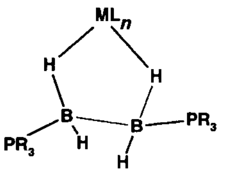
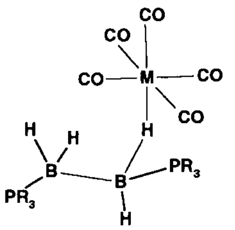
[8,8-η^2-{η^2-(BH$_3$)Ph$_2$PCH$_2$PPh$_2$}-*nido*-8,7-RhSB$_9$H$_{10}$]: A Rhodathiaborane with a Novel Bidentate Chelating Ligand[**]

Ramón Macías, Nigam P. Rath, and Lawrence Barton*

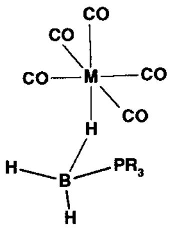
Although the B-H-M bridging bond is a common structural motif in the coordination and organometallic chemistry of boranes,[1] interactions of this nature are commonly found when the borane ligands are anionic species, for example, Cu(PPh$_2$Me)$_3$BH$_4$ and [BH$_4$Cr(CO)$_4$]$^-$, in which a BH$_3\cdot$H$^-$ adduct coordinates to the metal moiety through a single B-H-Cu bond[2] or two B-H-Cr bonds,[3] respectively. Compounds in which a neutral borane adduct coordinates to a metal center are less common. Examples exist in which the neutral 1,2-(PMe$_3$)$_2\cdot$B$_2$H$_4$ acts as a bidentate chelating ligand towards ZnCl$_2$,[4] Ni(CO)$_2$,[5] or M(CO)$_4$[6] (**I**; M = Cr, Mo, W). In related Cr and W complexes, 1,2-(PMe$_3$)$_2\cdot$B$_2$H$_4$[6] or BH$_3\cdot$PMe$_3$[7] coordinates through a single B-H-M bond (**II** and **III**). Herein we describe some novel chemistry involving the unsaturated eleven-vertex cluster **1**.[8] When treated with bis(diphenylphosphanyl)methane (dppm) **1** affords the saturated rhodathiaborane **2**, which contains a bidentate and a monodentate dppm ligand. Cluster **2** was obtained as a yellow crystalline solid in 48 % yield and identified by high-resolution mass spectrometry, multinuclear NMR spectroscopy, and a single-crystal structure determination (Figure 1).



I



II



III

[8,8-(PPh$_2$)$_2$-*nido*-8,7-RhSB$_9$H$_{10}$] **1**

[8,8-(η^2-dppm)(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] **2**

The existence of the dangling phosphane ligand in **2** suggested that it might be amenable to further reactions analogous to [(PPh$_3$)$_2$(CO)OsB$_4$H$_8$(BH$_2\cdot$dppp)] (dppp = bis(diphenylphosphanyl)propane), for which reactions of the free phosphane were observed.[9] Accordingly, reaction of a 20-fold excess of BH$_3\cdot$THF with **2** in CH$_2$Cl$_2$ at room temperature afforded the new rhodathiaborane **3** as an air-stable orange crystalline solid in 71 % yield. It was characterized by multinuclear NMR spectroscopy, elemental analysis, mass spectrometry, and a crystal structure determination (Figure 2).

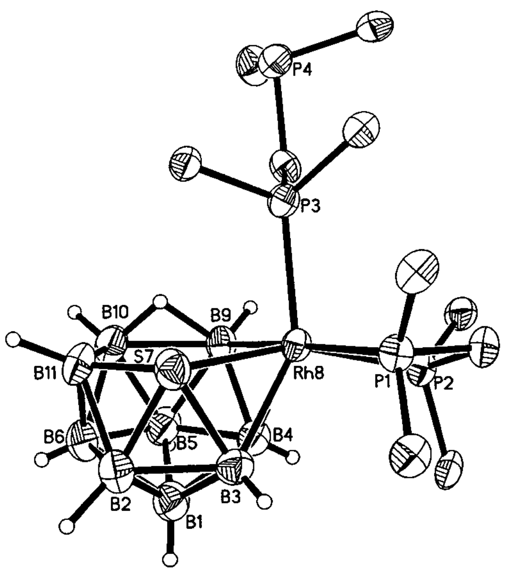


Figure 1. Projection of the molecular structure of **2**. Ellipsoids are drawn at the 50 % probability level. Selected interatomic distances [Å] and angles [°]: Rh8–S7 2.370(2), Rh8–P1 2.393(2), Rh8–P2 2.295(2), Rh8–P3 2.411(2), Rh8–B9 2.280(9), Rh8–B3 2.251(10), Rh8–B4 2.235(10); P1-Rh8-P2 71.3(7), P1-Rh8-S7 96.34(8), P1-Rh8-B9 174.4(2), P3-Rh8-S7 97.24(7), P2-Rh8-P3 103.44(7), Rh8-P2-C13 96.1(3), P1-C13-P2 96.0(4).

