Communication

Aromatic Diosmatricyclic Nitrogen-Containing Compounds

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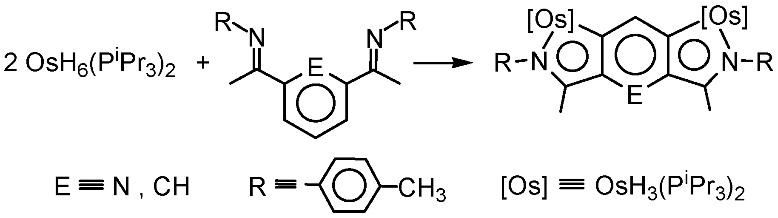

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Aromatic Diosmatricyclic Nitrogen-Containing Compounds

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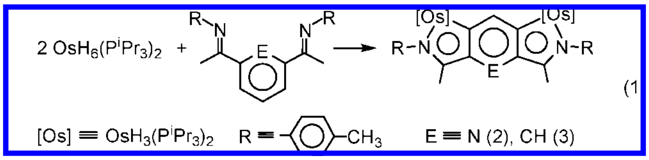
Aromatic metallacycles are transition metal containing ring systems that exhibit aromatic properties.[1] While much effort has been focused on metallabenzenes[2] and related metallacarbocycles,[3] important progress is also being made in synthesizing and studying the properties of heteroatom-containing species.[4]

Higher π-electron metallacyclic compounds are very rare. The isolation of the first metallanaphthalene by Paneque and co-workers[5] has extended the aromatic metallacycles to fused bicyclic compounds.[6] Evidence for the formation at −78 °C of a ruthenaphenanthrene oxide has been also reported,[7] and the intermediacy of renaphenanthrenes in reactions of 2,2′-dilithiobiphenyl with $ReBr(CO)_4(PPh_3)$ has been suggested.[8]

Bis(imino)pyridines are emergent tridentate ligands, which are receiving a lot of attention due to their metal complexation chemistry.[9] They are facilitating the entry into new families of transition metal complexes, which are being investigated for their potential use in a variety of catalytic metal-mediated organic transformations.[10]

The C−H bond activation reactions are promoted by low-valent metal complexes.[11] The use of high-valent metal compounds is rare, in particular hydride derivatives. Despite this, we have reported that the osmium(VI) complex $OsH_6(P^iPr_3)_2$ (**1**) activates C−H bonds of amines,[12] ketones,[13] aldehydes,[14] and imidazolium salts.[15] Now, we show that it is also able to produce the unprecedented activation of both *meta* C−H bonds of the pyridine ring of bis(imino)pyridines and related molecules, to afford aromatic dimetallatricyclic heteroatom-containing systems.

Treatment of toluene solutions of **1** with 0.5 equiv of 2,6-bis{1-[(4-methylphenyl)imino]ethyl}pyridine under reflux leads to a dark brown solution, from which the 1,7-diosma-2,4,6-triaza-*s*-indacene complex **2** is isolated as dark red crystals by addition of methanol and subsequent cooling of the mixture at 5 °C (eq 1).



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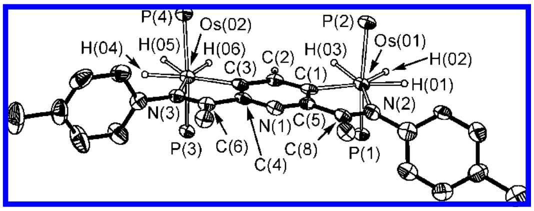

Figure 1. X-ray structure of complex **2** (isopropyl groups have been omitted for clarity).

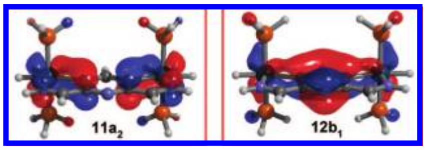

Figure 2. Plot of the valence $12b_1$ and $11a_2$ π orbitals of **2**. The value of the outermost contour line is 0.035.

The X-ray structure of **2** (Figure 1) proves the formation of the dimetallatricycle, which is planar (maximum deviation 0.1267(34) Å, N(2)). In agreement with a significant electron delocalization through the system, the bond lengths in the cycles are between those expected for single and double bonds. According to this, the Os(1)−N(2) (2.179(4) Å) and Os(2)−N(3) (2.183(4) Å) distances agree well with the Os−N bond lengths reported for osmapyrrole derivatives,[4i] whereas the Os(1)−C(1) (2.100(5) Å) and Os(2)−C(3) (2.100(6) Å) distances are similar to the Os−C bond lengths reported for both osmafuran[4f,k] and osmapyrrole complexes.[4i] The N(2)−C(8) (1.313(6) Å) and N(3)−C(6) (1.306(7) Å) distances of the five-membered rings are statistically identical with the N(1)−C(4) (1.320(7) Å) bond length of the pyridinic ring and slightly shorter than the N(1)−C(5) (1.346(6) Å) distance. All C−C bond lengths are statistically identical and lie between 1.454(6) and 1.420(7) Å.

