Synthesis and dynamic behaviour of new metallo-based sterically overcrowded alkenes

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The synthesis and crystal and molecular structures of novel metallo-based sterically overcrowded alkenes are reported and dynamic ^{1}H NMR studies reveals that the isomerization barriers are dramatically increased on metal coordination.

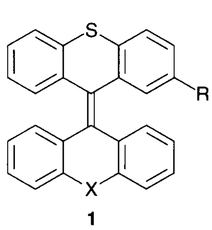
The intriguing thermochromic,[1] photochromic[2] and stereochemical properties[3] of sterically overcrowded alkenes have stimulated investigations towards the conformational behaviour and control of the dynamic processes of this class of compounds.

We have demonstrated a remarkable correlation between racemization barriers and aryl–X bond lengths in thioxanthene based inherently dissymmetric alkenes **1**.[4]

A conceptually simple strategy to novel overcrowded alkenes is based on the incorporation of metal binding sites and control of the conformation and dynamic processes by metal binding, *e.g.* replacement of covalent bridging moiety X in **1** by a metal ion as shown in **2**.

Here, we report the synthesis of 10-[bis(2-pyridyl)methylene]-9,9-dimethyl-9,10-dihydroanthracene **3** and the metal complexes **4** (M = ZnCl$_2$) and **5** (M = PdCl$_2$), which are the first examples of metallo-based sterically overcrowded ethylenes.

Alkene **3** was synthesized *via* a one-pot Peterson alkenation[5] sequence in 21% yield starting from 9,9-dimethyl-9,10-dihydroanthracene† and 2,2′-dipyridylketone (Scheme 1). The use of Bu^{t}OK–Bu^{n}Li (Schlosser's reagens) as a base for the deprotonation steps was essential for the successful preparation of **3**.



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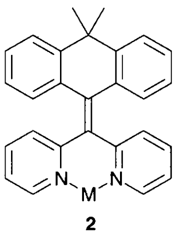

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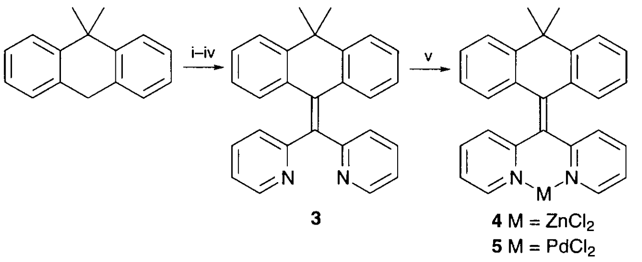

Scheme 1 *Reagents and conditions*: i, Bu^{t}OK–Bu^{n}Li, THF, −60 °C; ii, SiMe$_3$Cl; iii, Bu^{t}OK–Bu^{n}Li, −60 °C; iv, 2,2′-dipyridylketone; v, MX$_2$, MeCN

Interestingly, the X-ray structure determination of **3**‡ shows a *non-planar* structure with a folded 9,9-dimethyl-10-methylene-9,10-dihydroanthracene part [torsion angle: C(2)–C(1)–C(14)–C(13) −134.7(3)°] [Fig. 1(*a*)].

The central alkenic bond is almost planar [C(1)–C(14)–C(15)–C(21) 7.2(5), C(1)–C(14)–C(15)–C(16) 177.0(3), C(13)–C(14)–C(15)–C(16) −1.1(5), C(13)–C(14)–C(15)–C(2) −170.9(3)°] and the 2-pyridyl units are rotated out of the plane of the alkene [torsion angles: C(14)–C(15)–C(21)–N(2) −136.5(3), C(14)–C(15)–C(16)–N(1) −75.8(4)°]. Furthermore the 2-pyridyl units are oriented *anti* in the solid state.

The zinc complex **4** was prepared quantitatively by refluxing a solution of **3** and ZnCl$_2$ in a 1 : 1 ratio in acetonitrile for 16 h. The palladium complex **5**‡ was obtained in the same way by refluxing **3** and equimolar amounts of [Pd(MeCN)$_2$Cl$_2$] in acetonitrile for 2 h.

The molecular structure of **5** [Fig. 1(*b*)] clearly shows a folded configuration, whereby the tricyclic units at the upper and lower part of the molecule are positioned in opposite directions (*i.e. anti*-folded) with torsion angles: C(13)–C(14)–C(1)–C(2) −137.5(3), C(17)–C(16)–C(15)–C(21) 113.0(3)°. This folding diminishes the steric strain around the double bond, *i.e.* the *peri* hydrogen interactions of protons H(2)···H(22) and H(12)···H(17). The central alkenic bond is slightly elongated compared to a non-conjugated double bond with a bond length of 1.346(4) Å and is almost planar [dihedral angles: C(13)–C(14)–C(15)–C(16) −1.3(4), C(13)–C(14)–C(15)–C(21) −179.8(3), C(1)–C(14)–C(15)–C(21) 1.6(5), C(1)–C(14)–C(15)–C(16) −179.8(2)°]. It should be noted that previously described folded bistricyclic compounds have pyramidal double-bond carbon atoms,[6] and that thus compound **5** differs in an important aspect by having a nearly planar double bond. This may be ascribed to the deformation of the lower part of the molecule by the metal atom, leading to diminished contacts between the *peri* hydrogen atoms. The central six-membered ring in the lower part of the molecule containing palladium

