular structure of **3** will be published later [8].

The structure of complex **2** has been determined by an X-ray analysis.

Crystal data for **2** (obtained from a solution of *n*-hexane/THF): crystal dimensions $0.5 \times 0.2 \times 0.1$ mm, prism, green, $a = 8.388(2)$, $b = 20.464(3)$, $c = 22.246(3)$ Å, space group $P2_12_12_1$, $Z = 4$, MW = 760.64 for $C_{52}H_{40}Ti_2$, $d_{calc} = 1.323$ g cm⁻³, number of collected data at 20 °C 11393, number of unique data 5791, number of observed data with $I \geq 2\sigma(I)$ 3631, number of variables 487, $R_1 = 0.0426$ ($I \geq 2\sigma(I)$), $wR_2 = 0.0727$.

Positional parameters are given in Table 1. The

molecular structure (Fig. 1) exhibits a binuclear complex which contains fused titanacyclopentadiene and titanacyclopentene ring systems. The titanacyclopenta-

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**^a

Atom	x	y	z	U_{eq}
C(1)	-5215(5)	-4533(2)	-9223(2)	35(1)
C(2)	-4839(5)	-4666(2)	-8641(2)	34(1)
C(3)	-5784(4)	-5170(2)	-8304(2)	29(1)
C(4)	-6943(5)	-5537(2)	-8694(2)	31(1)
C(5)	-7750(5)	-6041(2)	-8447(2)	35(1)
C(6)	-8987(5)	-6451(2)	-8752(2)	47(1)
C(7)	-10564(6)	-6233(3)	-8802(2)	62(2)
C(8)	-11742(7)	-6621(4)	-9079(3)	98(3)
C(9)	-11336(11)	-7229(4)	-9310(4)	125(4)
C(10)	-9824(11)	-7448(3)	-9250(3)	107(3)
C(11)	-8654(7)	-7072(3)	-8981(2)	67(2)
C(12)	-4835(5)	-5665(2)	-10010(2)	44(1)
C(13)	-5840(6)	-6148(2)	-9774(2)	48(1)
C(14)	-7263(6)	-6147(2)	-10114(2)	53(1)
C(15)	-7105(6)	-5683(3)	-10558(2)	54(1)
C(16)	-5640(6)	-5370(2)	-10495(2)	50(1)
C(17)	-9383(5)	-4643(3)	-9154(3)	53(2)
C(18)	-9878(5)	-4940(3)	-9690(2)	53(1)
C(19)	-9205(5)	-4600(3)	-10169(2)	54(2)
C(20)	-8245(5)	-4108(3)	-9932(3)	56(2)
C(21)	-8359(5)	-4124(2)	-9309(3)	56(2)
C(22)	-5664(4)	-5303(2)	-7695(2)	30(1)
C(23)	-4891(5)	-4891(2)	-7238(2)	38(1)
C(24)	-5397(5)	-4243(3)	-7155(2)	51(1)
C(25)	-4836(7)	-3858(3)	-6690(3)	67(2)
C(26)	-3761(8)	-4106(4)	-6282(3)	86(2)
C(27)	-3208(7)	-4727(4)	-6357(3)	77(2)
C(28)	-3756(5)	-5127(3)	-6828(2)	58(2)
C(29)	-4452(5)	-6587(2)	-7593(3)	56(2)
C(30)	-5407(6)	-6939(2)	-8012(3)	54(2)
C(31)	-6501(6)	-7305(2)	-7678(3)	62(2)
C(32)	-6254(6)	-7194(3)	-7068(3)	64(2)
C(33)	-4998(6)	-6746(3)	-7018(3)	61(2)
C(34)	-9867(6)	-6220(3)	-7265(3)	59(2)
C(35)	-9040(7)	-6355(3)	-6745(3)	63(2)
C(36)	-8164(7)	-5797(3)	-6591(2)	66(2)
C(37)	-8517(6)	-5315(3)	-7015(3)	54(2)
C(38)	-9553(5)	-5580(3)	-7431(3)	53(1)
C(39)	-3523(5)	-4337(2)	-8344(2)	32(1)
C(40)	-2378(5)	-4043(2)	-8171(2)	38(1)
C(41)	-1044(5)	-3672(2)	-7938(2)	36(1)
C(42)	-251(5)	-3237(2)	-8311(2)	52(2)
C(43)	1038(6)	-2884(3)	-8088(3)	66(2)
C(44)	1526(6)	-2959(3)	-7513(4)	75(2)
C(45)	748(6)	-3386(3)	-7143(3)	69(2)
C(46)	-533(5)	-3746(2)	-7354(2)	51(2)
C(47)	-4427(5)	-3973(2)	-9532(2)	40(1)
C(48)	-3475(6)	-4038(3)	-10021(2)	65(2)
C(49)	-2868(8)	-3495(3)	-10316(3)	94(2)
C(50)	-3167(8)	-2881(3)	-10122(3)	92(2)
C(51)	-4073(7)	-2802(3)	-9625(3)	81(2)
C(52)	-4691(5)	-3338(3)	-9330(3)	62(2)
Ti(1)	-7105(1)	-5119(1)	-9605(1)	33(1)
Ti(2)	-7087(1)	-6160(1)	-7515(1)	35(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

