DOI: 10.1002/ejoc.200700613

Synthesis of Bis(catechol) Ligands Derived from Tröger's Base and Their Dinuclear Triple-Stranded Complexes with Titanium(IV) Ions

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Keywords: Tröger's base / Self-assembly / Catechol / Titanium / Helicates

Bis(catechol) ligands derived from 2,8-disubstituted analogues of Tröger's base and monofunctionalized MOM-protected or unprotected catechols bearing both rigid and flexible spacers were synthesized, which gave rise to dissymmetric oxygen donor ligands whose geometry is defined by the V-shaped and rigid structure of the core of Tröger's base. These racemic ligands undergo self-assembly to dinuclear triple-stranded helicates upon coordination to titanium(IV) ions as was proven by NMR spectroscopy and ESI-MS experiments; however, these processes are not diastereoselective.

Introduction

The last 15 years witnessed a lot of efforts made towards the use of chiral ligand structures to efficiently control the stereochemistry of metal centers of coordination compounds in a diastereoselective manner.[1] This is especially true for helicates[2] and in particular chiral N-donor ligands like 2,2′-bipyridines,[3–7] terpyridines,[8] quaterpyridine,[9] oxazolines,[10,11] or pyridylmethanimines[12–15] but also P-donor ligands,[16] and cationic complexes with suitable late-transition-metal or lanthanide ions were shown to be very effective in this sense. Our approach is aimed at the formation of self-assembled helical metal complexes from C_2-symmetric ligands that have cavities with inwardly directed functionalities; we recently showed that bis(2,2′-bipyridyl)-substituted 1,1-binaphthyl (BINOL) derivatives are very versatile in this respect.[17] During the course of this study, Tröger's base also attracted our interest as another dissymmetric chiral molecule.

Tröger's base (Figure 1) was first synthesized in 1887 by Julius Tröger,[18] and its V-shaped and rigid structure has attracted a lot of attention in the past years[19] that has led to applications in the design of various receptors for the recognition of neutral organic molecules such as menthol[20] or adenine[21] as well as for the recognition of dicarboxylic acids,[22] and it has been used as a chiral auxiliary for the enantioselective synthesis of aziridines.[23]

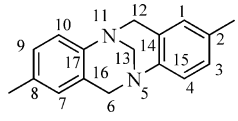

Figure 1. Tröger's base.

Very recently potentially restrictive α-amino acid based scaffolds were prepared starting from diiodo-substituted analogues of Tröger's base,[24] which were first synthesized in 2001 by Wärnmark.[25] The ability to access dihalo-substituted compounds allowed the formation of a variety of new valuable precursors for larger architectures with extended V-shaped cores through various cross-coupling methodologies.[26]

Thus, we started a study to find out if metallosupramolecular assemblies from ligands derived from Tröger's base could also be formed in a diastereoselective manner. We first synthesized racemic ligands bearing either 2,2′-bipyridine or 2-pyridylmethanimine moieties, and indeed we showed that they assemble diastereoselectively to form homoleptic D_{2d}-symmetric dinuclear double-stranded helicates upon coordination to silver(I) and copper(I) ions.[27] This was only the second example in which derivatives of Tröger's base were used as ligands for the formation of oligonuclear metal coordination compounds.[28]

Helicates, however, have not only been obtained from N- or P-donor ligands, but also from O-donor ligands like catechols and hard metal ions such as titanium(IV) or gallium(III).[2c,2g,2h] These helicates are anionic and hence do have different properties than the cationic aggregates self-assembled from ligands bearing N-heterocyclic metal chelation units and late-transition-metal ions. After the first examples of this kind published by Raymond,[29] Albrecht in

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particular extensively studied a variety of helical catecholato complexes,[2c,2g,2h,30] but there are also some examples published recently by Hahn.[31] So far, however, there have only been very few reports on the use of chiral ligands to control the stereochemistry of the newly formed stereogenic metal centers in these types of helicates, and the stereogenic information was introduced in the outer periphery of the bis(catechol) ligand structure[29c,32] rather than in the core structural element.[30c,33] Thus, we were eager to find out if Tröger's base substituted by catechol moieties could also self-assemble into helical dinuclear coordination compounds with hard titanium(IV) ions and whether these processes still proceeded in a diastereoselective fashion. Therefore, we prepared racemic bis(catechol) ligands **1** and **2** (Figure 2) and investigated their complexation behavior towards Ti^{IV} ions. Although this might sound somehow paradox, the results obtained with the use of racemic ligands to explore the degree of stereoselectivity of the self-assembly processes are better than those of enantiomerically pure ligands because in principle racemic ligands also allow the formation of heteroleptic complexes with differently configured ligands that are also diastereomers of the homoleptic complexes bearing only ligands that are equally configured.

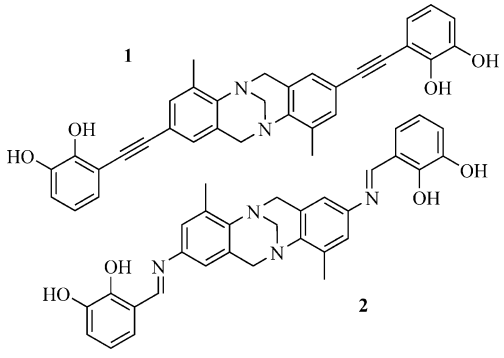
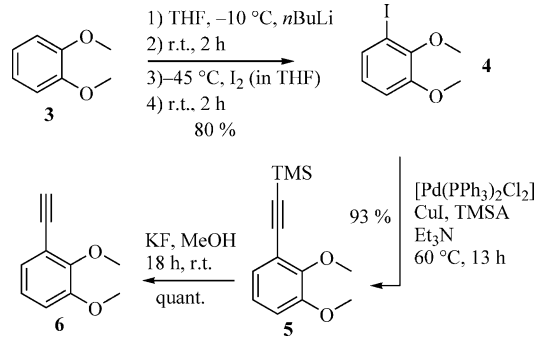


Figure 2. Bis(catechol) ligands **1** (ethynediyl bridged) and **2** (iminediyl bridged) derived from analogues of Tröger's base.

Results and Discussion

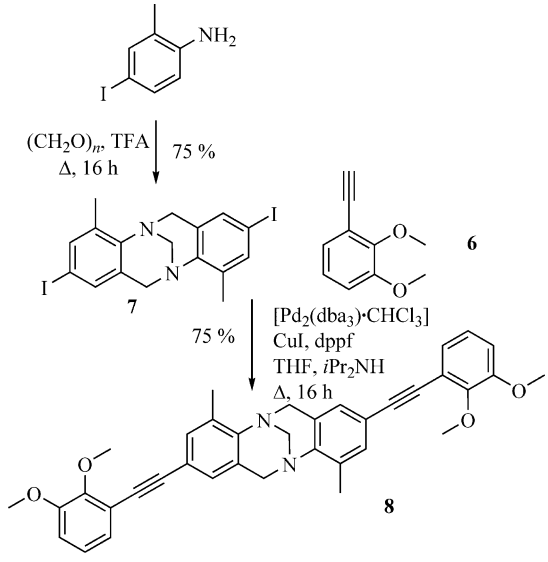
The synthesis of the desired bis(catechol) ligands in general requires disubstituted analogues of Tröger's bases and monofunctionalized catechols. As spacer units between the core of Tröger's base and the catechol units, we chose an ethynyl functionality as a rigid linker and an imine moiety as a more flexible spacer. Figure 2 shows the two ligand structures. Protection of the OH groups of the catechol is mandatory during the course of the synthesis of **1** as a result of lithiation and cross-coupling steps in the reaction sequence. Thus, we regarded veratrol (1,2-dimethoxybenzene) derivatives as especially promising OH-protected catechol derivatives for our purposes, because cleavage of the methyl groups can usually be achieved easily by applying boron tribromide as the demethylating agent.

Therefore, starting from commercially available veratrol (**3**), *ortho*-iodoveratrol **4** was prepared by *ortho* lithiation and quenching with iodine following the procedure of Thal (Scheme 1).[34] Compound **4** was transformed into **6** by applying Sonogashira conditions to yield **5**, which was deprotected to **6** by using potassium fluoride. A similar synthetic approach from *ortho*-bromoveratrole and slightly different reaction conditions was reported by Albrecht previously.[35] Our approach, however, allowed the isolation of **5** in much better yield. Additionally, deprotection of **5** to **6** could also be achieved in a better yield.



Scheme 1. Synthesis of monofunctionalized veratrol derivatives **4**–**6**.

ortho-Ethynylveratrol **6** and racemic 2,8-diiodo derivative **7** of Tröger's base[25] were subsequently subjected to a twofold Sonogashira reaction with the use of $[Pd_2(dba_3)_2 \cdot CHCl_3]$ as the palladium source and 1,1′-bis(diphenyphosphanyl)ferrocene (dppf) as a sterically demanding ligand to yield precursor **8** with methyl protected OH groups for the synthesis of racemic ligand **1** in excellent yield (Scheme 2).

