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Synthesis and characterisation of [6]-azaosmahelicenes: the first d^4-heterometallahelicenes†

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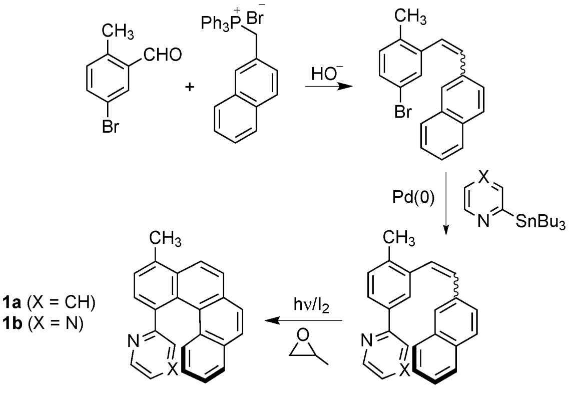
[6]-Azaosmahelicenes, the first d^4-heterometallahelicenes, have been synthesised and fully characterised. Their optical properties (UV-Vis absorption and luminescence) are reported.

Heterometallahelicenes constitute a class of [*n*]heterohelicenes[1] in which a CH group has been formally replaced by a transition metal and its associated ligands.[2] These interesting structures[3] would allow the study of the effect of the incorporation of the metal *d* electrons to a helical π-backbone, and hence, on the aromaticity and all the properties that rely on electronic coupling along the system. The first compounds of this type, which are d^8-, d^7-, d^6-azaplatinahelicenes[4] and d^6-azairidahelicenes,[4a] have been reported just a few months ago. Reported herein are the first d^4-heterometallahelicenes, which are also the first heteroosmahelicenes.

The organic fragments **1a** and **1b** used to build these structures were prepared by means of a Wittig C=C bond formation–Stille coupling–photocyclisation sequence starting from 5-bromo-2-methyl-benzaldehyde, 2-(naphthyl)methyltriphenyl phosphonium bromide, and 2-(tributylstannyl)pyridine or 2-(tributylstannyl)-pyrazine, respectively (Scheme 1). The 1-methyl-4-(2-pyridyl)-benzo[*g*]phenanthrene **1a** has been characterised by X-ray diffraction analysis (Fig. 1). The structure reveals a substantial distortion of the A/D ring planes with an angle between the terminal aromatic rings of 36.12(5)°. This helical curvature resembles that of 1,4-dimethylbenzo[*c*]phenanthrene (36.65°).[5] The separation between the pyridyl substituent and the polycyclic core (C(5)–C(6)) of 1.4903(18) Å is more than 0.04 Å longer than the longest C–C distance within the aromatic system (C(12)–C(16), 1.4587(18) Å), which indicates low electron delocalization between the polycycle and the aromatic substituent. As expected, the nucleus-independent chemical shifts (NICS), computed at the different [3, +1] ring critical points of the electron density, show that the terminal rings are the most aromatic.[6]



Scheme 1 Synthesis of **1a** and **1b**.

The UV-Vis spectra of **1a** and **1b** in dichloromethane contain bands between 250 and 380 nm, corresponding to the poly-π-conjugated system. A similar pattern is observed in the Diffuse Reflectance UV-Vis (DRUV) spectra, indicating that the absorption properties of the carbohelicenes do not depend upon the aggregation state. Furthermore, both **1a** and **1b** display emission in the blue region at about 400 nm in dichloromethane solution and in the solid state, at 77 K and at room temperature. Other emissions are not observed.

The activation of C–H bonds is usually promoted by low-valent compounds.[7] These types of reactions with high-valent complexes, in particular hydride derivatives, are rare. However, previous work has proven that the osmium(VI) complex $OsH_6(P^iPr_3)_2$ (**2**) efficiently activates C–H bonds of different organic substrates.[8] In agreement with this, the treatment of toluene solutions of **2** with 1.2 equiv. of **1a** and **1b** (3 h, reflux) led to the corresponding d^4-[6]azaosmahelicene derivatives **3a** and **3b**, which were isolated as racemic orange (**3a**) and dark red (**3b**) solids in 56% and 63% yield,

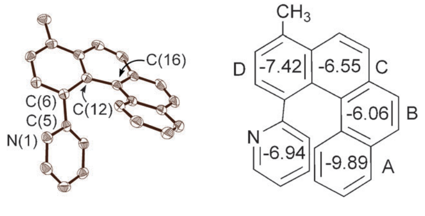


Fig. 1 Molecular diagram of **1a** and NICS (0) values for the aromatic rings.