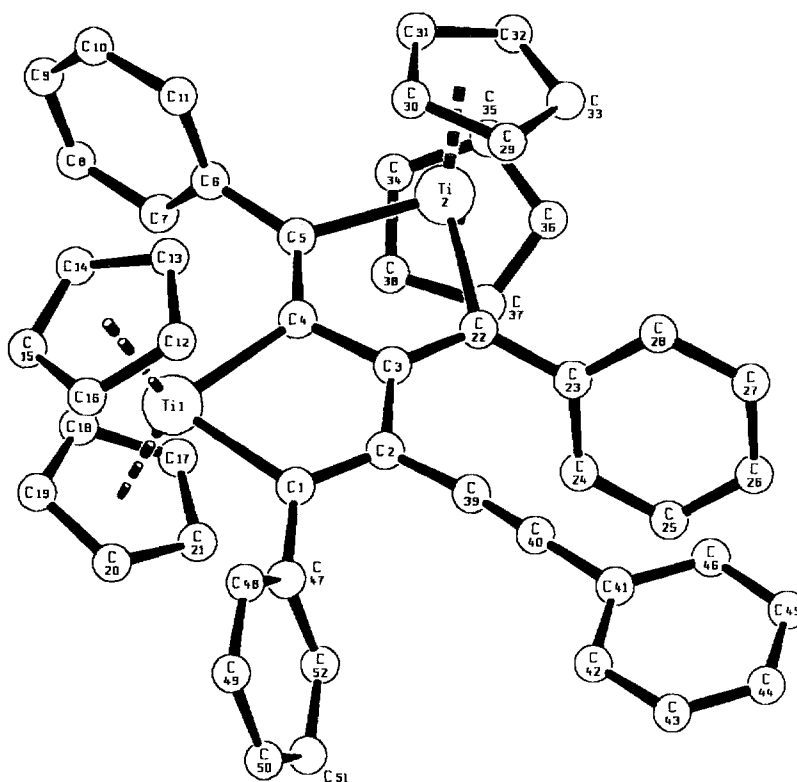


Fig. 1. Molecular structure of **2**, selected bond lengths (Å) and angles (°): Ti(1)–C(1) 2.160(4), Ti(1)–C(4) 2.204(4), C(4)–C(3) 1.505(5), C(2)–C(3) 1.500(5), C(1)–C(2) 1.361(6), Ti(2)–C(5) 2.159(4), Ti(2)–C(22) 2.159(4), C(5)–C(4) 1.351(5), C(3)–C(22) 1.387(5), C(39)–C(40) 1.197(5); C(4)–Ti(1)–C(1) 79.0(2), Ti(1)–C(1)–C(2) 115.7(3), C(1)–C(2)–C(3) 119.3(4), C(2)–C(3)–C(4) 113.4(4), C(3)–C(4)–Ti(1) 112.0(3), C(5)–Ti(2)–C(22) 82.7(2), C(5)–C(4)–C(3) 118.1(4), C(4)–C(3)–C(22) 120.8(4), C(3)–C(22)–Ti(2) 107.5(3).

diene is phenyl-substituted in the α and α' position and annellated at the β and β' carbon atoms. The titanacyclopentene has a phenyl at the α - and α' -phenylalkynyl substituent at β -olefinic carbon atoms. It is fused with the α' and β' carbon atoms. The structure shows the expected bond lengths consistent with such a description [single bonds C(2)–C(3) 1.500(5), C(3)–C(4) 1.505(5); double bonds C(1)=C(2) 1.361(6), C(4)=C(5) 1.351(5), C(3)=C(22) 1.387(5) and one triple bond C(39)≡C(40) 1.197(5) Å]. The Ti–C distances [Ti(1)–C(1) 2.160(4), Ti(1)–C(4) 2.204(4), Ti(2)–C(5) 2.159(4), Ti(2)–C(22) 2.159(4) Å] are in the typical region of such titanacycles [5].

