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# 4,5-Diazafluorene-Based Overcrowded Alkene: A New Ligand for Transition Metal Complexes

**Manel Querol,[†] Helen Stoekli-Evans,[‡] and Peter Belser*,[†]**

*Department of Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland, and Université de Neuchâtel, Institute of Chemistry, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

*peter.belser@unifr.ch*

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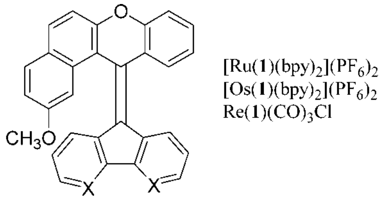
## ABSTRACT



(**1**) X= N

**A new ligand system, where a 4,5-diazafluorene-type chelate and a methoxybenzoxanthene unit are coupled by a double bond has been synthesized and fully characterized including X-ray structure. The synthesis and UV–vis spectra of Ru(II), Os(II), and Re(I) complexes with the above-mentioned ligand are also shown.**

The use of photochromic materials for reversible data storage is currently a growing field. This interest is based on their potential applications in the “bottom-up” approach adopted in nanotechnology.[1] Among them, overcrowded bistricyclic aromatic enes have been extensively studied since their “helicity” can be inverted by means of CPL (circularly polarized light) and such a change can be easily monitored by means of CD techniques. They have also been used as phototriggers in LCD technology.[2] These kinds of systems can be used either in a pure diastereomeric form (through a photodestruction process) or as a racemic MP mixture (through a photoenrichment process) as has been shown by Feringa et al.[3] To improve the photomodulation of these systems, several synthetic modifications have been introduced. These modifications are mainly oriented toward the increase of the encumbrance around the central double bond in order to achieve more and more overcrowding in the fjord region of these systems.[4]

In this Letter we will show the synthesis of an overcrowded polycyclic aromatic ene based on a 4,5-diazafluorene moiety which fulfills the steric requirements to adopt a helical shape. Moreover, the presence of a 4,5-diazafluorene moiety would allow us to introduce different metallo-based[5] sensitizers such as Ru(II), Os(II), and Re(I).

The synthesis of the target molecule was envisioned to have as coordinating site a 4,5-diazafluorene moiety due to its chelating ability. Keeping in mind this fragment, the upper part (methoxybenzoxanthene unit) had to provide enough substituents around the double bond in order to avoid thermal conformational inversion processes.[6] In this case, these processes should even be more important due to the planar geometry of the diazafluorene fragment (bottom part).[7] In

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[†] University of Fribourg, Department of Chemistry.

[‡] Université de Neuchâtel, Institute of Chemistry.

(1) (a) Special issue on Photochromism: Memories and Switches. *Chem. Rev.* **2000**, 1683. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1351. (d) Drexler, K. E. *Nanosystems. Molecular Machinery, Manufacturing, and Computation*; Wiley: New York, 1992.

(2) (a) Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686. (b) Feringa, B. L. *Acc. Chem. Res.* **2001**, *34*, 504. (c) Chen, C.-T.; Chou, Y.-Chen. *J. Am. Chem. Soc.* **2000**, *122*, 7662.

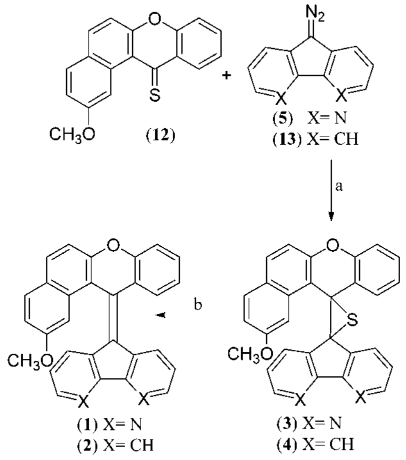
(3) Feringa, B. L.; van Delden, R. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 3418.

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

(5) For a related example of overcrowded alkenes as transition metal ligands, see: Wietske, I. S.; Schoevaars, A. M.; Kruizinga, W.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *Chem. Commun.* **1996**, 2265.

