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Helical Sense Bias Induced by Point Chirality in Cage Compounds**

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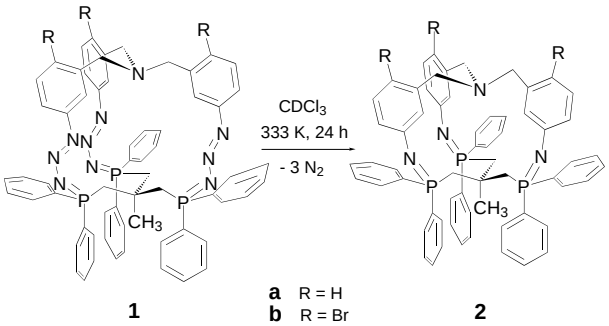
Dedicated to Professor José Elguero

At the molecular level, helical chirality[1] is usually a consequence of strong conformational preferences around covalent bonds. This is the case in molecular propellers, chiral molecules possessing two or more subunits which can be considered as "blades" (e.g., aryl or spirocyclic rings), which radiate from an axis of rotation (propeller axis).[2] Triarylmethanes are the most extensively studied structures of this class.[3] Bicyclic organic compounds of local C_3 symmetry, constructed by linking two propeller tripodal units exhibit this type of chirality. However, this propeller shape has been observed only for a limited number of such compounds in solution.[4] We have reported the preparation of several types of C_3 or pseudo-C_3 symmetric, chiral macrobicyclic triphosphazides (e.g. **1a**, Scheme 1), which possess propeller-like topology in solution and in the solid state.[5]



Scheme 1. Synthesis of **2** by dinitrogen expulsion from **1**.

Herein, we report that, when compound **1a** was kept at 333 K in $CDCl_3$ solution for 24 h, it cleanly converted into tri-λ^5-phosphazene **2a** in 75% yield, by triple expulsion of molecular N_2 (Scheme 1). The dinitrogen expulsion from

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

each PN_3 unit can be understood as the second mechanistic step of a Staudinger P^{III} imination reaction.[6]

The new cage compound **2a** was fully characterized by its analytical and spectroscopic data,[7] but we were unable to obtain a crystalline sample suitable for molecular structure determination by X-ray crystallography. To overcome this problem we prepared the new triphosphazide **1b**, by our well-established methodology,[5b,c] which was then heated in solution ($CDCl_3$) to yield the tri-λ^5-phosphazene **2b** (74%). Suitable crystals of **2b** enabled analysis of the molecular structure.[8] Two perspective views of the structure of **2b** are shown in Figure 1. The molecule is located on a non-crystallographic threefold axis passing through the two bridgehead atoms of the bicyclic cage, and its propeller-like shape is clearly apparent when the molecule is viewed along this axis (Figure 1b). Both propeller units, the upper tribenzylamine core and the lower *tert*-pentane fragment, present the same helical twist sense, *M*[9] (Figure 1b). The twist apparently arises from the need to minimize the volume of the unoccupied molecular cavity. The cavity is too small to include any available guest species and therefore screws down upon itself like the lid of a screw-top jar, which results in a cavity of almost negligible volume. Four molecules of chloroform cocrystallize with **2b**. One of these chloroform molecules engages in a CH···N hydrogen bond to one of the N=P nitrogen atoms (C···N 3.155 Å), while the others form strong CH···π-system interactions with H···centroid distances both approximately 2.45 Å (C···centroid 3.388 and 3.413 Å).