[8,8-(Ph$_2$PCH$_2$PPh$_2$BH$_3$)-*nido*-8,7-RhSB$_9$H$_{10}$] **3**

[8,8-(dppe)-*nido*-8,7-RhSB$_9$H$_{10}$] **4**

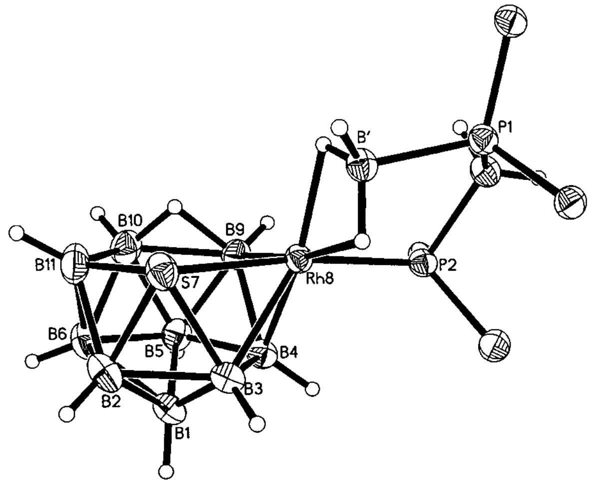


Figure 2. Projection of the molecular structure of **3**. Ellipsoids are drawn at the 50 % probability level. Selected interatomic distances [Å] and angles [°]: Rh8–S7 2.3658(5), Rh8–P2 2.2803(5), Rh8–B′ 2.323(2), Rh8–B3 2.195(2), Rh8–B4 2.193(2), Rh8–B9 2.174(2), B9–B10 1.848(4), B10–B11, 1.855(4), B2–B3 1.891(4); the other boron–boron distances are in the range of 1.725(4)–1.804(4); P2-Rh8-S7 172.92(2), P2-Rh8-B9 92.40(7), B′-Rh8-S7 93.46(6), P2-Rh8-B′ 88.36(6), Rh8- B′-P1 112.40(11), Rh8-P2-C1 108.74(7), P1-C1-P2 111.75(11), B9-Rh8-S7 90.42(7).

---

[*] Prof. L. Barton, Dr. R. Macías, Prof. N. P. Rath
Department of Chemistry
University of Missouri-St. Louis
St. Louis, MO 63121 (USA)
Fax: (+1) 314-516-5342
E-mail: lbarton@jinx.umsl.edu

[**] We acknowledge support from the Missouri Research Board and the Petroleum Research fund of the American Chemical Society. We thank Dr. David W. Berberich of Mallinckrodt Inc. and Professor Michael Gross of the Washington University Mass Spectrometry NIH Research Resource (Grant. No. P41RR094) for the mass spectra.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

The molecular structure of **3** can be described as an eleven-vertex *nido*-rhodathiaborane with a unique exopolyhedral ligand that chelates the rhodium atom through a phosphane group and a borane unit. The BH_3 end of this ligand can be regarded by itself as a neutral adduct of BH_3 that coordinates to the rhodium atom in a bidentate fashion through two three-center, two-electron Rh-H-B bonds. The bond lengths in the rhodathiaborane cage are within the ranges found for **2** and for other related metallathiaboranes;[8, 10] the Rh8–S7 distance of 2.3658(5) Å is close to those of **2** and the dppe derivative **4**[10] (dppe = $Ph_2P(CH_2)_2PPh_2$), but shorter than that of **1**.[8] The P2-Rh8-B′ chelate angle of **3** is 88.36(6)°, close to the value of 84.22(6)° found in **4**, but significantly larger than the corresponding chelate angle P1-Rh8-P2 of 71.45(98)° in the precursor **2**. The P1–B′ bond length of **3** is 1.921(2) Å, essentially the same value as is found in the dangling PPh_2MeBH_2 group of **5**[11] and for the Co-BH_2-PPh_2 interaction of the bridged cobaltaborane **6**,[12] which also contains a dangling phosphane. The Rh8–B′ bond length of 2.323(2) Å in **3** lies above the average value of 2.238 Å for rhodaboranes, but within the range of 1.951 – 2.477 Å so far reported.[13] The hydrogen atoms were refined successfully; the geometry around the BH_3 group is approximately tetrahedral.