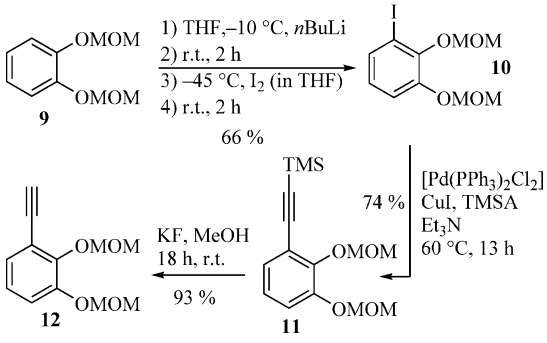


Scheme 2. Synthesis of racemic precursor **8**.

Surprisingly, the fourfold demethylation of **8** with the use of boron tribromide did not lead to the desired completely deprotected bis(catechol) ligand **1**, as expected, but rather gave rise to a complicated mixture of different products. ^1H NMR spectroscopic analysis of this mixture showed that the deprotection seemed to be incomplete; such an incomplete deprotection may lead to nine different possible prod-

ucts. Unfortunately, complete deprotection could not even be achieved when 40 equiv. of boron tribromide was used at room temperature or when trimethylsilyl iodide was used as a demethylating agent; this is most probably because partially deprotected species precipitate from the reaction mixture and thus evade further deprotection.

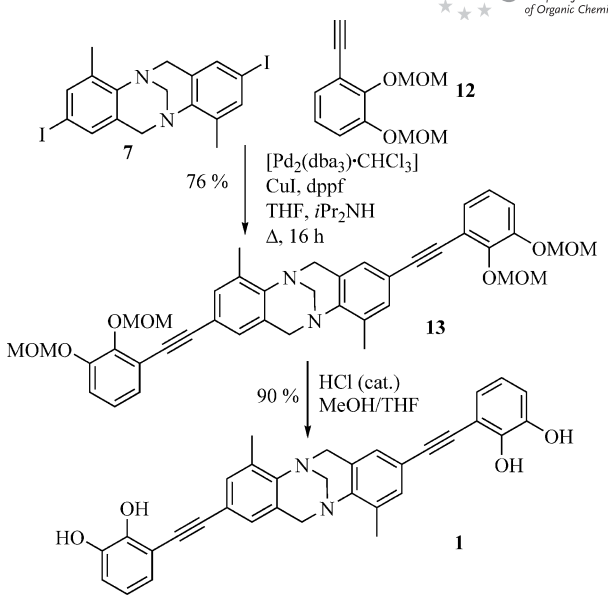
Because our initial approach did not yield desired ethynyl-bridged ligand **1** because of the problems encountered in the deprotection step of **8**, we focused on another protecting group for the OH groups of the catechol building block. During the course of our synthesis of the bis(bipyridine) ligands of BINOL,[17] we found the methoxymethyl group (MOM) to be also very useful for the protection of OH functionalities of the BINOL core. The MOM group can be cleaved easily by traces of HCl in methanol. Therefore, we synthesized MOM-protected catechol **9** by applying an adapted protocol for the introduction of the MOM groups.[36] The same reaction sequence that was used for the synthesis of the monofunctionalized veratrol derivatives including the iodination, Sonogashira cross-coupling reaction, and cleavage of the TMS functionality was then applied again and led to 1-ethynyl-2,3-bis(MOM) catechol **12** over three steps (Scheme 3).



Scheme 3. Synthesis of monofunctionalized MOM-protected catechol derivatives **10**–**12**.

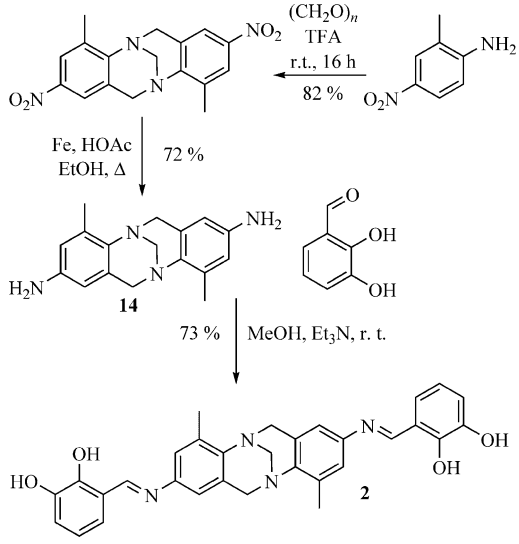
Again, a twofold Sonogashira reaction of **7** and **12** yielded MOM-protected precursor **13**, which finally could be completely deprotected without any complications to yield desired racemic ligand **1** with rigid ethynyl bridges (Scheme 4).

Next, we wanted to synthesize an additional ligand with a more flexible spacer as a linker between the core of Tröger's base and the catechol chelating units. Such a flexible spacer could be, as an example, an imine moiety, which is easily introduced by reaction of an amine and an aldehyde without any protection and deprotection steps of the OH groups. Recently we reported the synthesis of the racemic 2,8-diamino derivative of Tröger's base, **14**, through reduction of its 2,8-dinitro precursor.[27] An alternative approach to a diamino-substituted analogue of Tröger's base was reported recently by Sergeyev, and palladium-catalyzed C,N bond formation was the key step in the reaction sequence, which started from a diiodo derivative of Tröger's base.[37] However, in comparison to our approach, this sequence involves one more step and is much more expensive.



Scheme 4. Synthesis of precursor **13** and deprotection to racemic **1**.

The reaction of **14** and 2,3-dihydroxybenzaldehyde proceeded smoothly at room temperature and yielded racemic ligand **2** in 73% (Scheme 5).



Scheme 5. Synthesis of racemic ligand **2**.

With both racemic ligands **1** and **2** in hand, we then explored their ability to form dinuclear triple-stranded metallosupramolecular coordination compounds with titanium(IV) ions (Figure 3).

In earlier studies, the nature of the counterion of the base used to deprotonate the OH groups was sometimes found to be crucial for the successful formation of the helicates.[30b] Hence, racemic ligands **1** (3 equiv.) and **2** (3 equiv.), titanium(IV) oxide acetonylacetonate [TiO(acac)$_2$] (2 equiv.) as the Ti^{IV} source, and an alkali metal carbonate (2 equiv.; lithium, sodium, or potassium carbonate) were dissolved in DMF and stirred overnight. In general, in all cases a red color change of the solutions as well as for the solid com-

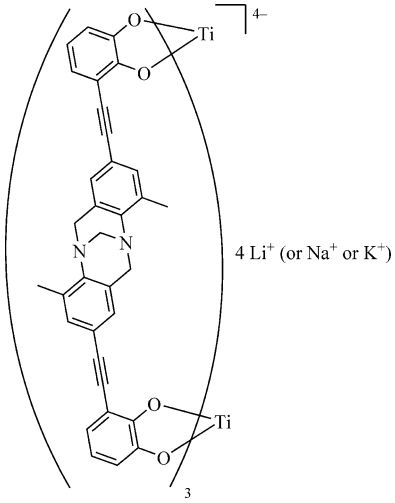


Figure 3. Schematic figure of dinuclear triple-stranded complex with Ti^{IV} derived from **1**.

plexes could be observed; a darker shade of red for the complexes with lithium as counterions and lighter shades for their sodium and potassium analogues.

Evaporation of the solvents yielded the desired complexes which were studied by ^{1}H NMR spectroscopy and ESI-mass spectrometric means. The ESI-MS spectrum of $Na_4[Ti_2(\mathbf{1})_3]$ is representatively shown in Figure 4, and it clearly shows signals of the negatively charged triple-stranded titanium(IV) complexes only and some water adducts of them (presumably coordinated to the nitrogen atoms of Tröger's base, as the first coordination sphere of the titanium is blocked and these adducts were found for the complexes of **1** and **2**) as the major peaks. These observations could be made for all six titanium(IV) complexes (containing lithium, sodium, or potassium counterions) of ligands **1** and **2**. In all cases, only signals for the expected triple-stranded helicates could be observed.

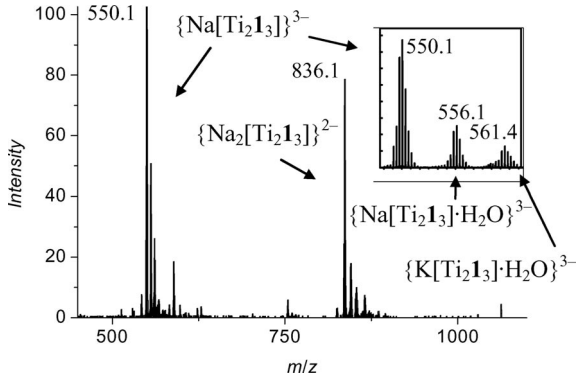


Figure 4. Negative ESI-MS of a solution of $Na_4[Ti_2(\mathbf{1})_3]$ in MeOH/DMF.

