Helicene-grafted vinyl- and carbene-osmium complexes: an example of acid-base chiroptical switching
Emmanuel Anger, Monika Srebro, Nicolas Vanthuyne, Christian Roussel, Loïc Toupet, Jochen Autschbach, Régis Réau, Jeanne Crassous

To cite this version:

HAL Id: hal-01058225
https://univ-rennes.hal.science/hal-01058225
Submitted on 26 Aug 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Helicene-grafted vinyl- and carbene-osmium complexes: an example of acid-base chiroptical switching

Emmanuel Anger, a,Monika Srebro, a Nicolas Vanthuyne, c Christian Roussel, bLoïc Toupet, a Jochen Autschbach, a, d Régis Réau, a and Jeanne Crassous, a, *

The first helicene-based carbene osmium complex has been prepared from a vinyl-osmium derivative and this system has been shown to behave as a potential acid-base triggered chiroptical switch.

Helicene derivatives have recently shown potential as molecular materials due to their inherent chirality, large magnitude chiroptical properties and π-conjugated electronic structure.1 For example, they have revealed fascinating optical, redox or chemical-stimuli induced chiroptical switching.2,3 These compounds may find applications invarious domains such as in optical displays, telecommunications, or molecular electronics. The design of new types of functional chiral molecular switches is needed and in this context, the switching of chiral metal-based systems has great potential,2,4 due to the possibility of reversibly modifying the molecule by changing the metal center’s properties (geometry, redox state, ...).2,4 In this communication, we describe the synthesis of an unprecedented enantiopure carbene-osmium helicene complex from an enantiopure helicene-grafted vinyl-osmium derivative. The potential use of these chiral organometallic systems as acid-base chiroptical switches is examined. The electronic interaction between the vinyl-osmium or carbene-osmium units and thecarb[6]helicenecore is investigated by DFT calculations.

Enantiopure vinyl-osmium-helicene complexes M- and P-2 (Scheme 1) were prepared in good yield (65-70%) using a known procedure,4 i.e. by hydro-osmylation of enantiopure M-(-) and P- (+)-I with 1 equivalent of OsHCl(PPr3)3 in CH2Cl2 at room temperature (r.t.). The NMR data fully support the proposed structure in accordance with previously reported analogues.4 For instance, the 1H NMR spectrum of 2 displays the fingerprint for trans-ethylene metal-substituted moieties with a doublet of triplets at 4.80 ppm (JH1H= 13.4 Hz, JH2H= 1.8 Hz) corresponding to the proton in the β position of the osmium center. Furthermore, according to 31P NMR spectroscopy the two PPr3 ligands are non-equivalent (23.96 and 23.92 ppm), indicating slightly different chemical environments for the two fragments. The X-ray structure of

![X-ray structure](image)

Scheme 1. Synthesis of enantiopure helicene-grafted vinyl-osmium complex P-2 and osmium-carbene-3 from enantiopure P-1/2 HOs[CO][Cl(PPr3)3], CH2Cl2, r.t., Ar, 3 days, 70%. ii) HCl, toluene, 10 min., 86%. iii) NEt3, CH2Cl2.

Complexes containing Os=C(H)=R units have been prepared.6 Such carbene complexes (also named alkylidene-osmium complexes) are an important class of compounds but to our knowledge their electronic and chiroptical properties have not yet been studied. The first enantiopure helicene-based carbene-osmium complexes M- and P-3 (Scheme 1) were straightforwardly prepared from vinyl-osmium complexes M- and P-2 by a simple addition of slight excess of HCl in toluene at r.t.4,6 and characterized by 1H, 31P{1H} and 13C{1H} NMR, along with IR, UV-vis and ECD spectroscopies. For example, the 1H NMR spectrum of monocarbene 3 in CH2Cl2 showed the presence of a triplet at 18.1 ppm (JH1= 6.6 Hz) which is typical of the CH=Os and two doublets of doublets at 2.85 and 3.13 ppm corresponding to the methylene group. In the 13C{1H} NMR spectrum, the sp2 carbon appears as a doublet of doublet (JC= 8.5 Hz) at 296.7 ppm. Furthermore, two singlets at 12.89 and 12.47 ppm are found in the 31P{1H} NMR spectrum. These are typical values for aryl-methylene-carbene-osmium species4b and correspond to the two P atoms in different chemical environments. Note that in such complexes the osmium centers are octahedral with a coordination sphere completed by a chloride ligand (see optimized structure in Figure 2). The Os-C1-C2-C3 dihedral angle in the calculated structure of 3 is 159.35°, which indicates a rotation of the helicene moiety around C1-C2 axis as compared to 2. See Supplementary Information, SI, for Cartesian coordinates of both calculated structures 2 and 3.