$[(PPh_3)_2(CO)OsB_4H_7](BH_2PPh_2Me)]$ **5**

$[(CO)(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$ **6**

The course of the reaction in which **3** is formed is not clear at this time. However, it is likely that the large excess of $BH_3 \cdot THF$ displaces the dangling dppm ligand in **2** as $Ph_2PCH_2PPh_2(BH_3)_2$ (also isolated from the reaction mixture)[14] and inserts into the Rh–P bond of the Rh(dppm) chelate to give the title compound. Conversely, BH_3 may remove the chelating ligand as dppm$(BH_3)_2$ and add to the dangling end of the monodentate dppm. The NMR data for **3** are consistent with the molecular structure described above. The ^{11}B NMR spectrum consists of ten broad signals in the range from $\delta = +17.2$ to -31.2. The peak at $\delta = -24.1$ shows coupling to a phosphorous atom and is assigned to the BH_3 group (B′ in Figure 2). All terminal hydrogen atoms were related to their corresponding boron atoms by selective $^1H\{^{11}B\}$ decoupling experiments. The signal of the bridging hydrogen atom on the B9–B10 edge appears at $\delta = -1.37$. The $^{31}P\{^1H\}$ spectrum shows a sharp doublet of doublets, which is assigned to the PPh_2 group *trans* to the sulfur atom, and a very broad signal for the phosphorous atom directly bound to the BH_3 unit. At room temperature, the three hydrogen atoms of the BH_3 group are equivalent on the NMR time scale and give rise to a broad single peak at $\delta = +0.85$. As the temperature is lowered this peak broadens and finally splits into three signals. This indicates that the BH_3 group is fluxional in solution, most likely undergoing rotation about the B–P bond ($\Delta G^{\neq} \approx 37\,kJ\,mol^{-1}$).

The resemblence of the NMR data of the BH_3 group to those of a pure borane adduct suggests that the BH_3–P interaction in **3** is best described as an adduct that coordinates to a rhodium center through two three-center, two-electron bonds. In terms of a metal complex, **3** could be formally regarded as an 18-electron species with bonding vectors towards the sulfur atom, the B4–B3 and B9–B4 edges of the cluster, the phosphane group, and the BH_3 unit; the novel exopolyhedral ligand $PPh_2CH_2PPh_2BH_3$ acts as a six-electron donor. Alternatively, **3** can be regarded as a saturated rhodathiaborane that conforms to the polyhedral skeletal electron pair theory description for an eleven-vertex *nido* cluster.[15]

In conclusion, **3** is the first polyhedral borane derivative in which a BH_3 adduct coordinates to a metal center in a bidentate fashion through the hydrogen atoms. We are currently investigating the reactivity of **3** and of related species.