Next, we focused on the investigation of the complexation behavior by ^{1}H NMR spectroscopy to elucidate their stereochemistry. The ^{1}H NMR spectra of ligand **2** and its titanium(IV) complexes are representatively shown in Figure 5. The signals of the complexes are significantly shifted relative to those of the free ligand, which again confirms the successful formation of the titanium(IV) complexes. In addition, the proton signals of the phenolic OH groups of free **2** completely disappeared in all cases. Generally, in the spectra of $Li_4[Ti_2(\mathbf{2})_3]$, the signals are much sharper than those in the spectra of $Na_4[Ti_2(\mathbf{2})_3]$ and $K_4[Ti_2(\mathbf{2})_3]$.

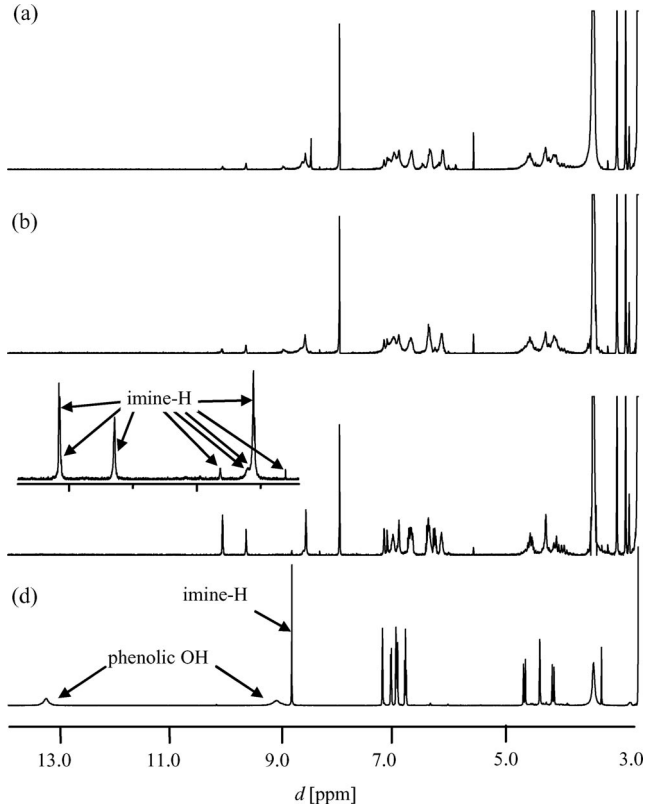


Figure 5. ^{1}H NMR spectroscopic complexation studies of **2** in [D_6]-DMSO: (a) $K_4[Ti_2(\mathbf{2})_3]$; (b) $Na_4[Ti_2(\mathbf{2})_3]$; (c) $Li_4[Ti_2(\mathbf{2})_3]$; (d) **2**.

However, a closer look at the spectra revealed that the formation of the dinuclear titanium coordination compounds is not diastereoselective in these cases. Whereas dinuclear double-stranded helicates derived from bis(bipyridine) ligands of the derivatives of Tröger's base gave rise to NMR spectra with the same number of signals as the free ligands, which is indicative of diastereoselectively formed helicates from dissymmetrical ligands that have equally configured ligands and metal centers,[17,27] the number of signals observed for the titanium complexes, however, is much higher than the number observed for the free ligand. This is best seen for the imine protons shown in the inset in Figure 5c. At least 10 different imine proton resonances − albeit in different intensities − can be distinguished. This indicates that all six possible diastereomeric homo- and heteroleptic coordination compounds − the (Δ,Δ)-, (Λ,Λ)-, and (Δ,Λ)-configured homoleptic complexes of the (5*S*,11*S*)-configured ligand as well as the (Δ,Δ)-, (Λ,Λ)-, and (Δ,Λ)-configured heteroleptic complexes containing two (5*S*,11*S*)-configured ligands and one (5*R*,11*R*)-configured ligand − are formed (together with their respective enantiomers, which of course cannot be distinguished by normal NMR spectroscopy).

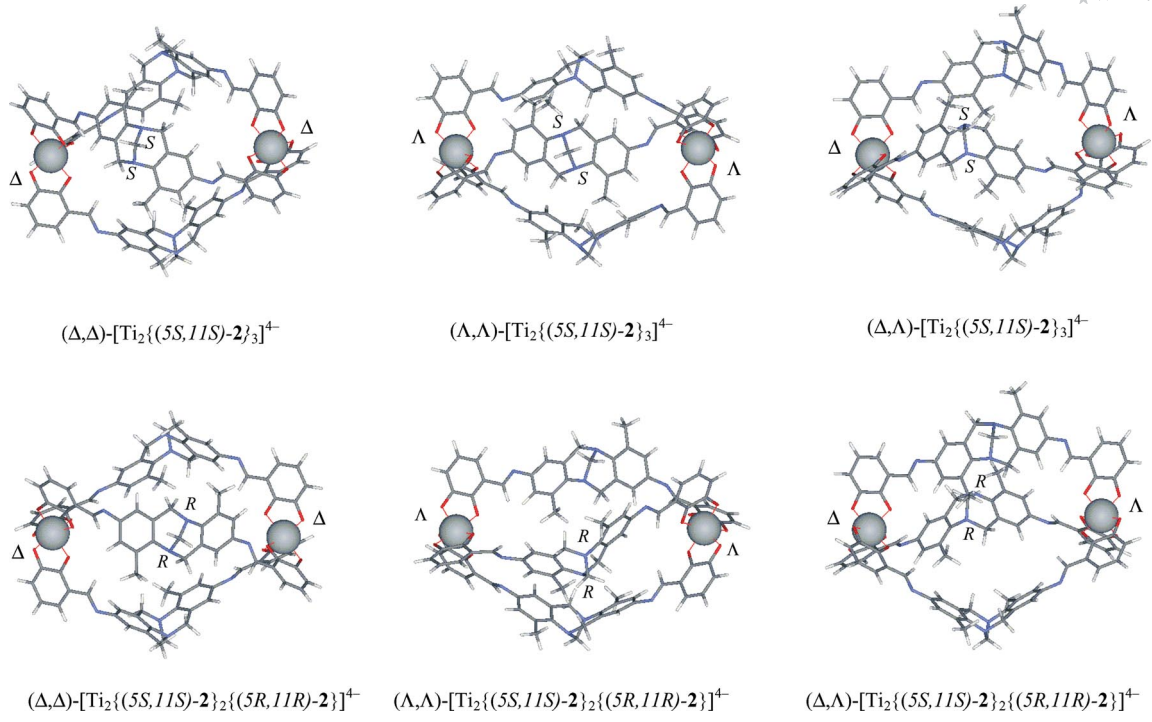


Figure 6. PM3-TM-minimized structures of diastereomeric homoleptic and heteroleptic dinuclear metal coordination compounds $[Ti_2\{\mathbf{2}\}_3]^{4-}$ formed upon self-assembly of racemic **2** and titanium(IV) ions [unlabeled ligands **2** in the structures are (5*S*,11*S*)-configured].

For these, one would expect a maximum of 12 different imine proton signals (1 + 1 + 2 + 2 + 2 + 4 = 12). Thus, the self-assembly process is clearly not diastereoselective in this case but rather leads to complex mixtures of all possible metallosupramolecular aggregates (Figure 6 shows the PM3-TM minimized structures of all six possible diastereomeric triple-stranded dinuclear titanium complexes of ligand **2**). The NMR spectroscopic interpretation of ligand **1** and its complexes indicates similar results; however, the signals were much broader than those in the spectra of the complexes of **2**.

Conclusions

We synthesized racemic bis(catechol) ligands **1** and **2**, which are derivatives of Tröger's base. These ligands undergo self-assembly to form dinuclear triple-stranded complexes of helical shape upon coordination to Ti^{IV} ions. This is only the third report of the formation of larger architectures by the self-assembly of ligands derived from Tröger's bases and transition-metal ions and the first one involving bis(catechols) as O-donor ligands. However, in contrast to similar bis(bipyridine) ligands derived from Tröger's base, the self-assembly processes of these ligands are not diastereoselective but lead to a complex mixture of all possible diastereomeric homo- and heteroleptic coordination compounds in racemic form instead. Although, this is a disappointing result, it is still very important, because it clearly demonstrates that the concept of diastereoselective self-assembly that has been well established for N-donor ligands and their coordination to late-transition-metal ions cannot simply be applied to O-donor ligands and their coordination to early-transition-metal ions like titanium(IV), at least not when 2,8-functionalized derivatives of Tröger's base are used to control the stereochemistry of the newly formed stereogenic metal centers.

