truncation gap of 53 μm). The radius of the cone was 20 mm, and the angle between the cone and plate was 2°. The experiments were performed at 35 °C for the single-headed surfactant **1** and at 25 °C for CTAB, **2**, and **3**. Both the steady shear (flow-step) and oscillatory shear (stress control) measurements were performed and the measurements were taken over a frequency sweep range of 0.001 to 100 s^{-1}. The rheometer has a built-in computer which converts the torque measurements into either G' (the storage modulus) and G'' (the loss modulus) in oscillatory shear experiments or viscosity in flow-step measurements.

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$R^*_4Tl_3Cl$ and $R^*_6Tl_6Cl_2$ ($R^* = SitBu_3$)—The First Compounds with Larger Clusters Containing Covalently Linked Thallium Atoms**

Nils Wiberg,* Thomas Blank, Hans-Wolfram Lerner, Dieter Fenske und Gerald Linti

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Many compounds of the compositions TlR_3 and TlR ($R =$ inorganic, organic group) exist with thallium in the oxidation states +III and +I,[1] (the Tl–R bonds in the former compounds are more covalent in nature, those in the latter more electrovalent), whereas very few compounds of the composition TlR_2 with thallium in the oxidation state +II are known to date. They form dimers $R_2Tl{-}TlR_2$ with a covalent Tl–Tl bond (Tl–Tl 2.914 ($R = Si(SiMe_3)_3$),[2] 2.966 ($R = SitBu_3$),[3] 2.881 Å ($R = SitBu_2Ph$)[4]). A few Tl^I compounds also have Tl–Tl bonds; however, as weak interactions with Tl–Tl distances > 3.3 Å these vary significantly from the strong interactions in the three reported dithallanes with Tl–Tl distances < 3.0 Å (e.g. $(PhCH_2)_5C_5Tl\cdots TlC_5(CH_2Ph)_5$: Tl–Tl 3.632 Å;[5] $[(Me_3Si)_3CTl]_4$: Tl–Tl 3.322 and 3.627 Å;[6] $\{MeSi[N(Tl)tBu]_3\}_2$ has a Tl–Tl distance in the intermediate range (3.146 Å) and in addition several very weak Tl–Tl interactions;[7] in $\{MeC[CH_2N(Tl)SiMe_3]_3\}_2$ and other Tl^I amides Tl–Tl interactions exclusively occur with very large Tl–Tl distances (> 3.6 Å)[8]). Thallium cluster compounds containing more than two covalently linked thallium atoms were hitherto unknown.

We obtained compounds of this type, namely the trithallane $R^*_4Tl_3Cl$ (**1**) and the hexathallane $R^*_6Tl_6Cl_2$ (**2**), in the attempt to synthesize sterically overloaded disupersilylthallium chloride R^*_2TlCl ($R^* = \text{supersilyl} = SitBu_3$) analogously to the preparation of R^*_2ECl ($E = Al, Ga, In$)[9] from the trihalide ECl_3 and two molar equivalents of supersilylsodium NaR^* in tetrahydrofuran (THF). Treatment of $TlCl_3$ in THF at −78 °C with NaR^* in the molar ratio 1:2 leads to the slow (several hours) formation of a red-brown reaction solution as well as a

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[+] Crystal structure analyses

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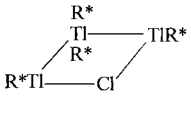

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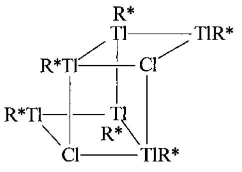