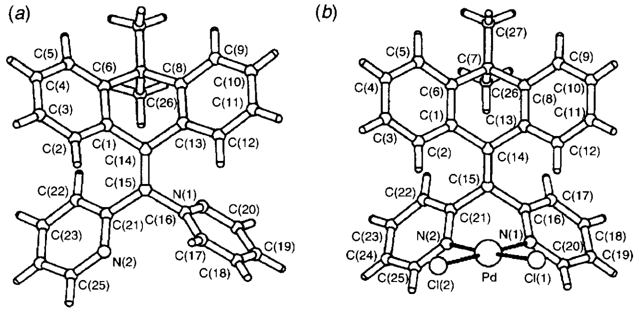

Fig. 1 PLUTON diagrams of (*a*) dipyridylalkene **3** and (*b*) the palladium complex **5**, with adopted numbering schemes

adopts a boat-like structure and a similar structural feature is found in the upper part of **5**. Pd–N bond distances of 2.028(2) Å are found. The molecular structure of **5** [Fig. 1(*b*)] shows that upon metal binding these new overcrowded alkenes adopt folded geometries comparable to folded structures of bis(thio)xanthylidenes.

Complex **5** (as well as **4**) shows two well separated singlets at δ 1.76, 1.99 (δ 1.81, 1.96 for **4**) in their ^1H NMR spectra ($CDCl_3$, 30 °C) for the methyl groups in the upper half of the molecule in contrast to alkene **3** for which one singlet (δ 1.87) is found under the same conditions, due to the non-planar configuration of **5** and slow movement of the aromatic moieties at room temperature. The interconversion of **A** into **B** leads to a conversion of $Me_{ax} \rightleftharpoons Me_{eq}$ and *vice versa*§ as is illustrated by the Newman projections in Fig. 2.

Upon lowering the temperature of a solution of **3** in CD_3OD the singlet (δ 1.84 at 30 °C) of the methyl groups broadened and two equal singlets (Δν 54.0 Hz) were found at −30 °C, $\Delta G^{\ddagger} = 11.8 \pm 0.2$ kcal mol^{-1} (cal = 4.184 J). The decoalescence is attributed to a slow interconversion process shown in Fig. 2. Alternative explanations involving slow rotation of the pyridyl groups are less likely, since extensive ^1H, ^{13}C and COSY NMR spectroscopy measurements show equivalent pyridyl groups in **3** under all conditions, indicating free rotation of the pyridyl moieties, in the temperature range studied.

Increasing the temperature to 200 °C of **4** or **5** dissolved in [$^2H_5$]nitrobenzene did not result in coalescence. Temperature-dependent NMR measurements (500 MHz) showed no significant line broadening of the methyl signals (**4**, δ 1.96, 2.00; **5**, δ 1.93, 2.01 in nitrobenzene at 60 °C) and an increase in Δν in the temperature range 60 °C (**4**, 20.6 Hz; **5**, 36.0 Hz) to 200 °C (**4**, 24.4 Hz, **5**, 51.8 Hz). These unexpected observations indicate considerable steric hindrance for the isomerization process (**A** ⇌ **B**) interconverting the folded structures in **4** and **5**.

The transition-state energies are largely determined by steric interactions during the 'edge' passages, whereby strong steric repulsions can occur between substituents around the central double bond. Comparing the metal-free alkene **3** and the metal complexes **4** and **5** shows that locking the pyridine rings in the lower part by metal binding drastically increases the barriers for the interconversion process between the folded structures (Fig. 2).

Since during isomerization two *peri*-H···*peri*-H [H(2)···H(22) and H(12)···H(17)] passages have to take place, the smaller aryl···aryl distance between the lower and upper halves will clearly enhance the steric barrier for this process. Metal binding eliminates free rotation of the pyridyl moieties and forces the two aromatic halves of the lower part of the molecule into the direction of the upper anthracene moiety. The isomerization barrier of metal-free **3** is clearly lower. This can be explained by the fact that the two aromatic rings of the lower half of the molecule can rotate freely around the single bonds. Because of this flexibility the steric hindrance during the isomerization process shown in Fig. 2 is quite low and as a consequence so is the isomerization barrier. In conclusion we have prepared the first metallo-based overcrowded ethylenes and demonstrated that metal binding results in folded structures completely stable towards interconversions.