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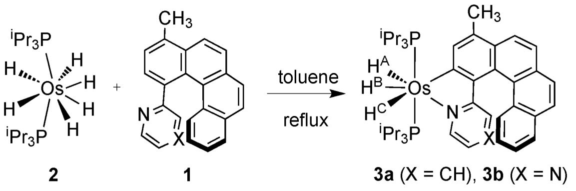

Scheme 2 Synthesis of complexes **3a** and **3b**.

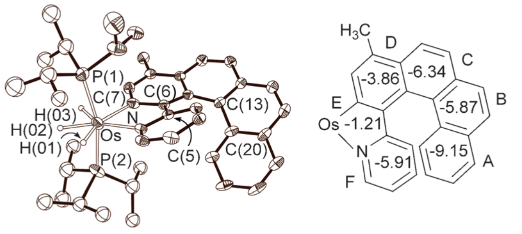

Fig. 2 Molecular diagram of **3a** and NICS (0) values for the aromatic rings.

respectively (Scheme 2). Complexes **3a** and **3b** result from the *ortho*-CH bond activation of the substituted ring of the starting [4]-carbohelicene, directed by the nitrogen atom of the aromatic substituent. Complex **3a** has been characterised by X-ray diffraction analysis and its structure proves the [6]-azaosmahelicene nature of the new d^4-species (Fig. 2).

Compared to **1a**, the interplanar angle between the external rings in **3a** increases by about 12°. This angle of 48.23(2)° agrees well with that of 9-methylphenanthro[4,3-*a*]dibenzothiophene (47.50(10)°),[9] which has also a five-membered ring between a six-membered cycle and a methylbenzophenanthrene moiety. As a consequence of the formation of the heterometallaring, the pyridyl group and the benzophenanthrene moiety approach. Thus, the C(5)–C(6) distance of 1.467(7) Å, which is about 0.02 Å shorter than that in **1a**, is statistically identical to the C(13)–C(20) bond length of cycle B (1.460(7) Å). This suggests some aromatic character for the five-membered metallacycle E. In agreement with this, the NICS values[10] computed at the [3, +1] ring critical point (NICS (0)) and at 1.0 Å above this point (NICS (1)) are −1.21 and −4.51 ppm, respectively. Furthermore, the reduction of the aromatic character of the pyridyl group and the rings D and B of the benzophenanthrene moiety also occurs, which is revealed by the decrease of the NICS (0) values of these rings of **3a** with regard to those of **1a**. As a consequence of the reduction of the aromaticity of the pyridyl group (cycle F), in contrast to **1a**, the terminal rings of the helicene are not now the most aromatic.

The coordination geometry around the osmium atom of **3a** can be rationalised as a distorted pentagonal bipyramid with *trans* phosphines (P(1)–Os–P(2) = 163.97(7)°). The $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^1H NMR spectra of **3a** and **3b** in toluene-d_8 at 193 K are consistent with this ligand distribution. The $^{13}C\{^1H\}$ NMR spectra show the C-metallated resonances at 191.9 (**3a**; t, J_{C-P} = 6.7 Hz) and 193.6 (**3b**; t, J_{C-P} = 5.7 Hz) ppm. In agreement with the asymmetry introduced by the screw of the polycycles, the $^{31}P\{^1H\}$ NMR spectra contain AB spin systems centered at about 24.5 ppm and defined by $\Delta\nu$ = 902 Hz and J_{AB} = 242 Hz (**3a**) and $\Delta\nu$ = 1115 Hz and J_{AB} = 228 Hz (**3b**). As expected for three inequivalent hydrides, the ^1H NMR spectra show three high field region resonances at −11.78, −10.89 and −6.35 (**3a**) and −10.87, −10.10, and −6.30 (**3b**), which were assigned to H^A, H^B, and H^C, respectively, on the basis of the NOESY spectra and $T_{1(min)}$ values.