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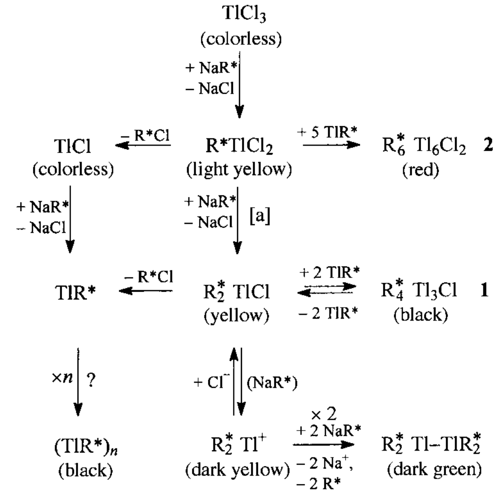
black-brown precipitate. From the THF solution at −25 °C or from a toluene solution obtained from extraction of the precipitate with toluene (−78 °C) and likewise kept at −25 °C, the compounds **1** and **2**, respectively (at least **1** forms in the THF solution very slowly at −25 °C), crystallized in the course of several months. The nature of fraction of the precipitate which remained after extraction with toluene has still to be clarified (oligomeric TlR*?).

The red trithallane **1** and the black hexathallane **2** probably form according to the Equations (1) and (2). Both Tl cluster compounds are air-, moisture-, and light-sensitive and thermolyze in C_6D_6 at room temperature slowly and very slowly, respectively, leading to the formation of R*Cl (dissolved in C_6D_6) and a black precipitate (oligomeric TlR*?), which at 100 °C in the presence of C_6D_6 slowly transforms into elemental thallium and deuterated supersilane R*D (supersilyl radicals probably form initially, which dimerize quickly and reversibly and stabilize slowly and irreversibly on addition of hydrogen: $2\,R^{*\bullet} \rightleftarrows (R^*)_2$; $R^{*\bullet} + C_6D_6 \rightarrow R^*D + C_6D_5^{\bullet}$).[10]

$$3\,TlCl + 6\,NaR^* \xrightarrow[-6\,NaCl]{THF,\ -78\,^{\circ}C,\ 20\,h,\ then\ -25\,^{\circ}C} \mathbf{1} + 2\,R^*Cl \qquad (1)$$

$$6\,TlCl + 11\,NaR^* \xrightarrow[-11\,NaCl]{THF,\ -78\,^{\circ}C,\ 20\,h,\ then\ -25\,^{\circ}C} \mathbf{2} + 5\,R^*Cl \qquad (2)$$

The mechanism of the reactions of $TlCl_3$ and NaR* leading to **1** and **2** is still not completely clear. Possibly, the supersilanation of $TlCl_3$ initially leads to the compounds R^*TlCl_2 and R^*_2TlCl (Scheme 1), which through R*Cl elimination decompose into TlCl and TlR*, respectively. The TlR* molecules formed directly in this way or indirectly after the supersilanation of TlCl oligomerize or insert into the Tl–Cl bonds of R^*TlCl_2 and R^*_2TlCl five and two times, respectively.



Scheme 1. The reaction of $TlCl_3$ with NaR*. [a] This reaction proceeds via an unidentified compound.

Studies on the reaction of $TlCl_3$ with varying amounts NaR* as well as on the thermolysis of the intermediate products formed hereby support these hypotheses for the formation of **1** and **2**. Thus, the reaction of $TlCl_3$ with the equimolar amount of NaR* in THF at −78 °C indeed leads to a solution of light yellow dichlorosupersilylthallane R^*TlCl_2.[11] With two molar equivalents of NaR* in THF at low temperatures it is not chlorodisupersilylthallane R^*_2TlCl that is formed but—as described—the trithallane **1** and the hexathallane **2** (rapid heating of a solution of $TlCl_3/2\,NaR^*$ cooled to −78 °C in THF to room temperature leads exclusively to R*Cl and a black precipitate). The yellow thallane R^*_2TlCl was obtained finally after many failed attempts (e.g. $TlCl_3 + NaR^*$, MgR^*_2, ZnR^*_2; $Tl_2R^*_4 + HCl$, Ph_3CCl) by addition of Me_3SiCl to a solution of $TlCl_3$ and three molar equivalents of NaR* in THF at −78 °C; Me_3SiR^* was formed as a by-product.[12] On heating the corresponding solution without adding Me_3SiCl, dark green tetrasupersilyldithallane $Tl_2R^*_4$ is formed, which is also accessible from TlBr and NaR*.[3] Possibly, in the present case a compound is formed initially that contains disupersilylthallonium $R^*_2Tl^+$ (counterion R^*NaCl^-?; see Scheme 1). The cations could react with Cl^- donors such as Me_3SiCl to give R^*_2TlCl, whereas in the absence of Me_3SiCl they would be slowly reduced by excessive NaR* to give $Tl_2R^*_4$ (Scheme 1). The dark yellow cation $R^*_2Tl^+$ also forms from R^*_2TlCl on addition of $AlCl_3$ in CD_2Cl_2.[13]