Experimental Section

General Information: All reactions except the synthesis of **1** from **13** and the preparations of the Ti^{IV} complexes were performed under an argon atmosphere by using standard Schlenk techniques and oven-dried glassware prior to use. TLC was performed on aluminium TLC plates silica gel 60 F_{254} from Merck. Detection was done by UV light (254 and 366 nm). Products were purified by column chromatography on silica gel 60 (70–230 mesh) from Merck. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 500 spectrometer at 300 K, at 500.1 and 125.8 MHz, respectively, with a Bruker AM 400 at 298 K, at 400.1 and 100.6 MHz, respectively, or a Bruker Avance 300 at 298 K, at 300.1 and 75.5 MHz, respectively. ^1H NMR chemical shifts are reported on the δ scale (ppm) relative to residual nondeuterated solvent as an internal standard. ^{13}C NMR chemical shifts are reported on the δ-scale (ppm) relative to deuterated solvent as an internal standard. Signals were assigned on the basis of ^1H, ^{13}C, HMQC, and HMBC NMR experiments. Mass spectra were taken with a Finnigan MAT 212 with data system MMS-ICIS (EI, CI, isobutane, NH_3) or a Finnigan MAT 95 with data system DEC-Station 5000 (CI, isobutane or NH_3; HiRes-CI, isobutane or NH_3; FD) or an A.E.I. MS-50 (EI; HiRes-EI). ESI-MS spectra were recorded with a Bruker APEX IV FT mass spectrometer. Melting points were measured with a hot-stage microscope SM-Lux from Leitz and are not corrected. Elemental analyses were carried out with a Fisons Instrument EA1108 or a Heraeus Vario EL. Molecular modeling studies were carried out

with Spartan Pro (Wavefunction). The geometry optimizations of the anionic dinuclear metal coordination complexes were performed on a semiempirical level of theory without taking into account the counterions or the solvent (mixture). Most solvents were dried, distilled, and stored under an argon atmosphere according to standard procedures. All chemicals were used as received from commercial sources. Compound **14** was prepared according to our previously published procedure.[27] Numbering of the ^1H and ^{13}C nuclei is according to Figure 1.

Synthesis of Catechol Derivatives

1-Iodo-2,3-dimethoxybenzene (4): THF (20 mL) and veratrol (3.5 g, 3.27 mL, 25.33 mmol) were cooled to –10 °C. A solution of *n*Buli (1.6 M in *n*-hexane, 17.29 mL, 27.87 mmol, 1.78 g, 1.1 equiv.) was added at this temperature, and the resulting mixture was allowed to come to room temperature and stirred for 2 h. The solution was then cooled to –45 °C followed by the addition of a solution of iodine (7.07 g, 27.87 mmol, 1.1 equiv.) in THF (30 mL). The resulting mixture was allowed to come to room temperature and stirred for another 2 h. The solvents were evaporated and dichloromethane was added. The organic layer was washed with aqueous $NaHSO_3$ (20%), aqueous saturated $NaHCO_3$, and aqueous saturated NaCl, and the layer was then dried with Na_2SO_4. The product was purified by column chromatography on silica gel [*n*-hexane/ethyl acetate (10:1), R_f = 0.49] and isolated as a yellow oil. Yield 5.30 g (20.1 mmol, 80%). Analytical data were in accordance with those previously published.[34] However, the ^{13}C NMR spectroscopic assignments were incorrect. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, -OCH_3@C-2_{Ph}), 3.85 (s, 3 H, -OCH_3@C-3_{Ph}), 6.79 (dd, ^3J = 8.2 Hz, ^3J = 8.2 Hz, 1 H, 5-H), 6.88 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 2 H, 4-H), 7.35 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 2 H, 6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.0 (-OCH_3@C-3_{Ph}), 60.4 (-OCH_3@C-3_{Ph}), 92.5 (C-1), 112.8 (C-4), 125.8 (C-5), 130.6 (C-4), 149.0 (C-2), 152.8 (C-3) ppm.

[2-(2,3-Dimethoxyphenyl)ethynyl]trimethylsilane (5): A Schlenk flask was charged with $[Pd(PPh_3)_2Cl_2]$ (80 mg, 114×10^{-3} mmol, 1 mol-%) and CuI (65 mg, 0.34 mmol, 3 mol-%). Et_3N (3 g) **4** (30 mL 11.36 mmol), and trimethylsilylacetylene (TMSA) (1.23 g, 12.50 mmol, 1.1 equiv.) were added, and the solution was stirred at room temperature for 16 h. Saturated aqueous NaCl and CH_2Cl_2 were added, and the reaction mixture was filtered through Celite. Aqueous saturated $NaHCO_3$ was added to the filtrate, the layers were separated, and the organic layer was dried with Na_2SO_4. The product was purified by column chromatography on silica gel [*n*-hexane/ethyl acetate (10:1) + 0.5% Et_3N, R_f = 0.35] and isolated as a yellow oil. Yield: 2.5 g (10.67 mmol, 93%). Analytical data were in accordance with those previously published.[34]

1-Ethynyl-2,3-dimethoxybenzene (6): Compound **5** (1.40 g, 5.97 mmol) and KF (1.04 g, 17.91 mmol, 3 equiv.) were dissolved in MeOH (50 mL), and the resulting solution was stirred for 18 h at room temperature. Evaporation of the solvent yielded the product, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 2:1 + 0.5% Et_3N; R_f = 0.81) and isolated as a colorless oil. Yield: 965 mg (5.97 mmol, quantitative). Analytical data were in accordance with those previously published.[34]

1,2-Bis(methoxymethoxy)benzene (9): To a suspension of NaH (60% dispersion in mineral oil, 1.86 g, 1.12 g, 46.51 mmol, 2.23 equiv.) in THF (30 mL) and DMF (15 mL) was added a solution of catechol (2.29 g, 20.83 mmol) in THF (15 mL) dropwise at 0 °C. A color change from white to green was observed while stirring at room temperature for 1 h. Chloromethyl methyl ether (5 mL, 5.3 g, 65.83 mmol, 3.16 equiv.) was added to the mixture, which slowly turned yellow and was then stirred for 18 h at room temperature. It was quenched with H_2O, and the aqueous layer was extracted with ethyl acetate (4×). The combined organic layers were washed with H_2O, aqueous saturated NaCl, and dried with Na_2SO_4. The product was purified by column chromatography on silica gel [*n*-hexane/ethyl acetate (2:1) + 0.5% Et_3N, R_f = 0.68] and obtained as a colorless oil. Yield: 3.70 g (18.67 mmol, 90%). Analytical data were in accordance with those previously published.[38] However, no NMR assignments were given. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.51 (s, 6 H, -OCH_3), 5.22 (s, 4 H, -OCH_2OCH$_3$), 6.96 (dd, ^3J = 6.0 Hz, ^4J = 3.2 Hz, 2 H, 3-H, 3′-H), 7.16 (dd, ^3J = 6.0 Hz, ^4J = 3.2 Hz, 2 H, 2-H, 2′-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.1 (-OCH_3), 95.5 (-OCH_2OCH$_3$), 116.9 (C-3, C-3′), 122.6 (C-2, C-2′), 147.3 (C-1, C-1′) ppm.

1-Iodo-2,3-bis(methoxymethoxy)benzene (10): A solution of **9** (1.5 g, 7.57 mmol) in THF (10 mL) was cooled to –10 °C. A solution of *n*Buli (1.5 M in *n*-hexane, 5.52 mL, 8.32 mmol, 0.53 g, 1.1 equiv.) was added at this temperature, and the resulting mixture was allowed to come to room temperature and stirred for 2 h. The solution was then cooled to –45 °C followed by the addition of a solution of iodine (2.11 g, 8.32 mmol, 1.1 equiv.) in THF (30 mL). The resulting mixture was allowed to come to room temperature and stirred for another 2 h. The solvents were evaporated and dichloromethane was added. The organic layer was washed with aqueous $NaHSO_3$ (20%), aqueous saturated $NaHCO_3$, and aqueous saturated NaCl, and the organic layer was then dried with Na_2SO_4. The product was purified by column chromatography on silica gel [*n*-hexane/ethyl acetate (10:1), R_f = 0.49] and isolated as a yellowish oil. Yield: 1.62 g (5.00 mmol, 66%). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.50 (s, 3 H, -OCH_3@C-2_{Ph}), 3.68 (s, 3 H, -OCH_3@C-3_{Ph}), 5.18 (s, 2 H, -OCH_2OCH$_3$@C-2_{Ph}), 5.19 (s, 2 H, -OCH_2-OCH$_3$@C-3_{Ph}), 6.78 (dd, ^3J = 8.2 Hz, ^3J = 8.2 Hz, 1 H, 5-H), 7.12 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1 H, 4-H), 7.44 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.3 (-OCH_3@C-2_{Ph}), 58.4 (-OCH_3@C-3_{Ph}), 92.7 (C-1), 95.3 (-OCH_2-OCH$_3$@C-2_{Ph}), 98.9 (-OCH_2OCH$_3$@C-3_{Ph}), 117.0 (C-4), 126.0 (C-5), 132.5 (C-6), 146.7 (C-2) ppm. 150.0 (C-3). MS (EI): *m*/*z* (%) = 324.0 (100) $[C_{10}H_{13}IO_4]^+$. $C_{10}H_{13}IO_4$(324.11)·1/9THF: calcd. C 37.77, H 4.22; found C 38.11, H 4.04. HRMS (EI): calcd. for $C_{10}H_{13}IO_4$ 323.9859; found 323.9852.