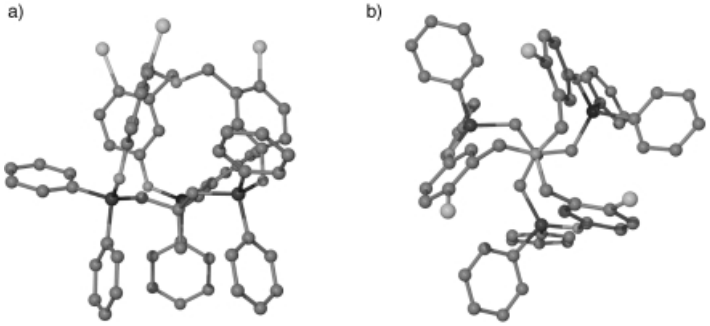
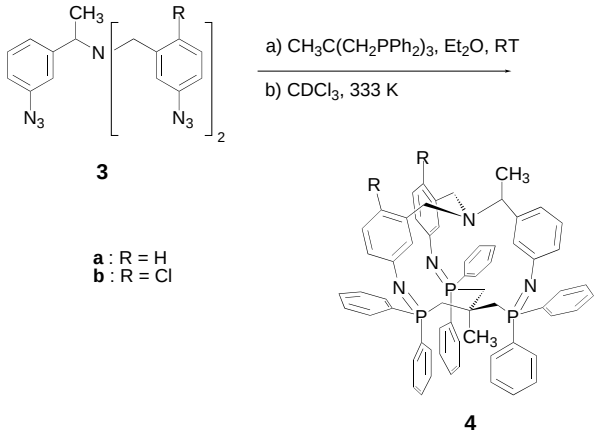


Figure 1. a) Molecular structure of **2b** (hydrogen atoms omitted for clarity), b) perspective view as projected along the threefold axis.

The NMR spectroscopic data of compound **2b** in $CDCl_3$ solution at 298 K (particularly the magnetic nonequivalence of the diastereotopic ligands), similar to those of **2a**, revealed that the solid state conformation of compounds **2** is probably retained in solution at 298 K. High-temperature ^1H NMR experiments (compound **2b**, *o*-$Cl_2C_6D_4$ solution) demonstrated the simultaneous coalescence of the signals of the methylene CH_2N and CH_2P protons at 423 K. At this temperature, the coalescence of signals for the two phenyl groups on the phosphorus atom was also observed in the $^{13}C\{^1H\}$ NMR spectrum. On cooling to 298 K, the spectrum recovered its original appearance. These results are explained by equilibration, at the coalescence temperature, between the two enantiomeric propeller-like forms of **2b** via a labile conformation with time-averaged C_{3v} symmetry. The calculated[10] activation energy of this racemization process, $\Delta G^{\neq} = 20.8\ kcal\,mol^{-1}$, is notably higher than the values found in other bicyclic molecular propellers[4b,d] and slightly higher than those of some tricyclic [4.4.4]propellanes[11] and the 1-azonia[4.4.4]propellane cation.[12] When a similar high-temperature NMR spectroscopy experiment was carried out with **2b** in wet [D_6]DMSO solution, the results were comparable to those above, but surprisingly no trace of hydrolysis of the tri-λ^5-phosphazene was observed, which reveals the chemical stability of compounds **2** to be in sharp contrast with the hydrolytic sensitivity of most of the λ^5 phosphazenes prepared to date.[13]

To our knowledge, compounds **2** are the first examples of bicyclic tri-λ^5-phosphazenes, a subclass of the rare species bearing intracyclic phosphazene units,[14] and the conversion of **1** into **2** is the first observation of nitrogen expulsion from a fully characterized cyclic phosphazide.[15]

We then wondered if the sense of twist (*P*/*M*) of the helical asymmetry of cages type **2** could be controlled by the configuration of a single chiral carbon atom on one of the arms. By using standard methods, we synthesized α-methyl substituted triazides **3** in racemic form, which were converted into tri-λ^5-phosphazenes **4** (Scheme 2).



Scheme 2. Preparation of α-methyl tri-λ^5-phosphazenes **4**.

Although two diasteroisomeric pairs (*R*,*P*/*S*,*M* and *R*,*M*/*S*,*P*) are possible for both **4a** and **4b**, these compounds were obtained as single diastereoisomers in 70 and 63% yield, respectively (based on the starting triazides). An X-ray crystal structure determination showed **4b** to be the *R*,*M*/*S*,*P* diastereoisomer (Figure 2). The same stereochemistry was assumed for **4a** as a consequence of the close similarity of its spectral data to that of **4b**.