Vinyl-osmium helicene complex 2 displays two strong high-energy absorption bands (258 and 314 nm, e ~70-105 M-1 cm-1 and 45-103 M-1 cm-1, respectively, see SI) that originate from the π-system of the
helicene ligand, along with abroawl-low-energy band at 405 nm of moderate intensity ($\sim 14 \times 10^3 \text{M}^{-1} \text{cm}^{-1}$) that does not exist in ligand 1 and is due to efficient electronic interaction between the vinyl-osmium moiety and the helicenic-$\pi$-core (see below). Interestingly, the carbene-osmium complex 3 displays the same high-energy absorption bands as 2 for the $\pi$-$\pi^*$ transition of the helicene-core while the low-energy band at 405 nm has disappeared and two new broad bands of low intensity are found at 500 nm ($\sim 5 \times 10^3 \text{M}^{-1} \text{cm}^{-1}$) and 785 nm ($\sim 3 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$), see SI. In addition, enantiopure complexes $M$- and $P$-2 display molar rotation (MR) values that are much higher than the corresponding ligand $\Delta [\varepsilon]^3$ in $\text{cm}^{-1}/\text{dmol}$: $P$-2: $+1800$ vs. $P$-1: $+11030$. The circular dichroism (CD) spectrum of the complex $P$-2 depicted in Figure 1 shows, aside from the regular strong bands present in the helicene core, new ECD-active bands between 380-480 nm as compared with the ethynyl-substituted precursor $P$-1. These new bands involve electronic interaction between the vinyl-metal-center and the helical $\pi$-system as confirmed by density functional calculations performed with the BHLYP/SV(P) level (see SI for Computational Details). For example, calculated excitations n°3 (367 nm) and n°4 (354 nm) manifest character of $\pi$ to $\pi^*$ transitions within the helicene ligand (HOMO–LUMO: 65% and HOMO–LUMO+1: 60%, respectively; see Figure 2 and SI). Both excitations are at low energy / long wavelength, due to an enlargement of the helicene chromophore by conjugation with the vinyl bridge and osmium $d$ orbital involvement. Yet, because of the chirality of the helicene moiety, the transitions carry significant rotatory strength and contribute predominantly to the positive CD intensity at long wavelengths. In addition, a metal-centered excitation (n°2, 373 nm, HOMO–4–LUMO+2: 78%) with moderate rotatory strength is present at lower energy. The resulting intense low-energy tail of the first positive ECD band is responsible for the increase in the molar rotation of the metal-grafted vinyl-helicene derivatives compared to the free ligands. Indeed, the calculated MR values of the $P$-isomers (2): 23915 with BHLYP and 17435 $\text{cm}^{-1}/\text{dmol}$ with LC-PBE0) reproduce well the strong increase relative to the helicene ligand (1: 17002 (BHLYP) and 13800 $\text{cm}^{-1}/\text{dmol}$ (LC-PBE0). See ref. 5 and SI for more details).

The osmium-carbene-helicene derivative revealed $\Delta [\varepsilon]^3$ values close to those of the ligands ($\Delta [\varepsilon]^3$ in $\text{cm}^{-1}/\text{dmol}$: $P$-3: $+9600$ vs. $P$-1: $+11030$). The ECD spectrum of complex $P$-3 shows a sharp negative band at 250 nm and a sharp positive one at 330 nm (Figure 1). Additionally, new weakly ECD-active bands at 500 and 785 nm ($\Delta \varepsilon \sim 3-14 \text{M}^{-1} \text{cm}^{-1}$) are also present in $P$-3. TDDFT calculations on the singlet osmium carbene complex reproduced well the high-energy strong positive ECD-active bands in $P$-3 originating from the purely helicenic-$\pi$-$\pi^*$ transitions (excitation n°5, 309 nm, HOMO–LUMO+2: 50% and HOMO–1–LUMO: 35%; see Figure 2 and SI), calculated in the same energy range where the strongest rotatory strength excitation of its organic precursor 1 occurs. As depicted in Figure 2 and SI, for $P$-3 these MOs are centered on the $\pi$-helical core without visible involvement of the osmium $d$ orbitals. Unlike complex 2, it appears that in the carbene-osmium derivative 3 the electronic coupling between metal center and the helicoidal-$\pi$-system is broken due to the presence of the CH$_2$.