Whereas the thermal decomposition of the thallane R^*TlCl_2 dissolved in THF into TlR* and TlCl (Scheme 1) already occurs at −50 °C, the thallane R^*_2TlCl decomposes very slowly (over a period of many days) in C_6D_6 even at room temperature via **1** to give R*Cl and the above-mentioned black precipitate (oligomeric TlR*?), which at higher temperatures—as already mentioned—is transformed into Tl and R*D. Thus, TlR*, which is formed slowly thermolytically from R^*_2TlCl, could in statu nascendi react with R^*_2TlCl to give trithallane **1**, which, in turn, would decompose even slower with the release of supersilylthallium, which has a tendency to oligomerize. Since R^*_2TlCl does not occur in the solutions of $TlCl_3/2\,NaR^*$ in THF, which at low temperatures lead to **1** and **2**, another compound (which still has to be identified; R*ClTl–TlClR*?) derived from R^*TlCl_2 and NaR* must be responsible for the formation of **1** and **2**.

Figures 1 and 2 show the structures of the molecules **1** and **2** in the crystal.[14] The central structural element of the trithallane **1** is a planar Tl_3Cl four-membered ring (sum of angles 359.91°) with a $R^*Tl\text{-}R^*_2Tl\text{-}R^*Tl$ chain (Tl–Tl 2.92 Å (av)). The Si_2Tl plane of the R^*_2Tl unit is almost perpendicular (89°) to the Tl_3Cl plane. The hexathallane **2** contains two Tl_3Cl four-membered rings with R*Tl-R*Tl-R*Tl chains (Tl–Tl 2.93 Å (av)), which are linked with each other through the central Tl atoms (Tl–Tl 2.85 Å). As a result of additional Tl–Cl bonds between the Tl_3Cl four-membered rings, these are, in contrast to those in **1**, no longer planar (sum of angles 344.3° (av); dihedral angle Tl-Tl-Cl-Tl in the rings 135.8° (av)).