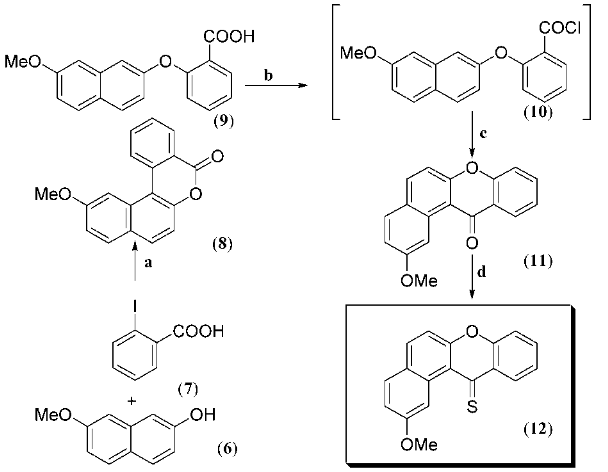
10.1021/ol017130c CCC: $22.00

**Scheme 1.** General Synthetic Scheme for the Preparation of Compounds **1** and **2**[a]



[a] Conditions: (a) toluene; (b) $PPh_3$/toluene.

**Scheme 2.** General Synthetic Scheme for the Obtention of the Upper Part of Compounds **1** and **2**[a]



[a] Conditions: (a) Cu(I), base, toluene; (b) $PCl_5$, benzene; (c) $SnCl_4$, benzene; (d) $P_2S_5$, toluene.

this sense, the upper part was envisioned to be a benzo[*a*]xantone in order to provide enough rigidity to the system as well as enough encumbrance around the double bond. In addition, substitution at the 2 position of the benzo[*a*]xantone unit could minimize the possibility of conformational inversion processes.

The synthesis of such highly hindered alkenes has been mainly obtained by means of Barton's 2-fold extrusion process.[8] Following this methodology, in principle, both the diazofluorene/xanthenethione and the fluorenethione/diazoxanthene could be adopted. Different attempts to obtain the fluorenethione over the 4,5-diazafluorenone starting material, using either $P_2S_5$ or Lawsson reagent[9] under different conditions including new procedures based on the use of microwaves,[10] were unsuccessful. In every case the obtention of the bis(4,5-diazafluore-9-ylidene) was the main product.[11] Therefore, the distribution of the functionalities needed was done as shown Scheme 1 The synthesis of the 9-diazo-4,5-diazafluorene **5** was accomplished as reported previously by Belser et al.,[12] taking as starting material 4,5-diazafluoren-9-one. The synthesis of the xanthone skeleton **11** (Scheme 2) has already been published in an overall yield below 10% using a methodology based upon a photooxidative cyclization of the corresponding substituted styrilchromone.[13] Due to this low yield, we decided to attempt the synthesis of such a moiety in a different way as shown in Scheme 2. In this sense, 7-methoxy-2-naphthol **6** was chosen as starting material and the preparation of the ether derivative **9** was attempted in two different ways. The first attempt was carried out by heating at 190 °C a mixture of the iodobenzoic acid **7** with a 3-fold excess of the sodium salt of the corresponding 7-methoxy-2-naphthol. Under these conditions, compound **9** was obtained in 37% yield. The relatively low yield obtained was correlated with the concomitant isolation of the biaryl lactone type compound **8** with a yield of 23%.

The second path chosen for the synthesis of the ether-type compound **9** was carried out by following the method described by Snieckus et al.[14] The method employs a toluene- or xylene-soluble Cu(I) complex as catalyst and $Cs_2CO_3$ as base. Under these conditions, compound **9** was obtained in 67% yield after two recrystallizations from toluene. When copper bronze was used as catalyst[15] and maintaining the same conditions, yields were always below 40%. The obtention of the benzo[*a*]xantone skeleton **11** was accomplished using $SnCl_4$ in benzene at 0 °C in a "one-pot" reaction starting from the corresponding ether **9**; this compound was transformed into the corresponding acyl chloride **10**, using an excess of $PCl_5$, which was further treated with $SnCl_4$ to afford the xantone-type skeleton in 76% yield after two recrystallizations using EtOH. This strategy can be an alternative not only to the use of polyphosphoric acid[15] (when acid sensitive groups are present) but also to the photooxidative cyclization of styrilchromones. The sulfurization step (Scheme 1) was achieved using $P_2S_5$ in boiling toluene for 7 h.

The diazo–thioketone coupling reaction was tested under various conditions. Conditions using low temperatures to avoid possible decomposition of compound **5** did not lead

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(6) For a definition of the conformational inversion process in overcrowded alkenes, folding angles, and pyramidalization angles, see: Biedermann, P. U.; Stezowski, J. J.; Agranat, I. *Eur. J. Org. Chem.* **2001**, 15.