Despite of the correct description of the high-energy part of the CD spectrum of 3, the very weak low-energy ECD-active bands could not be reproduced by a variety of non spin-orbit calculations. Absorptions to triplet excited states are often observed in heavy metal complexes because spin-orbit coupling weakens the spin selection rules. Calculations did indeed show the presence of triplet excitations in the wavelength range of interest. However, the appearance of triplet transitions above 600 nm was dependent on various approximations (see SI for more details). The calculated MR values of 3 were found to be overestimated as compared to the experimental result (17557 with BHLYP and 14173 with LC-PBE0) and similar to the calculated MR of 1. The trend among the set of complexes is thus correctly reproduced by the calculations. Another interesting question pertaining the electronic structure of 3 is the presence or absence of hyperconjugation($\sigma$–$\pi$ conjugation between CH$_2$ and C=Os helicene) which may affect structure and bonding in metal carbene complexes and leave signatures in UV-vis spectra. The optimized BP/SV(P) geometry of 3 does however not exhibit structural features that usually would be identified with hyperconjugation.

The ability of the helicene-osmium system to behave as an acid-base switch was examined. The reversible formation of helicene-vinyl-osmium $P$-2 from a solution of osmium-carbene-helicene $P$-3 in CH$_2$Cl$_2$ was performed by simply using NEt$_3$ and the UV-vis and ECD spectra of $P$-2 were almost recovered (see SI). Furthermore, the IR spectra of complexes 2 showed a characteristic CO stretching mode ($\nu_{\text{CO}}$) at 1895 cm$^{-1}$ that disappears upon adding HCl in toluene, while a new band grew up at 17435 cm$^{-1}$ corresponding to 3. This shows a stronger donating character of the helicene-vinyl ligand compared to the carbene. The reverse transformation to 2 could be conducted by using NEt$_3$, as followed by their IR $\nu_{\text{CO}}$ (Figure 3). This transformation is thought to involve a deprotonation of the acidic CH$_2$ group by the base.
followed by a 1,3-shift leading to HCl abstraction. As a consequence, this molecular system acts as an acid-base triggered chiroptical switch since the several ECD bands (330 nm, 800 nm, ...) are greatly modified upon $2 \rightarrow 3$ transformation. Although the system is not practically efficient due to the low stability of highly diluted solutions of carbene-osmium derivatives, to our knowledge this is the first time that a carbene derivative is used as a chiroptical switch.

In conclusion, the first enantiopure carbene-osmium based helicene derivative (3) has been prepared from unprecedented vinyl-osmium helicene derivative (2). The examination of the reversible transformation from $2 \rightarrow 3$ enabled to set up a new kind of an acid-base chiroptical switch due to the modification of the electronic interaction between the π-helicene core and a grafted osmium moiety. This example illustrates the inspiration from simple and well-known organometallic chemistry to the design of new kinds of helicene-based molecular switching systems.

![Figure 3. Reversibility test of the (carbene/vinyl)-osmium $2 \rightarrow 3$ transformation. IR spectra in CHCl$_3$ solution in the 1800-200 cm$^{-1}$ region ($\nu = \text{stretching band}$). Spectrum obtained after $3 \rightarrow 2$ transformation is indicated in dashed red lines.](image)

Notes and references

* Institute of Sciences Chimiques de Rennes, UMR 6262, Institut de Physique de Rennes, UMR 6251, CNRS - Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. Fax: (+33) 2-23-23-69-39; Tel: (+33) 2-23-23-57-09; E-mail: jeanne.crasou@univ-rennes1.fr

1. Faculty of Chemistry, Jagiellonian University, 30-062 Krakow, Poland. "Chirosciences, UMR 7313, Stérémichimie Dynamique et Chiralité, Aix-Marseille University, 13397 Marseille Cedex 20, France. Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260, USA. E-mail: jochenl@buffalo.edu"

Acknowledgements: The author thanks the Ministère de la Recherche et de l’Enseignement Supérieur, the CNRS, the Région Bretagne, Rennes Métropole, and the ANR (12 BS07-0004-METALHEL-01). The theoretical work has been supported by grants CHE 0952253 and 1265833 from the National Science Foundation (JA) and the Foundation for Polish Science Homing Plus programme co-financed by the European Regional Development Fund under the Operational ProgrammelnInnovative Economy (MS). The Center for Computational Research (CCR, Buffalo) has provided computational resources.

† Electronic Supplementary Information (ESI) available: experimental procedures, X-ray data and theoretical calculations. See DOI: 10.1039/b009000000x/

#Complex 3 is stable for several months if kept under rigorously inert atmosphere. However, it was not practically feasible to perform several reversible cycles due to successive adding of reagents in the solution and therefore changes in concentrations.