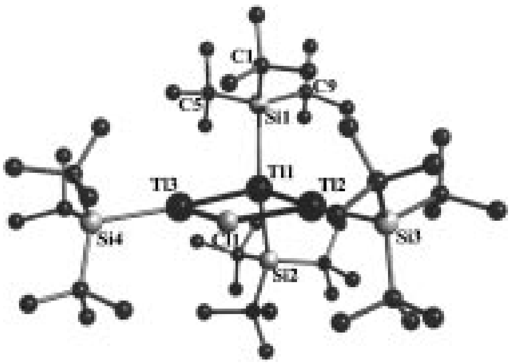


Figure 1. Molecular structure of **1** in the crystal (SCHAKAL plot; atoms with arbitrary radii; the hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Tl1-Tl2 2.9093(7), Tl1-Tl3 2.9262(8), Tl2-Cl1 2.808(3), Tl3-Cl1 2.803(3), Tl1-Si1 2.641(3), Tl1-Si2 2.645(3), Tl2-Si3 2.678(3), Tl3-Si4 2.696(3), Si-C 1.944 (av); Si1-Tl1-Si2 143.9(1), Si1-Tl1-Tl2 105.55(7), Si2-Tl1-Tl2 101.04(6), Si1-Tl1-Tl3 103.51(9), Si2-Tl1-Tl3 102.32(7), Tl2-Tl1-Tl3 85.85(3), Si3-Tl2-Cl1 101.24(11), Si3-Tl2-Tl1 166.70(9), Cl1-Tl2-Tl1 92.06(7), Si4-Tl3-Cl1 101.60(10), Si4-Tl3-Tl1 166.58(7), Cl1-Tl3-Tl1 91.82(7), C5-Si1-C9 111.5(10), C-Si-C 110.9 (av), C-Si-Tl 107.6 (av).

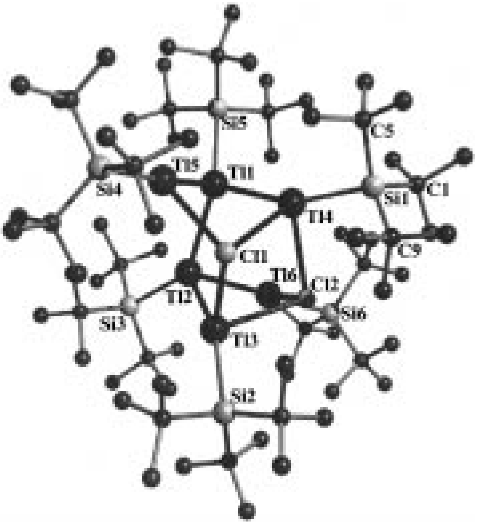


Figure 2. Molecular structure of **2** in the crystal (SCHAKAL plot; atoms with arbitrary radii; the hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] of one of the two almost identical $R^*_3Tl_3Cl$ units and its linkage with the other unit: Tl1-Tl2 2.854(2), Tl1-Tl5 2.908(2), Tl1-Tl4 2.944(2), Tl4-Cl2 2.918(6), Tl4-Cl1 2.984(7), Tl5-Cl1 2.866(7), Tl1-Si5 2.630(7), Tl4-Si1 2.715(6), Tl5-Si4 2.680(8), Si-C 1.951 (av); Si5-Tl1-Tl2 137.1(2), Si5-Tl1-Tl5 112.4(2), Tl2-Tl1-Tl5 94.83(5), Si5-Tl1-Tl4 113.8(2), Tl2-Tl1-Tl4 100.89(5), Tl5-Tl1-Tl4 84.11(4), Si1-Tl4-Cl2 99.7(2), Si1-Tl4-Tl1 159.6(2), Cl2-Tl4-Tl1 99.1(1), Si1-Tl4-Cl1 105.3(2), Cl2-Tl4-Cl1 82.0(2), Tl1-Tl4-Cl1 85.4(1), Si4-Tl5-Cl1 99.2(2), Si4-Tl5-Tl1 172.5(2), Cl1-Tl5-Tl1 88.3(1), Tl5-Cl1-Tl3 103.6(2), Tl5-Cl1-Tl4 84.1(2), Tl3-Cl1-Tl4 91.9(2), C-Si-C 111.7 (av), C-Si-Tl 107.3 (av).