These results demonstrate that the helical asymmetry of the bicyclic, propeller-like cages **4** is totally controlled by the absolute configuration of their single stereogenic benzylic carbon atoms. This control seems to be determined by the marked preference of the methyl group for the occupation of a 'pseudoaxial' position (parallel to the pseudo C_3 axis)

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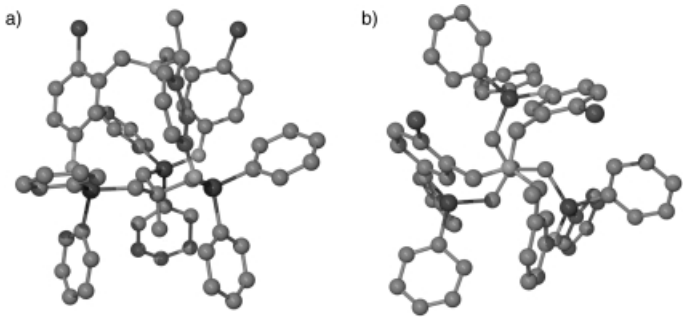

Figure 2. Molecular structure of **4b** with hydrogen atoms omitted for clarity a) side view, b) perspective view as projected along the *pseudo*-threefold axis.

instead of the alternative pseudoequatorial situation closer to the internal cavity, and therefore to the aryl groups. The sense of twist of the arm bearing the α-methyl group in turn determines those of the other two arms (Scheme 3).[16]

Scheme 3.

The calculated[17] difference in energy between both diastereoisomers of **4b** is 3.89 kcal mol^{-1} in favor of the one present in the crystal. When enantioenriched (−)-(*S*)-**3b** (98 % *ee*) was used in the procedure described in Scheme 2, optically active (*S*,*P*)-**4b** ($\alpha_D = +398.4^\circ$, $c = 6.20 \times 10^{-3}$ in $CHCl_3$) of definite helical sense was obtained.

The present case of point-to-helix chirality transfer at the molecular level in discrete organic compounds may be added to the limited number of such cases reported mainly in metal-coordinated systems[18] and polymeric superstructures.[19]

Experimental Section

General synthesis of **2**: A solution of compound **1** (5 mL, 1 mmol, 0.2 M in $CDCl_3$) placed in a loosely sealed round-bottom flask, immersed in an oil bath, was heated at 60 °C for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was crystallized from a mixture of dichloromethane and diethyl ether. In this way compounds **2a** and **2b** were obtained in 75 % and 74 % yield, respectively.

General synthesis of *rac*-tribenzylamines **3**: The corresponding 3-azidobenzyl iodide (4 mmol) was added to a solution of *rac*-1-(3-azidophenyl)ethylamine (30 mL, 2 mmol, 0.07 M in dioxane). The mixture was heated under reflux with stirring for 4 h. After cooling to room temperature, an excess of triethylamine (0.45 g, 4.5 mmol) was added at once, and the mixture stirred for 2 h. The precipitated triethylammonium iodide was separated by filtration. The dioxane was removed from the filtrate under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/*n*-hexane (1:9)). In this way compounds **3a** and **3b** were obtained in 44 % and 27 % yield, respectively.