Experimental Section

2: $PPh_2CH_2PPh_2$ (51 mg, 0.133 mmol) was added to a solution of **1** (32 mg, 0.042 mmol) in CH_2Cl_2. The bright red solution turned immediately bright yellow. The reaction mixture was stirred at room temperature under nitrogen. After 40 min the solvent was evaporated under vacuum. The yellow residue was subjected to thin layer chromatography (TLC) with CH_2Cl_2/pentane (3/2) as mobile phase, which gave rise to separation of **2** as a yellow component with $R_f = 0.4$ (20 mg, 0.02 mmol, 48 %). $^1H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 7.80 - 6.52$, (m, 40 H, C_6H_5), 3.85 (s, 1 H, BH), 3.74 (s, 1 H, BH), 3.27 (d, $J = 23$ Hz, 1 H, BH), 2.83 (d, $J = 12$ Hz, 1 H, BH), 2.11 (s, 1 H, BH), 1.71 (s, 1 H, BH), 1.68 (s, 2 H, BH), 1.10 (s, 1 H, BH), −4.38 (s, 1 H, μ-H); $^1H\{^{31}P\}$ NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 4.29$, 4.18 (both pairs of AB d, $^2J(H,H) = 14$ Hz, 2 H, CH_2), 3.58, 2.83 (each d, $^2J(H,H) = 16$ Hz, 2 H, CH_2); ^{11}B NMR (160.5 MHz, CD_2Cl_2, 25 °C): $\delta = 14.7$ (vbr, 1 B, BH), 8.1 (vbr, 3 B, BH), 1.2 (vbr, 1 B, BH), −13.5 (vbr, 1 B, BH), −14.9 (d, $^1J(H,B) = 126$ Hz, 1 B, BH), −19.0 (d, $^1J(H,B) = 126$ Hz, 1 B, BH), −29.2 (vbr, 1 B, BH); ^{31}P NMR (202.5 MHz, CD_2Cl_2, 25 °C): $\delta = 15.2$ (dt, $^1J(P,Rh) = 126$ Hz, $^2J(P,P) = 26$ Hz), −7.7 (ddd, $^1J(P,Rh) = 122$, $^2J(P,P) = 13$ and 63 Hz), −26.9 (d, $^2J(P,P) = 31$ Hz), −42.9 (br td, $^1J(P,Rh) + {}^2J(P,P) \approx 68$, $^2J(P,P) \approx 26$ Hz); HR-MS (FAB Kratos MS-50, 3-NBA/Ar gas): m/z calcd for $C_{50}H_{52}B_9P_4RhS$: 1010.2633 $[M^+ - H_2]$; found: 1010.2632.

3: A 20-fold excess of $BH_3 \cdot THF$ (0.34 mmol) was added to a solution of **2** (17 mg, 0.017 mmol) in CH_2Cl_2. The resulting orange solution was stirred at room temperature under nitrogen for 20 h. The solvent was removed in vacuum, and the resulting yellow residue was subjected to TLC with CH_2Cl_2/pentane (3/2) as eluent. Two components were isolated: yellow and UV-active bands with $R_f = 0.4$ and 0.5, respectively. Slow diffusion of pentane into a solution of the yellow component in CH_2Cl_2 yielded air-stable orange crystals of **3** (7.4 mg, 0.012 mmol, 71 %). $^1H\{^{11}B\}$ NMR (500 MHz, CD_2Cl_2, −80 °C): $\delta = 7.80 - 6.52$ (m, 20 H, C_6H_5), 4.19 (s, 1 H, BH), 3.58 (s, 1 H, BH), 3.12 (s, 1 H, BH), 2.91 (br s, 1 H, BH_3), 2.73 (br d, $J = 17$ Hz, 1 H, BH), 2.47 (s, 1 H, BH), 1.53 (s, 1 H, BH), 1.18 (s, 2 H, BH), 1.09 (s, 1 H, BH), −0.24 (br s, 1 H, BH_3), −0.52 (br s, 1 H, BH_3), −1.39 (s, 1 H, μ-H); $^1H\{^{31}P\}$ NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 3.06$, 3.36 (each d, $^2J(H,H) = 15$ Hz, 2 H, CH_2); $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_2Cl_2, 25 °C): $\delta = 17.2$ (vbr s, 1 B, BH), 13.1 (br s, 1 H, BH), 10.8 (s, 1 B, BH), 5.1 (s, 1 B, BH), 1.9 (s, 1 B, BH), −14.3 (s, 1 B, BH), −19.1 (s, 1 B, BH), −19.6 (s, 1 B, BH), −24.1 (br d, $^1J(B,P) = 17$ Hz, 1 B, BH_3), −31.2 (br s, 1 B, BH); ^{31}P NMR (202.5 MHz, CD_2Cl_2, −50 °C): $\delta = 49.3$ (dd, $^1J(P,Rh) = 151$, $^2J(P,P) = 6$ Hz), 14.43 (vbr, 1 P, PBH_3); elemental analysis: calcd: C 46.88, H 5.51; found: C 46.65, H 5.41; LR-MS (Finnegan TSQ-700, ESI, $CHCl_3$/TFA): m/z 644 $[M^+]$; parent envelope pattern conforms to values calculated from isotopic abundances.

Crystal data were collected for both compounds on a Siemens CCD area detector single-crystal X-ray diffractometer with ω scans. Data reduction and structure solutions were carried out with the SAINT and SHELXTL software packages, respectively. Least square refinements were performed with SHELXTL-97. Absorption correction was applied to the data by equivalent reflections (SADABS).