{2-[2,3-Bis(methoxymethoxy)phenyl]ethynyl}trimethylsilane (11): A Schlenk flask was charged with $[Pd(PPh_3)_2Cl_2]$ (46 mg, 64.8×10^{-3} mmol, 3 mol-%) and CuI (8.2 mg, 43.2×10^{-3} mmol, 2 mol-%). Et_3N (15 mL), **10** (700 mg, 2.16 mmol), and TMSA (254.6 mg, 2.59 mmol, 1.2 equiv.) were added, and the solution was stirred at room temperature for 16 h. Saturated aqueous NaCl and CH_2Cl_2 were added, and the reaction mixture was filtered through Celite. Aqueous saturated $NaHCO_3$ was added to the filtrate, the layers were separated, and the organic layer was dried with Na_2SO_4. The product was purified by column chromatography on silica gel [*n*-hexane/ethyl acetate (4:1) + 0.5% Et_3N, R_f = 0.45] and isolated as a yellow oil. Yield: 470 mg (1.60 mmol, 74%). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.24 [s, 9 H, -Si(CH_3)$_3$], 3.49 (s, 3 H, -OCH_3@C-3_{Ph}), 3.66 (s, 3 H, -OCH_3@C-2_{Ph}), 5.18 (s, 2 H, -OCH_2-OCH$_3$@C-3_{Ph}), 5.25 (s, 2 H, -OCH_2OCH$_3$@C-2_{Ph}), 6.96 (dd, ^3J = 8.2 Hz, ^3J = 8.2 Hz, 1 H, 5-H), 7.11 (d, ^3J = 8.2 Hz, 2 H, 4-H, 6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = –0.1 [Si(CH_3)$_3$], 56.2 (-OCH_3@C-3_{Ph}), 57.4 (-OCH_3@C-2_{Ph}), 95.3 (-OCH_2OCH$_3$@C-3_{Ph}), 98.6 (C≡C TMS), 98.7 (-OCH_2OCH$_3$@C-2_{Ph}), 101.3 (C≡CTMS), 117.6 (C-6), 118.5 (C-1), 124.1 (C-5) 127.2 (C-4), 148.3 (C-2), 150.1 (C-3) ppm. MS (EI): *m*/*z* (%) = 294.1 (100) $[C_{15}H_{22}O_4Si]^+$. HRMS (EI): calcd. for $C_{15}H_{22}O_4Si$ 294.1287; found 294.1291.

1-Ethynyl-2,3-bis(methoxymethoxy)benzene (12): Compound **11** (400 mg, 1.36 mmol) and KF (158 mg, 2.70 mmol, 2 equiv.) were dissolved in MeOH (30 mL), and the resulting solution was stirred for 18 h at room temperature. Evaporation of the solvent yielded the product, which was purified by column chromatography on silica gel [*n*-nexane/ethyl acetate (4:1) + 0.5% Et_3N, R_f = 0.29] and isolated as a colorless oil. Yield: 281 mg (1.26 mmol, 93%). ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.26 (s, 1 H, C≡C*H*), 3.50 (s, 3 H, -OCH_3@C-3_{Ph}), 3.65 (s, 3 H, -OCH_3@C-2_{Ph}), 5.19 (s, 2 H, -OCH_2OCH$_3$@C-3_{Ph}), 5.26 (s, 2 H, -OCH_2OCH$_3$@C-2_{Ph}), 6.99 (dd, ^3J = 7.7 Hz, ^3J = 8.2 Hz, 1 H, 5-H), 7.13–7.16 (m, 2 H, 4-H, 6-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 56.2 (-OCH_3@C-3_{Ph}), 57.5 (-OCH_3@C-2_{Ph}), 80.0 (*C*≡CH), 81.2 (C≡*C*H), 95.3 (-OCH_2OCH$_3$@C-3_{Ph}), 98.8 (-OCH_2OCH$_3$@C-2_{Ph}), 117.6 (C-1), 117.8 (C-4), 124.2 (C-5), 127.2 (C-6), 148.4 (C-2), 150.2 (C-3) ppm. MS (EI): *m*/*z* (%) = 222.1 (100) $[C_{12}H_{14}O_4]^+$. $C_{12}H_{14}O_4$ (222.24)·1/3CH_2Cl_2: calcd. C 59.12, H 5.90; found C 58.78, H 5.88. HRMS (EI): calcd. for $C_{12}H_{14}O_4$ 222.0892; found 222.0887.

Synthesis of the Derivatives of Tröger's Base

2,8-Diiodo-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzodiazocine (7): 4-Iodo-2-methylaniline (7.5 g, 32.02 mmol) and paraformaldehyde (2.02 g, 67.25 mmol, 2.1 equiv.) were dissolved in trifluoroacetic acid (64 mL, 0.80 mol, 26 equiv.), which resulted in a dark-purple-colored reaction mixture. The mixture was stirred for 16 h and poured into H_2O (200 mL) to yield a brown precipitate. Aqueous NaOH (6 N) was added to this suspension (pH 9), the precipitate was filtered off, and recrystallized from acetone, and the solution was stored at –20 °C for 12 h. A first product fraction was obtained by collecting the precipitate. A second crop could be isolated by concentrating the mother liquor and purification of the crude product by column chromatography on silica gel (toluene + 0.5% Et_3N, R_f = 0.25). Yield: 6.03 g (12.01 mmol, 75%; 55% after recrystallization and the remaining 20% by column chromatography). Analytical data were in accordance with those previously published.[25]

2,8-Bis(2,3-dimethoxybenzene-1-ylethynyl)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzodiazocine (8): THF (10 mL) and diisopropylamine (145 mg, 1.43 mmol, 2.4 equiv.) were added to a mixture of **7** (300 mg, 0.70 mmol), CuI (4.6 mg, 24×10^{-3} mmol, 4 mol-%), $[Pd_2(dba)_3{\cdot}CHCl_3]$ (19 mg, 36×10^{-3} mmol, 6 mol-% Pd), dppf (20 mg, 36×10^{-3} mmol, 6 mol-%), and **6** (214 mg, 1.31 mmol, 2.2 equiv.). The resulting mixture was stirred at 60 °C for 18 h. Saturated aqueous NaCl and dichloromethane were added, and the mixture was filtered through Celite. The residue was washed with dichloromethane. The filtrate was washed with saturated aqueous $NaHCO_3$, and the organic layer was dried with Na_2SO_4. The product was purified by column chromatography on silica gel [toluene/THF (9:1) + 5% Et_3N, R_f = 0.50] and obtained as a colorless solid. Yield: 260 mg (0.46 mmol, 75%). M.p. 179–181 °C. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 2.42 (s, 6 H, -CH_3), 3.86 (s, 6 H, -OCH_3@C-3_{Ph}), 3.95 (s, 6 H, -OCH_3@C-2_{Ph}), 4.02 (d, ^2J = –17.0 Hz, 2 H, 6_{endo}-H, 12_{endo}-H), 4.37 (s, 2 H, 13-H), 4.62 (d, ^2J = –17.0 Hz, 2 H, 6_{exo}-H, 12_{exo}-H), 6.88 (s, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 2 H, 4_{Ph}-H,$4'_{Ph}$-H), 6.97–7.00 (m, 4 H, 1-H, 7-H, 5_{Ph}-H, $5'_{Ph}$-H), 7.03 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 2 H, 6_{Ph}-H, $6'_{Ph}$-H), 7.26 (s, 2 H, 3-H, 9-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 17.0 (-*C*H$_3$), 54.8 (C-6, C-12), 56.0 (-O*C*H$_3$@C-3_{Ph}), 61.0 (-O*C*H$_3$@C-2_{Ph}), 67.6 (C-13), 84.8 (C≡*C*-Ph), 93.2 (*C*≡C-Ph), 112.8 (C-4_{Ph}, C-$4'_{Ph}$), 118.1 (C-1_{Ph}, C-$1'_{Ph}$), 118.7 (C-2, C-8), 123.8 (C-5_{Ph}, C-$5'_{Ph}$), 125.0 (C-6_{Ph}, C-$6'_{Ph}$), 127.8 (C-1, C-7), 128.0 (C-14, C-16), 132.1 (C-3, C-9), 133.0 (C-4, C-10), 146.2 (C-15, C-17), 150.3 (C-3_{Ph}, C-$3'_{Ph}$), 152.7 (C-2_{Ph}, C-$2'_{Ph}$) ppm. MS (EI): *m*/*z* (%) = 570.3 (100) $[C_{37}H_{34}N_2O_4]^+$. $C_{37}H_{34}N_2O_4$ (570.68)·1/4toluene: calcd. C 78.39, H 6.11, N 4.72; found C 78.40, H 6.19, N 4.81. HRMS (EI): calcd. for $C_{37}H_{34}N_2O_4$ 570.2519; found 570.2521.