Preparation of (*S*)-**3b**: *rac*-1-(3-Azidophenyl)ethylamine (1.84 g, 11.3 mmol) and (*R*,*R*)-tartaric acid (1.70 g, 11.3 mmol) were dissolved in hot methanol (40 mL). The solution was cooled to room temperature. After 12 h, the supernatant liquid was separated and the white solid was recrystallized from hot methanol (25 mL). After 16 h at room temperature, the solid was collected by filtration and dried to give the amine–tartrate salt (0.84 g). The salt was suspended in dichloromethane (30 mL), 1 M NaOH (20 mL) was added and the mixture was stirred for 1 h. The organic layer was separated, the aqueous layer was extracted twice (CH_2Cl_2, 2 × 20 mL), and the combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure to give (*S*)-1-(3-azidophenyl)-ethylamine (0.41 g, 45 %). The α-methoxy-α-phenyl-α-(trifluoromethyl)-acetamide of this material was prepared from (*R*)-(+)-α-methoxy-α-trifluoromethylbenzeneacetic acid (MPTA) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) and analyzed by ^{1}H and ^{19}F NMR spectroscopy to reveal a diastereoisomeric ratio of 95:5, the major isomer was the (*S*)-1-(3-azidophenyl)ethylamine. A third recrystallization of the amine–tartrate salt from methanol (15 mL) afforded 0.63 g of the salt, which yielded (*S*)-1-(3-azidophenyl)ethylamine upon addition of base $\alpha_D^{20} = -26.2^\circ$ ($c = 8.3 \times 10^{-3}$ in $CHCl_3$, 98 % *ee*). Mosher amide of (*S*)-1-(3-azidophenyl)ethylamine: yield 94 %; m.p. 69–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.49$ (d, $J = 6.8$ Hz, 3H, CH_3), 3.43 (d, $J = 6.8$ Hz, 3H, OCH_3), 5.14 (q, $J = 6.8$ Hz, 1H, CH), 7.12 (m, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): $\delta = 21.53$ (CH_3), 48.65 (OCH_3), 54.94 (CH), 84.15 (q, ^2J(C,F) = 26.7 Hz, CCF_3), 116.66, 118.08, 122.72, 123.75 (q, ^1J(C,F) = 289.5 Hz, CF_3), 127.56, 128.19, 128.51, 129.00, 129.50, 130.04, 132.37 (q), 140.42 (q), 144.70 (q), 165.46 (q, CO); ^{19}F NMR (282.4 MHz, $CDCl_3$, 25 °C): $\delta = 9.07$; IR (Nujol): $\tilde{\nu} = 2121$ (N_3), 1690 (C=O) cm^{-1}. The alkylation of (*S*)-1-(3-azidophenyl)ethylamine with 3-azido-6-chlorobenzyl iodide as above yielded (*S*)-**3b** in 22 % yield. $\alpha_D^{20} = -33.0^\circ$ ($c = 6.0 \times 10^{-3}$ in $CHCl_3$).

General synthesis of **4**: Two solutions of the corresponding tribenzylamine **3** (5 mL, 0.5 mmol, 0.1 M in $CDCl_3$) and [2-((diphenylphosphino)methyl)-2-methyl-1,3-propanediyl]bis[diphenylphosphine](TRIPHOS; 5 mL, 0.5 mmol, 0.1 M in $CDCl_3$) were simultaneously added to a round-bottom flask containing $CDCl_3$ (10 mL) under nitrogen at room temperature, over a period of 1 h with stirring. The resulting mixture was then stirred for about 3 h (monitoring by IR) at room temperature. After this time, the mixture was placed in an oil bath and heated at 60 °C for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was crystallized from a mixture of chloroform and hexane. The compounds **4a** and **4b** were obtained in 70 % and 64 % yield, respectively.

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[7] New compounds have been fully characterized by spectroscopic methods and elemental composition (see Supporting Information).

[8] Crystal structure analysis of **2b** · 4 $CHCl_3$: $C_{66}H_{58}Br_3Cl_{12}N_4P_3$, M_r = 1665.20 g mol^{-1}, triclinic space group $P\bar{1}$, a = 12.8432(4), b = 14.7484(6), c = 19.5242(5) Å, α = 85.839(2), β = 89.058(2), γ = 72.373(2)°, V = 3515.2(2) Å^3, Z = 2, unique data 15993 ($2\theta \leq 55°$), parameters 795, R_1 [$F^2 > 2\sigma(F^2)$] 0.044, wR_2 (all data) 0.094. Crystal structure analysis of **4b**: $C_{67.5}H_{59}Cl_{15.26}N_4P_3$, M_r = 779.85 g mol^{-1}, triclinic space group $P\bar{1}$, a = 12.453(3), b = 14.853(3), c = 19.456(6) Å, α = 85.522(14), β = 89.845(15), γ = 72.399(12)°, V = 3419.0(15) Å^3, Z = 2, unique data 10508 ($2\theta \leq 48°$), parameters 796, R_1 [$F^2 > 2\sigma(F^2)$] 0.190, wR_2 (all data) 0.422. The poor overall precision resulted from the presence of a great deal of disordered chloroform, coupled with poor overall crystal quality as a result of decomposition. The structural details of the macrobicycle are clear and unambiguous, however. CCDC-143862 (**2b**), and -172792 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[9] The conventional assignment of the stereochemical descriptor *P* or *M* (helical twist sense) to the propeller units of the chiral macrobicycles was made by looking at the molecule along its threefold axis from the side of the tribenzylamine fragment.