Experimental Section

NaR* (0.513 g, 11.3 mmol) in THF (25 mL) was added dropwise to a solution of $TlCl_3$ (1.74 g, 5.60 mmol) in THF (50 mL) at −78 °C. The initially orange solution (NaR*) was transformed slowly at −78 °C into a dark red-brown suspension. After a reaction time of 20 h the mixture was filtered at −78 °C to separate the insoluble components. Compound **1** (0.350 g, 0.240 mmol; 13 %) precipitated as red crystals from the filtrate, which had been concentrated to about 30 mL and kept at −25 °C, over the course of six months. The separated dark brown precipitate was extracted with toluene (30 mL; −78 °C). Black crystals of **2** (0.500 g, 0.200 mmol; 21 %) precpitated from the extract at −25 °C over the course of six months. **1**: ^{1}H NMR (C_6D_6, TMS, internal): $\delta = 1.395$ (br.; 2Si*t*Bu$_3$), 1.410 (br.; 2Si*t*Bu$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, internal): $\delta = 23.10$ (6*C*Me$_3$), 23.70 (6*C*Me$_3$), 33.70 (6C*Me$_3$*), 33.89 (6C*Me$_3$*); $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, external): $\delta = 99.1$ (d; $^1J(Si,^{203,205}Tl) = 1431$, 1436 Hz; 2Si*t*Bu$_3$), 100.2 (d; $^1J(Si,^{203,205}Tl) = 1450$, 1455 Hz; 2Si*tBu$_3$*). **2**: ^{1}H NMR ([D$_8$]toluene, TMS, internal): $\delta = 1.371$ (d; $^4J(H,Tl) = 1.33$ Hz; 4Si*t*Bu$_3$), 1.393 (br.; 2Si*t*Bu$_3$); ^{13}C and ^{29}Si NMR in [D$_8$]toluene: not observed. Note: In a repeat of the reaction, NMR spectra (^{1}H, ^{13}C, ^{29}Si) of the filtrate cooled to −25 °C were recorded immediately after heating to room temperature and thereafter at certain intervals (replace THF for C_6D_6). They show that at −25 °C the trithallane **1** is formed only slowly (in the course of weeks) from an unidentified precursor (R*ClTl−TlClR*?) (^{1}H NMR (C_6D_6, TMS, internal): $\delta = 1.36$ (d; $^4J(H,Tl) = 3.74$ Hz); $^{29}Si\{^1H\}$ NMR (C_6D_6, TMS, external): $\delta = 97.1$ (d; $^1J(Si,^{203,205}Tl) = 1447$, 1441 Hz). According to the NMR spectra the solution contained only traces of hexathallane **2.**

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[11] The existence of the thallane R^*TlCl_2 at low temperatures ($^{29}Si\{^1H\}$ NMR (THF, −50 °C): $\delta = 62.2$ (d, $^1J(Si,^{203,205}Tl) = 513.6$, 516.7 Hz; Si*t*Bu$_3$) is supported not only by the smooth thermolytic decomposition into R*Cl and TlCl, but also by the reaction with LiPh, which affords diphenylsupersilylthallane R^*TlPh_2. ^{1}H NMR (C_6D_6, TMS, internal): $\delta = 1.120$ (br.; Si*t*Bu$_3$), 7.18, 7.43 (each m; *o*-, *p*-, *m*-H of 2Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, internal): $\delta = 28.45$, 32.77 (3*C*Me$_3$, 3C*Me$_3$*), 127.41, 127.50, 129.00, 141.70 (*m*-, *p*-, *o*-, *i*-C of 2Ph); ^{29}Si NMR: not observed.

[12] According to X-ray structure analysis (in collaboration with H. Nöth, M. Warchhold), the air-, water-, and light-sensitive thallane R^*_2TlCl, which is obtained from pentane at −23 °C in the form of yellow plates, has a planar Si_2TlCl framework and thus contains—unlike Me_2TlCl[1]—no linear $[RTlR]^+$ ions (possibly the very different sizes of the ions $R^*_2Tl^+$ and Cl^- prevent the formation of an energy-poor ionic crystal). ^{1}H NMR (C_6D_6, TMS, internal): $\delta = 1.319$ (br.; 2Si*t*Bu$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS, internal): $\delta = 28.35$, 32.75 (each v br.; 6*C*Me$_3$, 6C*Me$_3$*; the former signal is a doublet with $^3J(C,Tl) = 55$ Hz); ^{29}Si NMR: not observed; MS: *m*/*z* (%): 603 (67) [$M^+ - Cl$], 581 (22) [$M^+ - C_4H_9$], 405 (90) [$M^+ - \mathrm{Si}t\mathrm{Bu}_3$], 205 (100) [$Tl^+$] (each correct isotopic pattern).