2: $C_{102}H_{114}B_{18}Cl_4OP_8S_2Rh_2$, $M_r = 2210.01$, triclinic, space group $P\bar{1}$, $a = 13.6177(1)$, $b = 18.8835(2)$, $c = 22.6213(2)$ Å, $\alpha = 102.61$, $\beta = 92.675(1)$, $\gamma = 103.587(1)°$, $V = 5488.30(9)$ Å^3, $\rho_{calcd} = 1.337$ Mg m^{-3}, $Z = 2$,

$\mu(\mathrm{Mo}_{K\alpha}) = 0.599\ \mathrm{mm}^{-1}$, $T = 223(2)$ K. A total of 19166 ($R_{\mathrm{int}} = 0.100$) independent reflections were collected up to $2\theta_{\max} = 55.00°$. The final $\omega R(F^2)$ for all unique reflections was 0.2162 with a conventional $R(F)$ of 0.08123 for 19166 reflections with $I > 2\sigma(I)$ and 1259 parameters. The molecule crystallizes with two molecules of CH_2Cl_2 and a molecule of H_2O in the lattice. The unit cell contains two unique molecules of the metallaborane, only one of which is shown in Figure 1 without solvent molecules.

3: $C_{25}H_{35}B_{10}P_2RhS$, $M_r = 640.54$, monoclinic, space group $P2_1/n$, $a = 13.2721(1)$, $b = 11.5727(1)$, $c = 19.9181(2)$ Å, $\beta = 94.898\ (1)°$, $V = 3048.13(5)$ Å^3, $\rho_{\mathrm{calcd}} = 1.396\ \mathrm{Mg\,m^{-3}}$, $Z = 4$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.750\ \mathrm{mm}^{-1}$, $T = 223(2)$ K. A total of 6964 ($R_{\mathrm{int}} = 0.07$) independent reflections were collected up to $2\theta_{\max} = 55.00°$. The final $\omega R(F^2)$ for all unique reflections was 0.0597 with a conventional $R(F)$ of 0.0303 for 6943 reflections with $I > 2\sigma(I)$ and 492 parameters.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103258 and 103259 for **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: June 22, 1998 [Z12027IE]
German version: *Angew. Chem.* **1999**, *111*, 203–206

Keywords: boron · clusters · P ligands · rhodium

[1] R. N. Grimes in *Metal Interactions with Boron Clusters* (Ed.: R. N. Grimes), Plenum Press, New York, **1982**, chap. 7, pp. 269–319.
[2] F. Takusagawa, A. Fumigalli, T. F. Koetzle, S. G. Shore, T. Schmitkons, A. V. Fratini, K. W. Morse, C.-Y. Wei, R. Bau, *J. Am. Chem. Soc.* **1981**, *103*, 5165–5171.
[3] M. Y. Darensbourg, R. Bau, M. W. Mark, R. R. Burch, Jr., J. C. Deaton, S. Slater, *J. Am. Chem. Soc.* **1982**, *104*, 6961–6969.
[4] S. A. Snow, M. Shimoi, C. D. Ostler, B. K. Thompson, G. Kodama, R. W. Parry, *Inorg. Chem.* **1984**, *23*, 511–512.
[5] S. A. Snow, G. Kodama, *Inorg. Chem.* **1985**, *24*, 795–796.
[6] K. Katoh, M. Shimoi, H. Ogino, *Inorg. Chem.* **1992**, *31*, 670–675.
[7] M. Shimoi, K. Katoh, M. Uruichi, S. Nagai, H. Ogino in *Current Topics in the Chemistry of Boron*, *Vol. 143* (Ed.: G. W. Kabalka), Royal Society of Chemistry, Cambridge, **1994**, pp. 293–296.
[8] G. Ferguson, M. C. Jennings, A. L. Lough, S. Coughlan, T. R. Spalding, J. D. Kennedy, X. L. R. Fontaine, B. Štíbr, *J. Chem. Soc. Chem. Commun.* **1990**, 891–894.
[9] P. McQuade, R. L. Thomas, H. Fang, N. P. Rath, L. Barton, *Abstr. Pap. 6th Boron-USA Workshop* (Athens, GA, USA) **1998**.
[10] G. M. Rosair, A. J. Welch, A. S. Weller, *Acta Crystallogr. Sect. C* **1996**, *52*, 3020–3024.
[11] L. Barton, J. Bould, H. Fang, K. Hupp, N. P. Rath, C. Gloeckner, *J. Am. Chem. Soc.* **1997**, *119*, 631–632.
[12] D. J. Elliot, C. J. Levy, R. J. Puddephatt, D. G. Holah, A. N. Hughes, V. R. Magnuson, I. M. Moser, *Inorg. Chem.* **1990**, *29*, 5014–5015.
[13] Cambridge Structural Database, QUEST-3D query, with the Rh–B distance in the fragment Rh-B-H constrained to be between 1.8 and 2.5 Å.
[14] $[Ph_2PCH_2PPh_2(BH_3)_2]$: $^1H\{^{11}B\}$ NMR (299.9 MHz, $CDCl_3$, 25 °C): $\delta = 7.66–7.34$ (m, 20H, C_6H_5), 3.24 (t, $^2J(H,P) = 17.0$ Hz, 2H, CH_2), 0.92 (d, $^2J(H,P) = 15.6$ Hz, 6H, BH_3); ^{11}B NMR (96.2 MHz, $CDCl_3$, 25 °C): $\delta = -37.1$; ^{31}P NMR (121.4 MHz, $CDCl_3$, 25 °C): $\delta = 15.2$.
[15] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.