2,8-Bis[2,3-bis(methoxymethoxy)benzene-1-ylethynyl]-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzodiazocine (13): THF (7 mL) and diisopropylamine (85 mg, 0.84 mmol, 3 equiv.) were added to **7** (141 mg, 0.28 mmol), CuI (2 mg, 11×10^{-3} mmol, 4 mol-%), $[Pd_2(dba)_3{\cdot}CHCl_3]$ (9 mg, 17×10^{-3} mmol, 6 mol-% Pd), dppf (9.3 mg, 17×10^{-3} mmol, 6 mol-%), and **12** (150 mg, 0.67 mmol, 2.4 equiv.). The resulting mixture was stirred at 60 °C for 16 h. Saturated aqueous NaCl and dichloromethane were added, and the mixture was filtered through Celite. The residue was washed with dichloromethane. The filtrate was washed with saturated aqueous $NaHCO_3$, and the organic layer was dried with Na_2SO_4. The product was purified by column chromatography on silica gel [toluene/THF (9:1) + 5% Et_3N, R_f = 0.56] and obtained as a yellow solid. Yield: 148 mg (0.21 mmol, 76%). M.p. 202–204 °C. ^1H NMR (500.1 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, -CH_3), 3.50 (s, 6 H, -OCH_3@C-3_{Ph}), 3.65 (s, 6 H, -OCH_3@C-2_{Ph}), 3.98 (d, ^2J = –17.0 Hz, 2 H, 6_{endo}-H, 12_{endo}-H), 4.02 (s, 2 H, 13-H), 4.58 (d, ^2J = –17.0 Hz, 2 H, 6_{exo}-H, 12_{exo}-H), 5.20 (s, 4 H, -OCH_2OCH$_3$@C-3_{Ph}), 5.27 (s, 4 H, -OCH_2OCH$_3$@C-2_{Ph}), 6.97 (s, 2 H, 1-H, 7-H), 6.99 (d, ^3J = 7.7 Hz, 2 H, 5_{Ph}-H, $5'_{Ph}$-H), 7.11 (dd, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 4 H, 4_{Ph}-H, $4'_{Ph}$-H, 6_{Ph}-H, $6'_{Ph}$-H), 7.23 (s, 2 H, 3-H, 9-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 17.0 (-*C*H$_3$), 54.8 (C-6, C-12), 56.2 (-O*C*H$_3$@C-3_{Ph}), 57.5 (-O*C*H$_3$@C-2_{Ph}), 67.4 (C-13), 85.0 (C≡*C*-Ph), 93.3 (*C*≡C-Ph), 95.3 (-O*C*H$_2$OCH$_3$@C-3_{Ph}), 98.7 (-O*C*H$_2$OCH$_3$@C-2_{Ph}), 117.1 (C-6_{Ph}, C-$6'_{Ph}$), 118.5 (C-2, C-8), 118.8 (C-1_{Ph}, C-$1'_{Ph}$), 124.2 (C-5_{Ph}, C-$5'_{Ph}$), 126.7 (C-4_{Ph}, C-$4'_{Ph}$), 127.6 (C-1, C-7), 128.1 (C-14, C-16), 132.1 (C-3, C-9), 133.1 (C-4, C-10), 146.4 (C-15, C-17), 147.7 (C-2_{Ph}, C-$2'_{Ph}$), 150.2 (C-3_{Ph}, C-3_{Ph}) ppm. MS (EI): *m*/*z* (%) = 690.3 (100) $[C_{41}H_{42}N_2O_8]^+$. $C_{41}H_{42}N_2O_8$ (690.78)·H_2O: calcd. C 69.48, H 6.26, N 3.95; found C 69.42, H 6.20, N 3.93. HRMS (EI): calcd. for $C_{41}H_{42}N_2O_8$ 690.2941; found 690.2937.

2,8-Bis(2,3-dihydroxybenzene-1-ylethynyl)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzodiazocine (1): Compound **13** (340 mg, 0.49 mmol) was dissolved in MeOH (10 mL) and THF (10 mL). Concentrated hydrochloric acid (2 mL) was added to this solution, which was then stirred for 24 h at room temperature. The solvents were evaporated, and the crude product was dissolved in ethyl acetate. After the addition of H_2O, the layers were separated, and the aqueous phase was extracted with ethyl acetate (3×). The combined organic layers were dried with Na_2SO_4, and the product was dried in vacuo. Yield: 226 mg (0.44 mmol, 90%). M.p. >250 °C. ^1H NMR (500.1 MHz, [D$_6$]DMSO): δ = 2.38 (s, 6 H, -CH_3), 4.12 (d, ^2J = –17.0 Hz, 2 H, 6_{endo}-H, 12_{endo}-H), 4.38 (s, 2 H, 13-H), 4.57 (d, ^2J = –17.0 Hz, 2 H, 6_{exo}-H, 12_{exo}-H), 6.60 (dd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, 2 H, 5_{Ph}-H, $5'_{Ph}$-H), 6.77–6.78 (m, 4 H, 4_{Ph}-H, $4'_{Ph}$-H, 6_{Ph}-H, $6'_{Ph}$-H), 7.05 (s, 2 H, 1-H, 7-H), 7.24 (s, 2 H, 3-H, 9-H), 8.85 (br. s, 2 H, O*H*), 9.46 (br. s, 2 H, O*H*) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 16.6 (-*C*H$_3$), 54.0 (C-6, C-12), 67.0 (C-13), 86.1 (C≡*C*-Ph), 92.2 (*C*≡C-Ph), 110.4 (C-1_{Ph}, C-$1'_{Ph}$), 115.9 (C-4_{Ph}, C-$4'_{Ph}$), 118.4 (C-2, C-8), 119.2 (C-5_{Ph}, C-$5'_{Ph}$), 122.9 (C-6_{Ph}, C-$6'_{Ph}$), 127.6 (C-1, C-7), 128.3 (C-14, C-16), 131.5 (C-3, C-9), 132.9 (C-4, C-10), 144.9 (C-15, C-17), 145.5 (C-3_{Ph}, C-$3'_{Ph}$), 152.7 (C-2_{Ph}, C-$2'_{Ph}$) ppm. MS (EI): *m*/*z* (%) = 514.2 (100) $[C_{33}H_{26}N_2O_4]^+$. $C_{33}H_{26}N_2O_4$ (514.57)·7/2H_2O: calcd. C 68.62, H 5.76, N 4.85; found C 68.49, H 5.56, N 4.50. HRMS (EI): calcd. for $C_{33}H_{26}N_2O_4$ 514.1892; found 514.1894.

2,8-Bis(2,3-dihydroxybenzenemethanimine)-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzodiazocine (2): Compound **14** (250 mg,