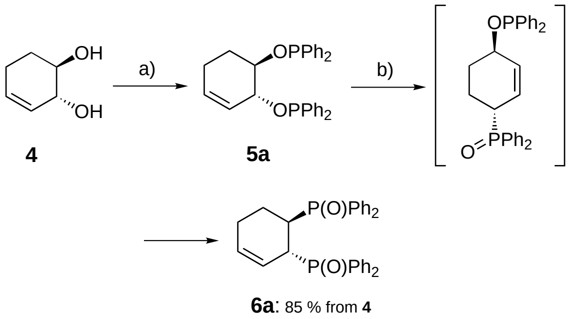
[13] Disupersilylthallonium tetrachloroaluminate $[R^*_2Tl]^+[AlCl_4]^-$, which had hitherto not been obtained as crystals suitable for an X-ray structural analysis: ^{1}H NMR (CD_2Cl_2, TMS, internal): $\delta = 1.40$ (br.; 2Si*t*Bu$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, TMS, internal): $\delta = 27.39$, 33.25 (each v br.; 6*C*Me$_3$, 6C*Me$_3$*); ^{29}Si NMR: not observed; ^{27}Al NMR (CD_2Cl_2, $Al(NO_3)_3$ in D_2O, external): $\delta = 101.14$ ($AlCl_4^-$; full width at half maximum 140 Hz).

[14] Crystal structure analyses: **1**: monoclinic, space group $C2/c$, $a = 2511.8(5)$, $b = 1309.2(3)$, $c = 4291.8(9)$ pm, $\beta = 101.37(3)°$, $V = 13.84(1)$ nm^3, $Z = 4$; $\rho_{calcd} = 1.473$ Mg m^{-3}, $\mu = 7.109$ mm^{-1}, $F(000) = 6040$. Data collection: $2\theta = 3.86 - 48.14°$, $-18 \leq h \leq 28$, $-13 \leq k \leq 13$, $-49 \leq l \leq 49$, 24666 reflections, of which 9010 were independent ($R_{int} = 0.0781$) and 611 refined. All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions, $R_1 = 0.0663$, $wR_2 = 0.1794$ ($F > 4\sigma(F)$), GOF(F^2) = 1.083; max. residual electron density 2.556 e Å^{-3}. **2**: triclinic, space group $P\bar{1}$, $a = 1548.9(3)$, $b = 1738.7(4)$, $c = 2097.4(4)$ pm, $\alpha = 78.37(3)$, $\beta = 68.79(3)$, $\gamma = 77.12(3)°$, $V = 5.0877(18)$ nm^3, $Z = 2$; $\rho_{calcd} = 1.473$ Mg m^{-3}, $\mu = 9.621$ mm^{-1}, $F(000) = 2396$. Data collection: $2\theta = 4.22 - 51.84°$, $-18 \leq h \leq 18$, $-21 \leq k \leq 21$, $-25 \leq l \leq 25$, 55309 reflections, of which 18432 were independent ($R_{int} = 0.0939$) and 829 refined. All non-hydrogen atoms were refined anisotropically and the H atoms were included in calculated positions, $R_1 = 0.1313$, $wR_2 = 0.4136$ ($F > 4\sigma(F)$), GOF(F^2) = 1.851; max. residual electron density 17.506 e Å^{-3}. The crystals of **2** are extremely thin, very small platelets, and therefore the data set was strongly influenced by absorption effects. An absorption correction could not be performed. Several maxima of similar size occur which are all located at the periphery of the molecule (60–150 pm from the H atoms). If only data up to $2\theta = 44°$ are considered for the refinement of the structure, the structural parameters are altered only slightly: $R_1 = 0.128$; max. residual electron density 13.40 Å^{-3}. The intensities were measured with a STOE-IPDS diffractometer with a CCD area detector (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The crystals were mounted in perfluoropolyether oil; $T = 183(2)$ and 193(2) K, respectively. The structures were solved by using direct methods and refined against F^2 for all observed reflections. (Structure solution with SHELXS 94, refinement using SHELXL 93). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-150538 (**1**) and CCDC-150539 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). .