Insect Desaturases as Unique Analytical Tools To Unravel the Stereochemical Course of the Reduction of Vicinal Ditosylates with Lithium Aluminum Deuteride[**]

Isabel Navarro, Gemma Fabrias,[*] and Francisco Camps

The biosynthetic pathways of lepidopteran sex pheromones involve the action of rather unusual desaturases, among which the Δ^{11}-acyl-CoA desaturases are the most common ones.[1] As part of our ongoing studies on the determination of the stereospecificity of fatty acyl desaturases from insects, we have recently demonstrated that in the moth, *Spodoptera littoralis*, formation of (*E*)-11-tetradecenoic acid takes place by stereospecific removal of the *pro*-(*R*) C11-H and the *pro*-(*S*) C12-H from myristic acid.[2] In contrast, desaturation of myristic acid to (*Z*)-11-tetradecenoic acid occurs by stereospecific cleavage of *pro*-(*R*) C11-H and *pro*-(*R*) C12-H, in agreement with the previously reported stereospecificities of the related (*Z*)-11-palmitoyl CoA[3] and (*Z*)-9-stearoyl-CoA desaturases.[4–6]

To continue our investigations, we required an expeditious procedure for the synthesis of *vic*-dideuterated, enantiomerically pure fatty acids.[7] In this context, we thought that asymmetric olefin dihydroxylation followed by tosylation and reduction of the resulting ditosylate with lithium aluminum deuteride might be an appropriate method. However, a recent report on the occurrence of anchimeric effects in the nucleophilic substitution of a *vic*-dimesylate[8] suggested that the stereochemical outcome of the above procedure might be not so straightforward as anticipated. Thus, the evaluation of the stereochemical course of the proposed sythetic pathway was a complex issue, since the determination of the relative stereochemistry of deuterium atoms in the resulting *vic*-dideuterated fatty acids is very cumbersome by current analytical methods.

To solve this problem, we applied the above synthetic procedure to the preparation of a *vic*-dideuterated fatty acid suitable as substrate for a desaturase of known stereospecificity so that the result of the enzymatic reaction would reveal the relative configuration of the vicinal deuterium atoms in the probe. Since the stereochemical courses of both (*Z*)- and (*E*)-11 desaturations of myristic acid in *S. littoralis* is known,[2] the mass of the most abundant isotopomer of both (*Z*)- and (*E*)-11-tetradecenoic acids formed in pheromone glands of insects incubated with both the racemic mixtures of the diastereomers of [11,12,13,13,14,14,14-$^2H_7$]myristic acid

---

[*] Dr. G. Fabrias, Dr. I. Navarro, Prof. Dr. F. Camps
Department of Biological Organic Chemistry (CID-CSIC)
Jordi Girona 18-26, E-08034-Barcelona (Spain)
Fax: (+349) 3-2045904
E-mail: gfdqob@cid.csic.es

[**] This work was supported by Comisión Asesora de Investigación Científica y Técnica (grant AGF 98-0844), Comissionat per a Universitats i Recerca from the Generalitat de Catalunya (grant GRQ 93-8016) and SEDQ S.A.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.