The C–C single bond between the two titanacycles [C β –C β' 1.505(5) Å] is significantly longer compared with the corresponding bond in the Ni(0) complexed [1.419(6) Å] [7] or in the free titanacyclocumulene [1.339(13) Å] [5], but in the typical region of titanacyclopentadienes [1.495(6) Å] [5].

Complex **1** reacts with acetone to give the red zirconadihydrofuran **4** in a yield of 36% (Scheme 1), with the phenyl group in β position to the metal. With water complex **1** forms the yellow titanoxane **5**, with phenyl groups in α and β position, in a yield of 60% (Scheme 1). The structures of complexes **4** and **5** were deter-

mined by an X-ray structure analysis and will be published later [8]. The unusual regioselectivity obtained for complex **5** is under investigation [8] with respect to recent results of metallocene–alkyne complexes [9,10].

3. Conclusion

In the reactions of titanocene fragments with 1,4-disubstituted 1,3-butadiynes $RC\equiv C-C\equiv CR$, the stability and reactivity of the five-membered titanacyclocumulenes obtained depends strongly on the substituents used. With $R = Me_3Si$ the cyclocumulene is too unstable and a C–C bond cleavage is favored. With $R = ^tBu$ the cyclocumulenes are very stable and unreactive toward, for example, carbon dioxide, water, acetone, etc. For $R = Ph$ the titanacyclocumulene is stable in the solid state but not in solution. In principle, this complex can react (i) like a cyclocumulene, e.g. with Ni(0) complexes; (ii) like an alkyne complex, e.g. with acetone or water; or (iii) simultaneously as a cyclocumulene and an alkyne complex, e.g. in the dimerization. These results are best explained by an equilibrium between both types of complex (**1a** and **1b**, Scheme 1).

4. Experimental section

4.1. General

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400; IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus; X-ray diffraction data were collected on a STOE-IPDS diffractometer using Mo K α radiation. The structures were solved by direct methods (SHELXS-86 [11]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93 [12]); structural representation SCHAKAL-92 [13].

4.2. Synthesis of complexes

4.2.1. Preparation of **1**

0.865 g (4.41 mmol) of $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ was dissolved by heating in 15 ml of *n*-hexane. The warm solution was added to 1.537 g (4.41 mmol) $\text{Cp}_2\text{Ti}(\text{Me}_3\text{SiC}_2\text{SiMe}_3)$ in 5 ml of *n*-hexane. The color of the mixture changed from yellow to dark, and a precipitate was formed. After 30 min the solution was decanted, the precipitate washed with *n*-hexane and dried in vacuum. The residue was extracted with 60 ml of *n*-hexane/THF (2:1) mixture, and the solution was filtered, evaporated to 20 ml and cooled to -75°C . After 1 h at -75°C the solution was decanted, the precipitate washed with cold *n*-hexane and dried in vacuum to give 0.931 g of an orange–brown solid which contains 80% complex **1** (analysis by NMR), green and red–brown impurities (decomp. $>240^\circ\text{C}$). Anal. Found: C, 79.12; H, 5.59 (acceptable in view of the formation of titaniumcarbides). $\text{C}_{26}\text{H}_{20}\text{Ti}$ (380.32) Calc.: C, 82.11; H, 5.30% [14].

^1H NMR (THF- d_8) δ /ppm: 5.16 (s, 10H, Cp); 7.42 (t, 2H, *para*); 7.56 (t, 4H, *meta*); 8.09 (d, 4H, *ortho*). ^{13}C NMR (THF- d_8) δ /ppm: 103.1 (C β); 104.4 (Cp); 129.1 (*p*-Ph); 129.4 and 133.7 (*o*-, *m*-Ph); 136.1 (*i*-Ph); 176.8 (C α). MS (70 eV): 381 $[\text{M} + 1]^+$, 202 $[\text{Ph}_2\text{C}_4]^+$, 178 $[\text{Cp}_2\text{Ti}]^+$. IR (Nujol mulls): 1853, 1589, 1566 cm^{-1} .

4.2.2. Preparation of **2**

0.352 g of complex **1** was dissolved in 10 ml of toluene under argon. The orange–brown solution was filtered and after three days at room temperature 0.064 g of red–brown crystals of **3** (m.p. $256\text{--}259^\circ\text{C}$): C, 81.52; H, 5.38% had formed in the green solution. The solution was decanted, treated with 10 ml of *n*-hexane and allowed to stand under argon at room temperature. After

two days green crystals deposited, which were washed with *n*-hexane and dried in vacuum to give 0.160 g of complex **2** (decomp. $>210^\circ\text{C}$). Anal. Found: C, 81.13; H, 5.52 (acceptable in view of the formation of titaniumcarbides). $\text{C}_{32}\text{H}_{40}\text{Ti}_2$ (760.64) Calc.: C, 82.11; H, 5.30% [14].