New C_2-Symmetrical 1,2-Diphosphanes for the Efficient Rhodium-Catalyzed Asymmetric Hydroboration of Styrene Derivatives**

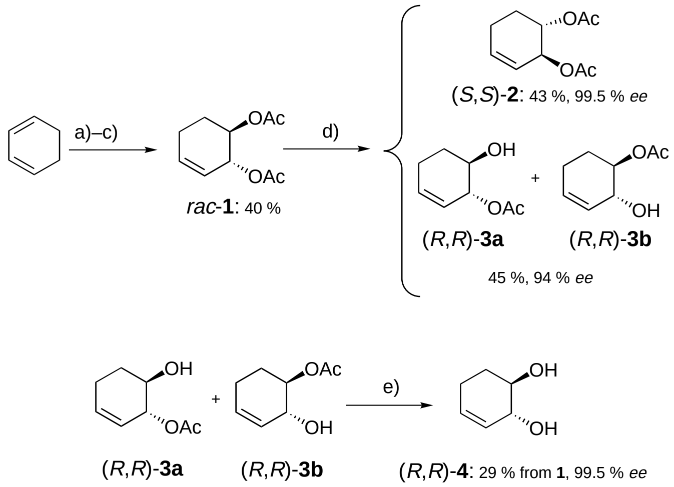
Stéphane Demay, Florence Volant, and Paul Knochel*

Chiral 1,2-diphosphanes are important ligands for asymmetric metal catalysis.[1] Their synthesis is challenging especially if the stereoselective formation of secondary carbon–phosphorus bonds is desired. Recently, we have developed a method[2] that provides a stereoselective synthesis of cyclic 1,2-diphosphane oxides using a tandem [2,3] sigmatropic rearrangement of diphenylphosphinites that are readily available from the corresponding unsaturated 1,2-diols (Scheme 1). Herein we report the use of this rearrangement for a practical preparation of new chiral 1,2-diphosphanes and their application in highly efficient rhodium-catalyzed asymmetric hydroborations.



Scheme 1. Tandem [2,3] sigmatropic rearrangement of diphenylphosphinite. a) ClPPh$_2$, 4-DMAP, Et$_2$O, RT; b) toluene, reflux, 42 h.

The racemic mixture of the diacetate **1** is prepared in three steps in about 40% overall yield starting from 1,3-cyclohexadiene.[3] This diacetate is easily resolved using *Pseudomonas fluorescens* lipase[4] to afford the chiral diacetate (*S*,*S*)-**2** (43% yield, 99.5% *ee*) and a mixture of monoacetates (*R*,*R*)-**3** (45% yield, 94% *ee*; Scheme 2). The two enantiomeric diols (*R*,*R*)-**4** and (*S*,*S*)-**4** are obtained in optically pure forms after saponification and recrystallization from AcOEt in yields of 29 and 31%, respectively (from **1**). These compounds have been prepared on a multigram scale and are a convenient starting material for a range of new chiral phosphanes of interest for metal catalysis.



Scheme 2. Preparation of the optically pure diol (*R*,*R*)-**4**. a) Br$_2$ (1 equiv), CHCl$_3$, 5 °C; b) 1 M KOH, H$_2$O, RT, 96 h; c) Ac$_2$O (2 equiv), pyridine, RT, 12 h; d) *Pseudomonas fluorescens* lipase, pH 7, buffer, 38 °C; e) NaOMe (1 equiv), MeOH, RT, 1 h; f) recrystallization from AcOEt.

The reaction of (*R*,*R*)-**4** with several diarylchlorophosphanes[5] provides the corresponding diphosphinites **5a–c** which undergo a smooth [2,3] sigmatropic rearrangement in

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