(7) Levy, A.; Biedermann, P. U.; Agranat. I. *Org. Lett.* **2000**, *2*, 1811.

(8) (a) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. I* **1976**, 2079. (b) Krebs, A.; Kaletta, B.; Nickel, W.-U.; Rüger, W.; Tikwe, L. *Tetrahedron* **1986**, *42*, 1693.

(9) Scheibye, S.; Kristensen, J.; Lawesson. S.-O. *Tetrahedron* **1979**, *35*, 1339.

(10) Varma, R. S.; Kumar, D. *Org. Lett.* **1999**, *1*, 697.

(11) For synthesis description and X-ray structure of bis(4,5-diazafluore-9-ylidene), see: Riklin, M.; von Zelewsky, A.; Bashall, A.; McPartlin, M.; Baysal, A.; Connor, J. A.; Wallis, J. D. *Helv. Chim. Acta* **1999**, *82*, 1666.

(12) Bernhard, S.; Belser, P. *Synthesis* **1996**, 192.

(13) (a) Kumar, K. A.; Srimannarayana, G. *Indian J. Chem., Sect. B* **1980**, 615. (b) Ichiro, Y.; Kyoko, H.; Yoshiaki; S.; Manki, K. *Chem. Pharm. Bull.* **1981**, *29*(9), 2670.

(14) Kalinin, A. V.; Bower, J. F.; Riebel, P.; Snieckus, V. *J. Org. Chem.* **1999**, *64*, 2986.

(15) Barf, T.; Jansen, J. F. G. A.; van Bolhuis, F., Antony, L.; Feringa, B. L. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 376.

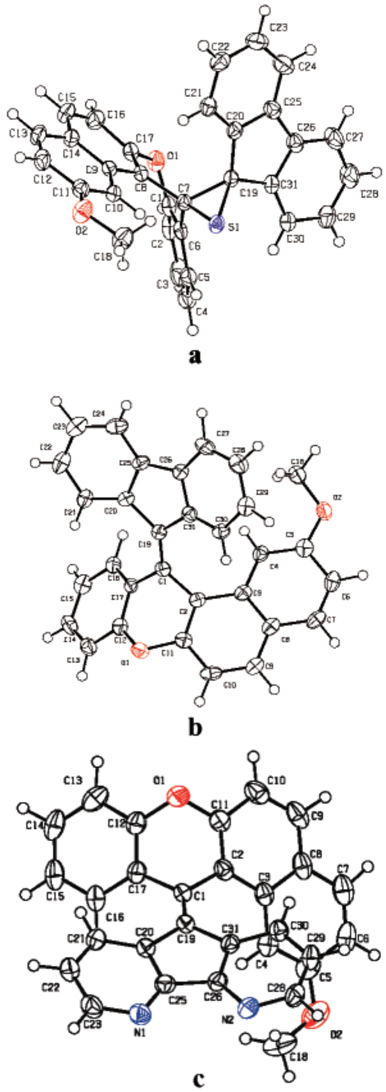

**Figure 1.** Crystal structures Platon[14] representation of compound (*R*)-**4** (a), (*P*)-**2** (b), and (*P*)-**1** (c). See ref 16.

to thiirane-type compound **3**. The thioxanthene-type compound **12** was recovered in quantitative yield. When the reaction was carried out in toluene at 110 °C for a minimum of 48 h, and using a 2-fold excess of the 9-diazo-4,5-diazafluorene **5** moiety, the corresponding alkene **1** was isolated without detection of the thiirane intermediate. Different attempts to isolate this intermediate, consisting of temperature/time tuning, never showed the presence of this compound. The structure of the newly formed molecule was confirmed by X-ray crystallography (Figure 1c). To understand the behavior of this system in further photophysical studies, the model compound **2** was also synthesized. In this case the diazafluorene moiety was replaced by the simple fluorene moiety **13**. The synthesis of this fragment following the previous synthetic idea was carried out by oxidation of the corresponding hydrazone to the azo compound using an excess of $MnO_2$ in THF at 0 °C.