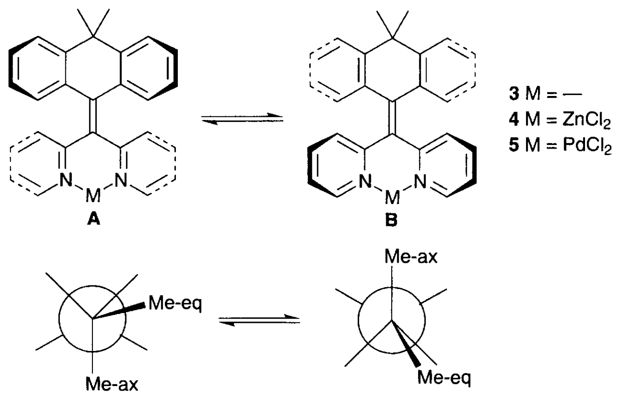

Fig. 2 Isomerization process **A** ⇌ **B** of compounds **3–5**

Footnotes

† The upper part of the molecule was prepared starting from 2-benzylbenzoic acid following the method described by Taylor *et al.*[7]

‡ Crystals of **3**, suitable for X-ray analysis, were obtained by crystallization from ethanol. Half a molecule of ethanol per molecule of **3** was included in the crystals. Crystals of **5**, suitable for X-ray analysis, were grown by slow diffusion of acetonitrile into a chloroform solution of **5**. One molecule of chloroform per molecule **5** was included in the crystals of the palladium complex.

Crystal data: **3**, $C_{27}H_{22}N_2 \cdot 0.5C_2H_5OH$, colourless block-shaped crystal (0.40 ×0.40 × 0.25 mm), monoclinic, space group $P2_1/c$, a = 8.4714(4), b = 17.6318(14), c = 14.8589(11) Å, β = 107.934(5), U = 2111.6(3) Å^3, Z = 4, D_c = 1.250 g cm^{-3}. X-Ray data (4229) were collected on an Enraf-Nonius CAD4T [Mo-Kα, graphite monochromated, λ = 0.71073 Å, θ_{max} = 25°, ω-scan, T = 150 K]. The structure was solved by direct methods (SHELXS 96) and refined on F^2 (SHELXL-93). Hydrogen atoms were taken into account at calculated positions. Final R_1 value 0.0690 [2397 reflections with $I > 2\sigma(I)$], wR_2 = 0.1837 (3715 reflections), S = 1.039, 303 parameters.

5, $C_{27}H_{22}Cl_2N_2Pd \cdot CHCl_3$, bright orange block-shaped crystal (0.25 × 0.38 × 0.50 mm), triclinic, space group $P\bar{1}$, a = 8.9341(6), b = 12.7169(8), c = 13.3759(8) Å, α = 72.98(1), β = 88.48(1), γ = 71.52(1)°, U = 1374.48(16) Å^3, Z = 2, D_c = 1.622 g cm^{-3}. X-Ray data (8711) were collected as above (θ_{max} = 27.5°). The structure was solved by Patterson methods (DIRDIF 92) and refined on F^2 (SHELXL-93). Hydrogen atoms were taken into account at calculated positions. Final R_1 value 0.0310 [5799 reflections with $I > 2\sigma(I)$], wR_2 = 0.0786 [6302 reflections], S = 1.070, 327 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/216.

§ This process can easily be followed by temperature-dependent ^1H NMR studies. At low temperatures the molecular motion is slow on the NMR timescale, which leads to two well separated singlets for both methyl groups in the spectrum. The isomerization barrier was measured using the coalescence temperature T_c and the difference in chemical shift Δν, by substituting these numbers in the following equation, which is derived from the Eyring equation: $\Delta G^{\ddagger} = 4.57\ T_c\ [9.97 + \log (T_c/\Delta\nu)]$. No decomposition of **4** and **5** was seen up to 200 °C.

References

1 J. Sandstrøm, *Top. Stereochem.*, 1983, **14**, 160; I. R. Gault, W. D. Ollis and I. O. Sutherland, *Chem. Commun.*, 1970, 269; I. Agranat and Y. Tapuhi, *J. Am. Chem. Soc.*, 1978, **100**, 5604; I. Agranat and Y. Tapuhi, *J. Org. Chem.*, 1979, **44**, 1941.

2 *Photochromism: Molecules and Systems in Studies in Organic Chemistry 40*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990; B. L. Feringa, W. F. Jager, J. C. de Jong, B. de Lange, N. P. M. Huck and A. Meetsma, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 348; B. L. Feringa, N. P. M. Huck and H. A. van Doren, *J. Am. Chem. Soc.*, 1995, **117**, 9929; for a review see: B. L. Feringa, W. F. de Jager and B. de Lange, *Tetrahedron*, 1993, **49**, 8267.

3 I. Agranat and Y. Tapuhi, *J. Chem. Soc., Chem. Commun.*, 1993, 213; N. P. M. Huck, A. Meetsma, R. Zijlstra and B. L. Feringa, *Tetrahedron Lett.*, 1995, **36**, 9381.

4 B. L. Feringa, W. F. Jager and B. de Lange, *Tetrahedron Lett.*, 1992, **33**, 2887.

5 D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.

6 Reviews on pyramidalization in enes: W. T. Borden, *Chem. Rev.*, 1989, **89**, 1095; R. C. Haddon, *J. Am. Chem. Soc.*, 1990, **112**, 3385; T. P. Radhakrishnan and I. Agranat, *J. Struct. Chem.*, 1991, **2**, 107.

7 G. A. Taylor, C. P. Falshaw and N. A. Hashi, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1837.

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