[10] The activation energy was calculated from the equation: $\Delta G^{\neq} = (4.57 \times 10^{-3})\ T_c\ (10.32 + \log(T_c 2/\pi\Delta\nu))$ following: D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., McGraw-Hill, New York, **1989**, p. 103.

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[17] Semi-empirical calculations were carried out by using the MNDO method as implemented in the Gaussian 98 set of programs. The geometries of both stationary points were optimized, and harmonic frequency calculations were performed in order to characterize both structures as minima.

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Alkene C–H Activations at Dinuclear Complexes Promoted by Oxidation**

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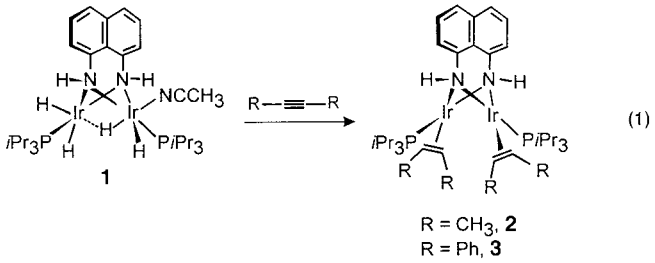
Several recent discoveries in the chemistry of transition metal di- and polynuclear complexes have disclosed new methods of hydrocarbon activation and functionalization, favored by polynuclear environments.[1, 2] In parallel, considerable progress has been made in understanding the reactivity features resulting from multimetallic reaction sites.[1, 3, 4] Together, such advances may contribute to the rational design of new catalysts and applications based on this type of compound. However, the proximity of the metal centers is likely to have significant repercussions for the reactivity, which remain to be determined.

In our recent studies on "open-book" d^8 diiridium complexes with N-donor bridges, we have observed a remarkable substrate selectivity in the reactions of these compounds towards oxidative addition reactants. Whereas the d^8 diiridium complexes underwent fast S_N2 oxidative additions with substrates such as halocarbons,[4] the additions of less-polar reactants such as dihydrogen were not observed. The oxidation of these d^8d^8 diiridium compounds, to species of d^6d^8 or d^7d^7 electronic configurations, gave dihydrogen-activating compounds.[5] Here we report that such an oxidation strategy also allows the transformation of nonreactive d^8d^8 compounds into dinuclear C–H activating species.

The treatment of the diamidonaphthalene ((NH$_2$)naphth)-bridged diiridium(III) complex [Ir$_2$(μ-1,8-(NH)$_2$naphth)-(μ-H)H$_3$(NCCH$_3$)(P*i*Pr$_3$)$_2$] (**1**) with two equivalents of an internal alkyne such as 2-butyne or diphenylacetylene afforded diiridium(I) derivatives of the formula [Ir$_2$(μ-1,8-(NH)$_2$naphth)(η^2-*Z*-RHC=CHR)$_2$(P*i*Pr$_3$)$_2$] (R = Me (**2**), Ph (**3**)) [Eq. (1)]. The solution NMR spectra of both compounds indicate symmetric C_2 structures with a transoid arrangement of nonrotating *Z*-alkene ligands. These features have been confirmed by the X-ray crystallographic determination of the structure of **2**,[6] (Figure 1).



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