The previous coupling conditions applied to this new molecule afforded, after 24 h, a mixture mainly formed by the desired alkene-type compound **2** and the thiirane-type precursor **4**. When the reaction was allowed to react for longer times, decomposition of the thiirane-type compound toward the thioxanthene starting material was detected. After this observation, the reaction was repeated using the same conditions for a period of 7 h. After this time, the solvent was removed in vacuo and after two crystallizations of the crude product using EtOH the thiirane-type compound was isolated in 78% yield. The structure of this compound was further confirmed by X-ray crystallography (Figure 1a). Desulfurization of compound **4** was achieved using $PPh_3$ in boiling toluene for a period of 12 h. The resulting alkene **2** structure was also confirmed by X-ray crystallography (Figure 1b).

Crystals suitable for X-ray analysis were obtained from compounds **4**, **2**, and **1**. Figure 1a shows one of the two possible enantiomers. All three structures showed a butterfly shape in the benzoxanthene part of the structure and a boat-like conformation for the central six-membered ring. Compound **4** shows as the main features folded conformation[6] for the upper part with a folding angle of 47.0° and a nearly planar conformation for the lower part (folding angle 3.9°). This folding in the upper part of the molecule could be attributed to the small angle defined by C(20)−C(19)−C(31) of 104.6° that pushes up the benzoxanthene-based moiety. The dihedral angles around the thiirane ring [C(6)−C(7)−C(19)−C(31) and C(8)−C(7)−C(19)−C(20)] are −1.48° and 8.73°, respectively, and the thiirane ring plane is twisted by 2.2° from the plane defined by C(20)−C(31)−C(8)−C(6). The crystal structure of compound **2** shows three independent molecules in the asymmetric unit; all of them show anti-folded conformations with pyramidalization angles of 5.1/−5.0°, 10.1/−4.2°, and 7.3/−8.6°, respectively, and folding angles for the upper/lower part of 47.3/15.8°, 41.9/12.9°, and 43.3/12.9°, respectively. The crystal structure of compound **1** showed a half molecule of hexane per molecule of **1** in the asymmetric unit. This compound in the solid state also shows an anti-folded conformation with pyramidalization angles of 7.44/−3.43° and folding angles of 44.2/14.7° for the upper and lower part, respectively. In either case, compounds **2** and **1** show overcrowding[6] in the fjord region as can be seen in Table 1.

$^1H$ NMR spectra in $CDCl_3$ (Figure 2) show as the main feature a completely asymmetric pattern for the diazafluorene protons as well as for the fluorene ones.[18] This spectra shows that protons a and b are strongly upfield shifted when compared with the homologous protons c and d. This can be rationalized by considering the strong shielding effect due to the aromatic rings located close to these protons. This effect can be also seen in the resonance of the methoxy group protons. In this case those protons are shifted upfield by as much as 0.6 ppm when compared with those of the xanthione-based precursor. These features are consistent with

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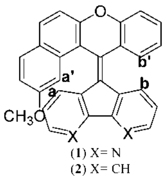
(16) Only one of the isomers of the racemate has been represented.

(17) Defined as deviation from the sum of the van der Waals radii. For the values of van der Waals radii of C and H, see: Levy, A.; Biedermann, P. U.; Cohen, S.; Agranat, I. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2329 and references therein.

(18) Full assignments of the aromatic protons of systems **1** and **2** are provided in the Supporting Information.

**Table 1.** Degree of Overcrowding in the Fjord Region for Compounds **1** and **2**[17]



| | compound | |
|---|---|---|
| | **1** | **2**[a] |
| Ca−Ca′ | 12% | 11% |
| Ca−Ha′ | 16% | 15% |
| Ca′−Ha | 4% | 7% |
| Cb−Cb′ | 12% | 13% |

[a] Average value from three different molecules in the asymmetric unit.

a system in which the "bottom half" and "top half" are in close proximity as has been shown previously by X-ray analysis. These NMR features are constant even when the sample was heated at 80 °C. This last observation can be correlated with the blocking of the conformational inversion processes associated with these systems.

$[Ru(bpy)_2(\mathbf{1})](PF_6)_2$, $[Os(bpy)_2(\mathbf{1})](PF_6)_2$, and $Re(\mathbf{1})(CO)_3Cl$ were prepared[20] by refluxing compound **1** with the appropriate metal source ($Ru(bpy)_2Cl_2$, $Os(bpy)_2Cl_2$, and $Re(CO)_5Cl$, respectively) for several hours using methoxyethanol for the ruthenium and osmium complexes and toluene for the rhenium complex formation. The ruthenium and osmium complexes were purified by recrystallization of their hexafluorophosphate salts from a mixture of acetone/hexane and a second recrystallization from methanol. For the rhenium complex the purification was achieved by crystallization from a mixture toluene/acetone.