0.89 mmol) was dissolved in MeOH (20 mL) and Et_3N (2 mL). 2,3-Dihydroxybenzaldehyde (246 mg, 1.78 mmol, 2 equiv.) was added, and the resulting yellowish solution was stirred at room temperature for 20 h. After a short time an intensively orange solid began to precipitate. The precipitate was filtered off, washed with small amounts of cold MeOH, and dried in vacuo. Yield: 338 mg (0.65 mmol, 73%). M.p. >250 °C. ^{1}H NMR (500.1 MHz, [D$_6$]-DMSO): δ = 2.42 (s, 6 H, -CH_3), 4.06 (d, ^2J = –17.0 Hz, 2 H, 6$_{endo}$-H, 12$_{endo}$-H), 4.30 (s, 2 H, 13-H), 4.58 (d, ^2J = –17.0 Hz, 2 H, 6$_{exo}$-H, 12$_{exo}$-H), 6.75 (dd, ^3J = 8.7 Hz, ^3J = 7.2 Hz, 2 H, 5$_{Ph}$-H, 5′$_{Ph}$-H), 6.90 (d, ^3J = 8.7 Hz, 4 H, 4$_{Ph}$-H, 4′$_{Ph}$-H), 6.93 (s, 2 H, 1-H, 7-H), 7.01 (d, 2 H, 6$_{Ph}$-H, 6′$_{Ph}$-H), 7.17 (s, 2 H, 3-H, 9-H), 8.62 (s, 2 H, -N=CH) 9.11 (br. s, 2 H, OH@C-3$_{Ph}$), 13.30 (br. s, 2 H, OH@C-2$_{Ph}$) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 16.8 (-CH$_3$), 54.5 (C-6, C-12), 67.0 (C-13), 117.2 (C-1, C-7), 118.6 (C-1$_{Ph}$, C-1′$_{Ph}$, C-5$_{Ph}$, C-5′$_{Ph}$), 119.3 (C-4$_{Ph}$, C-4′$_{Ph}$), 121.5 (C-3, C-9), 122.5 (C-6$_{Ph}$, C-6′$_{Ph}$), 129.1 (C-14, C-16), 133.5 (C-4, C-10), 142.8 (C-2, C-8), 144.8 (C-15, C-17), 145.5 (C-3$_{Ph}$, C-3′$_{Ph}$), 149.3 (C-2$_{Ph}$, C-2′$_{Ph}$), 162.4 (C=N) ppm. MS (EI): m/z (%) = 520.3 (100) [$C_{31}H_{28}N_4O_4$]$^+$, 520.3 (100) [$C_{31}H_{28}N_4O_4$]$^+$, 520.3 (100) [$C_{31}H_{28}N_4O_4$]$^+$. $C_{31}H_{28}N_4O_4$ (520.58)·3/4H_2O: calcd. C 69.71, H 5.57, N 10.49; found C 69.78, H 5.79, N 10.51. HRMS (EI): calcd. for $C_{31}H_{28}N_4O_4$ 520.2111; found 520.2111.

Preparation of the Titanium(IV) Complexes

Either **1** or **2** (3 equiv.), titanium(IV) oxide acteylacteonate {[TiO(acac)$_2$]} (2 equiv.), and Li_2CO_3 (or Na_2CO_3 or K_2CO_3, 3 equiv.) were dissolved in DMF, and the resulting mixture was stirred at room temperature for 16 h. An immediate color change to dark red was observed upon the addition of DMF. The solvents were evaporated and the remaining solid dried in vacuo.

Li$_4$[Ti$_2$(1)$_3$]: Compound **1** (40 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and Li_2CO_3 (3.8 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 542.5 (70) {H[Ti$_2$**1**$_3$]}$^{3-}$, 544.8 (100) {Li[Ti$_2$**1**$_3$]}$^{3-}$, 817.7 (30) {H$_1$Li$_1$[Ti$_2$**1**$_3$]}$^{2-}$, 820.7 (100) {Li$_2$[Ti$_2$**1**$_3$]}$^{2-}$. $C_{99}H_{66}Li_4N_6O_{12}Ti_2$ (1655.11)·6DMF·13H_2O: calcd. C 60.37, H 5.80, N 7.22; found C 60.16, H 5.70, N 7.11.

Na$_4$[Ti$_2$(1)$_3$]: Compound **1** (40 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and Na_2CO_3 (5.5 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 542.5 (5) {H[Ti$_2$**1**$_3$]}$^{3-}$, 550.1 (100) {Na[Ti$_2$**1**$_3$]}$^{3-}$, 556.1 (30) [{Na[Ti$_2$**1**$_3$]·H_2O}$^{3-}$ and some {K[Ti$_2$**1**$_3$]}$^{3-}$], 561.4 (15) {K[Ti$_2$**1**$_3$]·H_2O}$^{3-}$, 836.7 (50) {Na$_2$[Ti$_2$**1**$_3$]}$^{2-}$, 845.2 (15) {Na$_2$[Ti$_2$**1**$_3$]·H_2O}$^{2-}$, 853.6 (5) [{Na$_1$K$_1$[Ti$_2$**1**$_3$]·H_2O}$^{2-}$ and some {K$_2$[Ti$_2$**1**$_3$]}$^{2-}$]. $C_{99}H_{66}Na_4N_6O_{12}Ti_2$ (1719.31)·4DMF·15H_2O: calcd. C 58.42, H 5.48, N 6.14; found C 57.90, H 5.14, N 6.23.

K$_4$[Ti$_2$(1)$_3$]: Compound **1** (40 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and K_2CO_3 (7.2 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 542.5 (5) {H[Ti$_2$**1**$_3$]}$^{3-}$, 555.5 (100) {K[Ti$_2$**1**$_3$]}$^{3-}$, 561.5 (30) {K[Ti$_2$**1**$_3$]·H_2O}$^{3-}$, 833.7 (30) {H$_1$K$_1$[Ti$_2$**1**$_3$]}$^{2-}$, 844.2 (15) {Na$_1$K$_1$[Ti$_2$**1**$_3$]}$^{2-}$, 852.7 (100) {K$_2$[Ti$_2$**1**$_3$]}$^{2-}$, 861.7 (10) {K$_2$[Ti$_2$**1**$_3$]·H_2O}$^{2-}$. $C_{99}H_{66}K_4N_6O_{12}Ti_2$ (1783.74)·3DMF·12H_2O: calcd. C 58.45, H 5.04, N 5.68; found C 58.37, H 5.01, N 5.63.

Li$_4$[Ti$_2$(2)$_3$]: Compound **1** (40.5 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and Li_2CO_3 (3.8 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 824.2 (20) {H$_2$[Ti$_2$**2**$_3$]}$^{2-}$, 827.2 (30) {H$_1$Li$_1$[Ti$_2$**2**$_3$]}$^{2-}$, 829.2 (80) {Li$_2$[Ti$_2$**2**$_3$]}$^{2-}$, 838.2 (100) {Li$_2$[Ti$_2$**2**$_3$]·H_2O}$^{2-}$, 845.7 (70) {Na$_2$[Ti$_2$**2**$_3$]}$^{2-}$, 854.7 (30) {Na$_2$[Ti$_2$**2**$_3$]·H_2O}$^{2-}$. $C_{93}H_{72}Li_4N_{12}O_{12}Ti_2$ (1673.14)·5DMF·13H_2O: calcd. C 57.07, H 5.90, N 10.48; found C 56.67, H 5.65, N 10.41.

Na$_4$[Ti$_2$(2)$_3$]: Compound **1** (40.5 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and Na_2CO_3 (5.5 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 834.7 (20) {H$_1$Na$_1$[Ti$_2$**2**$_3$]}$^{2-}$, 845.7 (100) {Na$_2$[Ti$_2$**2**$_3$]}$^{2-}$, 854.7 (40) {Na$_2$[Ti$_2$**2**$_3$]·H_2O}$^{2-}$. $C_{93}H_{72}N_{12}Na_4O_{12}Ti_2$ (1737.33)·5DMF·10H_2O: calcd. C 56.82, H 5.61, N 10.43; found C 56.27, H 5.52, N 10.47.

K$_4$[Ti$_2$(2)$_3$]: Compound **1** (40.5 mg, 77.73 mmol, 3 equiv.), [TiO(acac)$_2$] (13.6 mg, 51.82 mmol, 2 equiv.), and K_2CO_3 (7.2 mg, 51.82 mmol, 2 equiv.) were used as described above. Yield: quantitative. MS (ESI): m/z (%) = 824.2 (100) {H$_2$[Ti$_2$**2**$_3$]}$^{2-}$, 834.7 (10) {H$_1$Na$_1$[Ti$_2$**2**$_3$]}$^{2-}$, 842.2 (60) {H$_1$K$_1$[Ti$_2$**2**$_3$]}$^{2-}$, 853.7 (10) {Na$_2$[Ti$_2$**2**$_3$]·H_2O}$^{2-}$, 861.7 (25) {K$_2$[Ti$_2$**2**$_3$]}$^{2-}$. $C_{93}H_{72}K_4N_{12}O_{12}Ti_2$ (1801.77)·2DMF·13H_2O: calcd. C 54.49, H 5.17, N 8.99; found C 54.65, H 5.28, N 8.91.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG SPP 1118 and SFB 624) is gratefully acknowledged. T. Weilandt is thanked for performing the ESI-MS experiments of the complexes.