^1H NMR (THF- d_8) δ /ppm: 6.13 (s, 10H, Cp); 6.25 (s, 10H, Cp); 6.84–6.94 (m, 10H, Ph); 7.08–7.19 (m, 10H, Ph). ^{13}C NMR (THF- d_8) δ /ppm: 219.9, 200.6, 192.7, 171.1, 129.5, 128.8 (titanacycle); 116.4, 114.1 (Cp); 92.2, 91.9 ($-\text{C}\equiv$); 150.8, 150.0, 148.1, 131.8, 127.8, 127.6, 126.9, 126.3, 124.2, 123.7, 123.4, 122.2 (Ph). IR (Nujol mulls): 2188 cm^{-1} ($\nu\text{C}\equiv\text{C}$), 1585, 1561, 1486 cm^{-1} . MS (70 eV): 558 $[\text{M}-\text{Ph}_2\text{C}_4]^+$, 178 $[\text{Cp}_2\text{Ti}]^+$.

5. Supplementary material available

Tables of crystal structure and details of data collection, bond angles and distances, atomic positional and thermal parameters, listings of observed and calculated structure factors of **2** are available. Ordering information is given on any current masthead page.

Acknowledgements

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References

- [1] P.J. Slang and F. Diederich, *Modern Acetylene Chemistry*, VCH, Weinheim, 1995.
- [2] W.A. Nugent and D.F. Taber, *J. Am. Chem. Soc.*, **111** (1989) 6435 and references cited therein; S.S.H. Mao and T.D. Tilley, *J. Am. Chem. Soc.*, **117** (1995) 5365, 7031; D.P. Hsu, W.M. Davis and S.L. Buchwald, *J. Am. Chem. Soc.*, **115** (1993) 10394; B.P. Warner, W.M. Davis and S.L. Buchwald, *J. Am. Chem. Soc.*, **116** (1994) 5471; B. Du, M.F. Faron, D.B. McConville and W.J. Youngs, *Tetrahedron*, **51** (1995) 4359; T. Takahashi, K. Aoyagi, V. Denisov, N. Suzuki, D. Choueiry and E. Negishi, *Tetrahedron Lett.*, **34** (1993) 8301; T. Takahashi, K. Kasai, Z. Xi and V. Denisov, *Chem. Lett.*, (1995) 347; T. Takahashi, Z. Xi, Y. Obora and N. Suzuki, *J. Am. Chem. Soc.*, **117** (1995) 2665.
- [3] V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur, M.E. Vol'pin, U. Rosenthal and H. Görls, *J. Organomet. Chem.*, **476** (1994) 197 and references cited therein; A. Ohff, S. Pulst, N. Peulecke, P. Arndt, V.V. Burlakov and U. Rosenthal, *Synlett.*, **2** (1996) 111 and references cited therein.
- [4] U. Rosenthal, A. Ohff, W. Baumann, P. Kempe, A. Tillack and V.V. Burlakov, *Angew. Chem.*, **106** (1994) 1678; *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1605.
- [5] V.V. Burlakov, A. Ohff, C. Lefebvre, A. Tillack, W. Baumann, R. Kempe and U. Rosenthal, *Chem. Ber.*, **128** (1995) 967.
- [6] B. Temme, G. Erker, R. Fröhlich and M. Grehl, *Angew. Chem.*, **106** (1994) 1570; *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1480.

- [7] S. Pulst, P. Arndt, B. Heller, W. Baumann, P. Kempe and U. Rosenthal, *Angew. Chem.*, 108 (1996) 1175; *Angew. Chem., Int. Ed. Engl.*, 35 (1996) 1112.
- [8] V.V. Burlakov, N. Peulecke, W. Baumann, A. Spannenberg, P. Kempe and U. Rosenthal, *Organometallics*, in preparation.
- [9] C. Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov, H. Görls and U. Rosenthal, *J. Organomet. Chem.*, 501 (1995) 179.
- [10] C. Lefeber, A. Ohff, A. Tillack, W. Baumann, R. Kempe, V.V. Burlakov and U. Rosenthal, *J. Organomet. Chem.*, 501 (1995) 189.
- [11] G.M. Sheldrick, *SHELXS-86*, *Acta Crystallogr.*, A46 (1990) 467.
- [12] G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Germany, 1993.
- [13] E. Keller, *SCHAKAL-92*, University of Freiburg, Germany, 1992.
- [14] E. Samuel, Y. Ma, J.F. Harrod, Y. Dromzee and Y. Jeannin, *J. Am. Chem. Soc.*, 112 (1990) 3435 and references cited therein.