UV−vis absorption spectra of compound **1** and its metal complexes with Ru(II), Os(II), and Re(I) are shown in Figure 3. The absorption spectrum of ligand **1** shows a broad peak at 360 nm corresponding to a ligand-centered ($^1$LC) transition, mainly located in the methoxybenzoxanthene part of the molecule. At about 300 nm a transition associated with the diazafluorene part can be observed. In the UV part of the spectra of the ruthenium and osmium complexes an intense absorption band (280 nm) can be attributed to a $^1$LC transition from the bpy ligand. Moderately intense metal-to-ligand charge transfer ($^1$MLCT) bands are observed for both complexes in the 400−500 nm region. In the osmium-containing complex, spin−orbit coupling gives rise to broad and weak absorptions at wavelengths higher than 600 nm, corresponding to the spin forbidden, formally $^3$MLCT transition. The rhenium complex $Re(\mathbf{1})(CO)_3Cl$ shows a large absorption maximum at 370 nm attributed to a $^1$MLCT transition. This study shows that the possibility of a selective irradiation over the metal center can be done and therefore helicity tuning could be achieved trough a triplet−triplet sensitization mechanism.

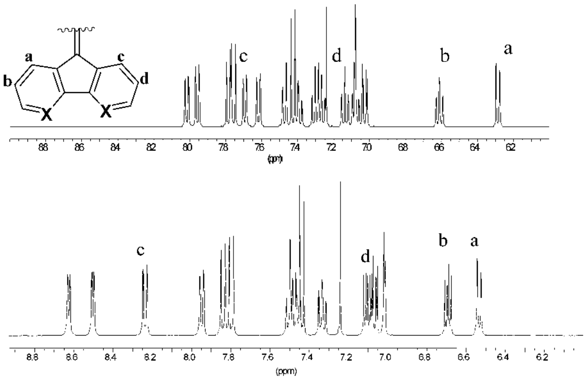


**Figure 2.** $^1$H NMR (400) of the aromatic region of compounds **2** (top) and **1** (bottom). See ref 19.

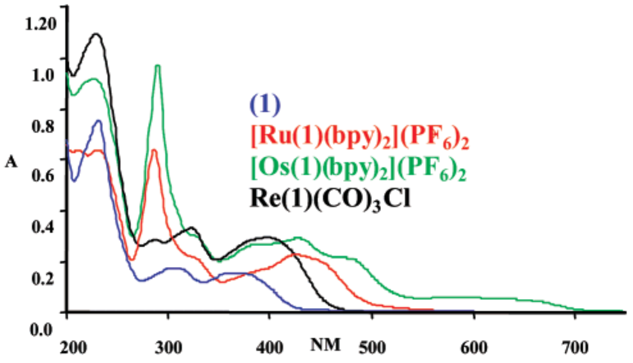


**Figure 3.** UV−vis absorption of compound **1** and its Ru(II), Os(II), and Re(I) complexes.

In conclusion, the helical character of compounds **1** and **2** has been proven by means of X-ray analysis. These compounds are potential candidates for chiroptical switches following a photoenrichment process. Moreover, the ability of compound **1** to form metal complexes with Ru(II), Os(II), and Re(I) has also been proven and the UV−vis absorption spectra shows well-differentiated bands where a metal-based irradiation can be performed and therefore the sensitization could be tested.

**Acknowledgment.** We thank the National Swiss Science Fundation for funding through the NFP 47 program.

**Supporting Information Available:** Experimental procedures for the synthesis of compounds **1** and **2**. Full $^1$H NMR aromatic region assignments for compounds **1** and **2**. Crystallographic data for compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystal structure data for compounds **1** (CCDC 173789), **2** (CCDC 173790), and **4** (CCDC 173788) have been deposited in the Cambridge Crystalographical Database.

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(19) Taken at 25 °C using the racemic mixture (*M*/*P*) of compounds **2** and **1**.

(20) For synthesis of related complexes, see: (a) Beyeler, A.; Belser, P.; De Cola, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2779. (b) De Cola, L.; Bazani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; Bernhard, S. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 534. All complexes gave satisfactory MS data.