The main characteristic of the orbital interactions in aromatic metallacyclic molecules is the involvement in the π bonding of two filled metal d orbitals, d_{xz} and d_{xy}, instead p orbitals of main group elements.[16] The orbital interactions in **2** are fully consistent with this. Figure 2 shows the $12b_1$ (π symmetry) and $11a_2$ (δ symmetry) interactions between the metal d_{xz} and d_{xy} orbitals and the $3b_1$ and $2a_2$ organic fragment orbitals.

The coordination geometry around each osmium atom can be rationalized as a distorted pentagonal bipyramid with axial phosphines (P(1)−Os(1)−P(2) = 160.11(5)°, P(3)−Os(2)−P(4) = 160.69(5)°) and the hydride ligands lying in the equatorial plane between the metallated atoms of the organic fragment. In agreement with this phosphine disposition, the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 contains a singlet at 23.8 ppm, which is temperature-invariant between 363 and 203 K. In contrast to the $^{31}P\{^1H\}$ NMR spectrum, the ^1H NMR spectrum is temperature-dependent. At temperatures higher than 363 K, it shows a single hydride resonance at −10.1 ppm, which is consistent with the operation of two thermally activated site exchange processes on each osmium atom, in agreement with the behavior of other trihydride derivatives.[17] At ∼353 K, the first decoalescence occurs, and at ∼258 K, the second one takes place. Thus, between 233 and 203 K, three resonances at −5.84 (H(01) and H(04)), −11.79 (H(02) and H(05)), and −12.42 (H(03) and H(06)) ppm are observed. These chemical shifts show no significant temperature dependence. However, the magnitude of the observed H(01)−H(02) (H(04)−H(05)) coupling constant is sensitive to the temperature, decreasing from 84 to 48 Hz as the temperature decreases from 233 to 203 K. This indicates the operation of quantum exchange coupling[18] between H(01) and H(02) and between H(04) and H(05), in addition to the thermally

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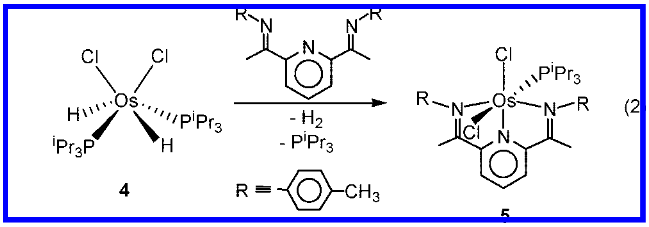
activated site exchanges. The value of $\Delta H^{\ddagger}$ for the processes involving H(01) and H(02) and H(04) and H(05) is 11 kcal·mol^{-1}, while the H(02)/H(03) and H(05)/H(06) exchanges cost 15 kcal·mol^{-1}.

The trend of **1** to activate aromatic C−H bonds allows preparation of other dimetallatricyclic heteroatom-containing systems by means of the same strategy, involving a double 1,3-C−H bond activation of aromatic rings with imino substituents *meta* disposed. Thus, the treatment of toluene solutions of **1** with 0.5 equiv of 1,3-bis{1-[(4-methylphenyl)imino]ethyl}benzene under reflux affords the 1,7-diosma-pyrrolo[3,4,*f*]isoindole complex **3** as dark red crystals (eq 1).

The X-ray structure of **3** (see Supporting Information) is consistent with that shown in Figure 1. The $^{31}P\{^1H\}$ and ^1H NMR spectra also agree well with those of **2**. The $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 contains a singlet at 24.0 ppm. In agreement with the X-ray structure, at 213 K, the ^1H NMR spectrum shows three hydride resonances at −6.04, −11.91, and −12.22 ppm. The hydride ligands of each osmium atom also are involved in two thermally activated site exchange processes. In this case the values of $\Delta H^{\ddagger}$ are 12 and 15 kcal·mol^{-1}. Furthermore the central hydrides and those cisoid disposed to the nitrogen atoms undergo quantum exchange coupling increasing the H−H coupling constant from 32 to 60 Hz as the temperature increases from 213 to 243 K.

The abnormal behavior of the 2,6-bis(imino)pyridine molecule giving rise to the formation of **2** is a consequence of the high trend of **1** to activate aromatic C−H bonds. In fact, in contrast to the hexahydride, the known complex $OsH_2Cl_2(P^iPr_3)_2$[19] (**4**) reacts with 2,6-bis{1-[(4-methylphenyl)imino]ethyl}pyridine to give the purple compound **5** in high yield, which contains a usual tridentate ligand (eq 2). Complex **5** has been also characterized by X-ray diffraction analysis (see Supporting Information).



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In conclusion tricyclic aromatic systems formed by a central six-membered ring fused with nitrogen-containing osma-five-membered rings can be easily prepared from the osmium(VI) hexahydride complex $OsH_6(P^iPr_3)_2$, by double 1,3-C−H bond activation of aromatic six-membered cycles with imino substituents *meta* disposed.

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Supporting Information Available: Experimental details for the synthesis, characterization and crystallographic data for **2**, **3**, and **5**, as well for the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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