The hydride resonances are temperature dependent. The coalescence of the H^B and H^C resonances occurs between 243 K and 263 K for **3a** and 235 K and 245 K for **3b**, whereas a single hydride resonance is observed at temperatures higher than 343 K for **3a** and 335 K for **3b**. This is consistent with the operation of two thermally activated site exchange processes, in agreement with the behaviour of related OsH_3-derivatives.[11] The exchange mechanism implies Os–H stretching, H–H shortening, and subsequent rotation of the resulting dihydrogen ligand. Since the activation barriers for the H^B–H^C exchanges (11 kcal mol^{-1} for **3a** and 10 kcal mol^{-1} for **3b**) are lower than those for the H^A–H^B exchanges (15 kcal mol^{-1} for **3a** and 12 kcal mol^{-1} for **3b**), the disposition *trans* of the metallated carbon atom to the dihydrogen ligand, in the hydride–dihydrogen transition state, appears to be favoured with regard to the disposition *trans* of the nitrogen atom. As expected for an easily accessible $Os(\eta^2\text{-}H^B\text{–}H^C)$ species, H^B and H^C undergo quantum exchange coupling[12] in addition to the thermally activated site exchange. Thus, for both **3a** and **3b**, the J_{HB-HC} value decreases with the temperature; from 30 to 18 Hz as the temperature decreases from 213 K to 183 K, for **3a** and from 50 to 32 Hz as the temperature decreases from 215 K to 205 K, for **3b**.

As expected, the involvement of the metal fragment in the helicene moiety provokes dramatic changes in the UV-Vis spectra of complexes **3a** and **3b** compared to those of the free ligands **1a** and **1b**. Thus, the spectra are characterised by the presence of a significant absorption around 500 nm (λ = 500 nm for **3a** and λ = 520 nm for **3b**). Our gas-phase TD-DFT calculations accurately assign this band to the HOMO → LUMO vertical transition (λ_{calc} = 489 nm for **3a** and λ_{calc} = 508 nm for **3b**). As readily seen in Fig. 3 for **3a**, the HOMO is mainly located in a d_π orbital of the metal whereas the LUMO is clearly a π^* molecular orbital delocalized in the helicene ligand. Therefore, this absorption can be assigned to a MLCT($\pi \rightarrow \pi^*$) type transition.

Luminescence studies of **3a** and **3b** in the solid state exhibit emissions in the red region at 77 K (λ = 624 nm for **3a** and λ = 683 nm for **3b**) and at room temperature (λ = 624 nm for **3a** and λ = 676 nm for **3b**). Emission bands in the red region are also observed in dichloromethane, toluene, tetrahydrofuran, acetone, and methanol at 77 K. However, in solution at room temperature a dual behaviour is observed (Fig. 12a, ESI†). The dominant bands are intense blue emissions (λ = 406 nm for **3a** and λ = 405 nm for **3b**) accompanied by weak bands in the red region (λ = 634 nm for **3a** and λ = 625 nm for **3b**). According to the lifetimes, Stokes shift and the published data for helicene platinum complexes,[4] the blue fluorescence can be explained in terms of emissions from the singlet excited state (S_1), whereas red

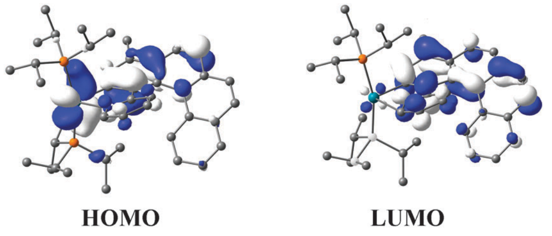

Fig. 3 Frontier molecular orbitals of **3a** (isosurface value of 0.04 au).

phosphorescence could derive from the first excited triplet state (T_1) and seems to be governed by the concentration of the solutions and not by the solvent polarity. Thus, a study of the emission spectra of **3a** in dichloromethane at room temperature has shown that the intensity ratios between blue and red bands decrease as the concentration of **3a** increases, leading to the disappearance of the blue fluorescence at concentrations of *ca.* 10^{-3} M. At high concentrations only the red emission is observed with low intensity, suggesting an efficient intersystem crossing (ISC) process.[13] Thus, molecules would emit from the T_1 state. The intensity of these red emissions is not high and no blue emission is observed, which could indicate quenching of the S_1 state. At low concentrations, the blue emission (emission from S_1) governs the luminescence. Solvent effects could also account for these facts.[14]

In summary, the first d^4-heterometallahelicenes have been prepared by reaction of the hexahydride $OsH_6(P^iPr_3)_2$ with pyridyl and pyrazinyl substituted benzo[*g*]phenanthrenes. The participation of the *d*-orbitals of the metal in the helical π-backbone of the resulting [6]-azaosmahelicenes produces significant perturbations in the aromaticity of the six-membered rings compared to that in the starting [4]-carbohelicenes, which gives rise to notable differences between the optical properties of the [6]-azaosmahelicene products and the [4]-carbohelicene reagents.

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