[1] A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, **1995**.
[2] a) E. C. Constable, *Tetrahedron* **1992**, *48*, 10013–10059; b) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; c) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–287; d) A. von Zelewsky, *Coord. Chem. Rev.* **1999**, *190–192*, 811–825; e) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; f) A. von Zelewsky, O. Mamula, *J. Chem. Soc. Dalton Trans.* **2000**, 219–231; g) M. Albrecht, *Chem. Eur. J.* **2000**, *6*, 3485–3489; h) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; i) O. Mamula, A. von Zelewsky, *Coord. Chem. Rev.* **2003**, *242*, 87–95.
[3] W. Zarges, J. Hall, J. M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991**, *74*, 1843–1852.
[4] a) N. C. Fletcher, F. R. Keene, H. Viebrock, A. von Zelewsky, *Inorg. Chem.* **1997**, *36*, 1113–1121; b) O. Mamula, A. von Zelewsky, G. Bernardinelli, *Angew. Chem.* **1998**, *110*, 302–305; *Angew. Chem. Int. Ed.* **1998**, *37*, 289–293; c) H. Murner, A. von Zelewesky, G. Hopfgartner, *Inorg. Chim. Acta* **1998**, *271*, 36–39; d) O. Mamula, A. von Zelewsky, T. Bark, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 3129–3133; *Angew. Chem. Int. Ed.* **1999**, *38*, 2945–2948; e) O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. von Zelewsky, *Chem. Eur. J.* **2001**, *7*, 533–539; f) O. Mamula, A. von Zelewsky, P. Brodard, C.-W. Schläpfer, G. Bernardinelli, H. Stoeckli-Evans, *Chem. Eur. J.* **2005**, *11*, 3049–3057.
[5] a) C. R. Woods, M. Benaglia, F. Cozzi, J. S. Siegel, *Angew. Chem.* **1996**, *108*, 1977–1980; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1830–1833; b) R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, C. R. Woods, J. S. Siegel, *Eur. J. Org. Chem.* **2001**, 173–180.
[6] G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Commun.* **1999**, 195–196.
[7] a) R. Prabaharan, N. C. Fletcher, M. Nieuwenhuyzen, *J. Chem. Soc. Dalton Trans.* **2002**, 602–608; b) R. Prabaharan, N. C. Fletcher, *Inorg. Chim. Acta* **2003**, *355*, 449–453.
[8] a) E. C. Constable, T. Kulke, M. Neuburger, M. Zehnder, *Chem. Commun.* **1997**, 489–490; b) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Commun.* **1998**, 2659–2660; c) G. Baum, E. C. Constable, D. Fenske, E. Hou-

secroft, T. Kulke, M. Neuburger, M. Zehnder, *J. Chem. Soc. Dalton Trans.* **2000**, 945–959.
[9] a) G. Baum, E. C. Constable, D. Fenske, T. Kulke, *Chem. Commun.* **1997**, 2043–2044; b) E. C. Constable, T. Kulke, G. Baum, D. Fenske, *Inorg. Chem. Commun.* **1998**, *1*, 80–82; c) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862–1873.
[10] C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J.* **1999**, *5*, 3487–3494.
[11] F. G. Gelalcha, M. Schulz, R. Kluge, J. Sieler, *J. Chem. Soc. Dalton Trans.* **2002**, 2517–2521.
[12] G. C. van Stein, G. van Koten, K. Vrieze, C. Brevard, A. L. Spek, *J. Am. Chem. Soc.* **1984**, *106*, 4486–4492.
[13] M. A. Masood, E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 973–977; *Angew. Chem. Int. Ed.* **1998**, *37*, 928–932.
[14] V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, E. Roboli, M. Zema, *Inorg. Chem.* **2000**, *39*, 5803–5806.
[15] J. Hamblin, L. J. Childs, N. W. Alcock, M. J. Hannon, *J. Chem. Soc. Dalton Trans.* **2002**, 164–169.
[16] a) A. L. Airey, G. F. Swiegers, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1997**, *36*, 1588–1597; b) V. C. Cook, A. C. Willis, J. Zank, S. B. Wild, *Inorg. Chem.* **2002**, *41*, 1897–1906; c) P. K. Bowyer, V. C. Cook, N. Gharib-Naseri, P. A. Gugger, A. D. Rae, G. F. Swiegers, A. C. Willis, J. Zank, S. B. Wild, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4877–4882.
[17] a) A. Lützen, M. Hapke, J. Griep-Raming, D. Haase, W. Saak, *Angew. Chem.* **2002**, *114*, 2190–2194; *Angew. Chem. Int. Ed.* **2002**, *41*, 2086–2089; b) C. A. Schalley, A. Lützen, M. Albrecht, *Chem. Eur. J.* **2004**, *10*, 1072–1080.
[18] J. Tröger, *J. Prakt. Chem.* **1887**, *36*, 225.
[19] M. Valik, R. M. Strongin, V. Kral, *Supramol. Chem.* **2005**, *17*, 347–367.
[20] a) M. D. Cowart, I. Sucholeiki, R. R. Bukownik, C. S. Wilcox, *J. Am. Chem. Soc.* **1988**, *110*, 6204–6210; b) T. H. Webb, H. Suh, C. S. Wilcox, *J. Am. Chem. Soc.* **1991**, *113*, 8554–8555.
[21] a) J. C. Adrian Jr, C. S. Wilcox, *J. Am. Chem. Soc.* **1989**, *111*, 8055–8057; b) J. C. Adrian Jr, C. S. Wilcox, *J. Am. Chem. Soc.* **1991**, *113*, 678–680; c) J. C. Adrian Jr, C. S. Wilcox, *J. Am. Chem. Soc.* **1992**, *114*, 1398–1403.
[22] a) S. Goswami, K. Ghosh, *Tetrahedron Lett.* **1997**, *38*, 4503–4506; b) S. Goswami, K. Ghosh, S. Dasgupta, *J. Org. Chem.* **2000**, *65*, 1907–1914.
[23] Y.-M. Shen, M.-X. Zhao, J. Xu, Y. Shi, *Angew. Chem.* **2006**, *118*, 8173–8176; *Angew. Chem. Int. Ed.* **2006**, *45*, 8005–8008.
[24] S. P. Bew, L. Legentil, V. Scholier, S. V. Sharma, *Chem. Commun.* **2007**, 389–391.
[25] J. Jensen, K. Wärnmark, *Synthesis* **2001**, 1873–1877.
[26] a) U. Kiehne, A. Lützen, *Synthesis* **2004**, 1687–1695; b) C. Solano, D. Svensson, Z. Olomi, J. Jensen, O. F. Wendt, K. Wärnmark, *Eur. J. Org. Chem.* **2005**, 3510–3517; c) F. Hof, M. Schar, D. M. Scofield, F. Fischer, F. Diederich, S. Sergeyev, *Helv. Chim. Acta* **2005**, *88*, 2333–2344.
[27] U. Kiehne, T. Weilandt, A. Lützen, *Org. Lett.* **2007**, *9*, 1283–1286.
[28] M. S. Khoshbin, M. V. Ovchinnikov, C. A. Mirkin, J. A. Golen, A. L. Rheingold, *Inorg. Chem.* **2006**, *45*, 2603–2609.
[29] a) R. C. Scarrow, D. L. White, K. N. Raymond, *J. Am. Chem. Soc.* **1985**, *107*, 6540–6546; b) Z. Hou, C. J. Sunderland, T. Nishio, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 5148–5149; c) B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 7221–7222.
[30] a) M. Albrecht, I. Janser, H. Houjou, R. Froehlich, *Chem. Eur. J.* **2004**, *10*, 2839–2850; b) M. Albrecht, I. Janser, S. Kamptmann, P. Weis, B. Wibbeling, R. Froehlich, *Dalton Trans.* **2004**, 37–43; c) M. Albrecht, I. Janser, J. Fleischhauer, Y. Wang, G. Raabe, R. Fröhlich, *Mendeleev Commun.* **2004**, 250–253; d) M. Albrecht, I. Janser, A. Lützen, M. Hapke, R. Froehlich, P. Weis, *Chem. Eur. J.* **2005**, *11*, 5742–5748.
[31] a) F. E. Hahn, C. S. Isfort, T. Pape, *Angew. Chem.* **2004**, *116*, 4911–4915; *Angew. Chem. Int. Ed.* **2004**, *43*, 4807–4810; b) C. S. Isfort, T. Kreickmann, T. Pape, R. Froehlich, F. E. Hahn, *Chem. Eur. J.* **2007**, *13*, 2344–2357.
[32] M. Albrecht, *Synlett* **1996**, 565–567.
[33] a) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1995**, *107*, 1082–1084; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996–998; b) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1998**, *110*, 977–981; *Angew. Chem. Int. Ed.* **1998**, *37*, 932–935.
[34] M. Essamkaoui, J. Mayrargue, J. M. Vierfond, A. Reynet, H. Moskowitz, C. Thal, *Synth. Commun.* **1992**, *22*, 2723–2728.
[35] M. Albrecht, *Synthesis* **1996**, 230–236.
[36] X.-W. Yang, J.-H. Sheng, C.-S. Da, H.-S. Wang, W. Su, R. Wang, A. S. C. Chan, *J. Org. Chem.* **2000**, *65*, 295–296.
[37] D. Didier, S. Sergeyev, *Tetrahedron* **2007**, *63*, 3864–3869.
[38] R. Stern, J. English Jr, H. G. Cassidy, *J. Am. Chem. Soc.* **1957**, *79*, 5792–5797.

Received: July 4, 2007
Published Online: October 1, 2007

