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Stabilization of NH Tautomers of Quinolines by Osmium and Ruthenium

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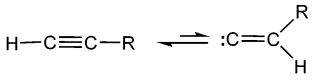
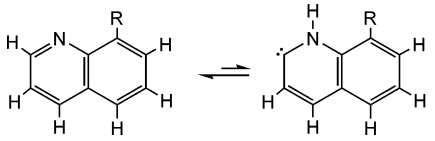
Intramolecular transfer of a proton in tautomeric systems is the key step in numerous important biological processes. It is not always clear which tautomeric form is responsible for the biological activity. For many biological transformations, the energetically less stable tautomer is often an active intermediate, which dictates the mechanism and the formed product. Noncovalent H-bonding interactions are also responsible for the stability of some tautomers.[1]

Transition-metal elements have the remarkable ability to coordinate organic molecules. A crucial consequence of this ability is the essential modification of the chemical behavior of the organic species. An attractive illustration may be found in the alkyne−vinylidene tautomerization (eq 1).[2] Although the activation energy for the acetylene−vinylidene isomerization is 76 kcal·mol^{-1} and the latter lies 44 kcal·mol^{-1} above the former in energy, numerous transition-metal vinylidene complexes have been reported in recent years.[3] In the presence of the transition metal and its associated ligands, the barrier for the isomerization diminishes, and the coordination of the vinylidene to the metal produces an inversion of the relative energy between the two tautomers.

Quinoline, also known as 1-azanaphthalene, is an aromatic nitrogen compound characterized by a double-ring structure that contains a benzene fused to pyridine at two adjacent carbon atoms. DFT calculations indicate that, like acetylene, it has a NH tautomer resulting from a C,N-1,2-hydrogen shift (eq 2), which lies 44.3 kcal·mol^{-1} above the usual CH tautomer.



(1)



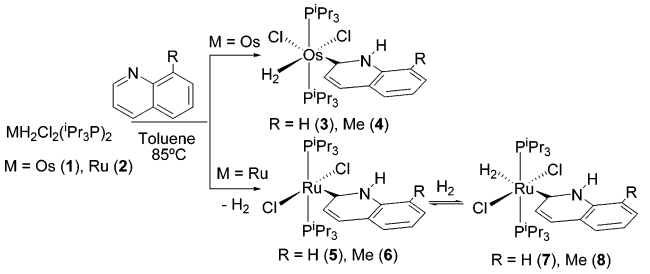
(2)

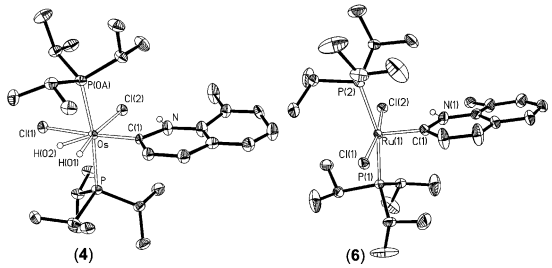
Complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) has been one of the cornerstones in the development of the modern osmium organometallic chemistry.[4] In this communication, we prove that **1** and its ruthenium counterpart $RuH_2Cl_2(P^iPr_3)_2$[5] (**2**) promote the transformation shown in eq 2 and stabilize the NH tautomer. Recently, Bergman has shown a related Rh-mediated rearrangement of 3-methyl-3,4-dihydroquinazoline via C−H bond activation.[6]

Treatment of a toluene solution of **1** with 2.0 equiv of quinoline at 85 °C for 10 h leads to the elongated dihydrogen complex **3** (Scheme 1), which is isolated as an orange solid in 70% yield. Under the same conditions, the reaction of **1** with 8-methylquinoline affords **4** in 90% yield. The formation of **3** and **4** involves, in addition to the tautomerization of the heterocycles, the transformation of the osmium−dihydride unit of **1** into osmium-elongated dihydrogen.[7]

The X-ray structure of **4** proves the stabilization of the NH tautomer, which coordinates to the metal center through the carbon

Scheme 1





at the 2-position (C(1)). The Os−C(1) distance (2.005(6) Å) compares well with the Os−NHC (NHC = N-heterocyclic carbene) distance in [(η^6-p-cymene)OsCl(=CHPh)(IPr)]OTf and [(η^6-p-cymene)OsCl(IPr)]OTf (2.090(3) and 2.078(2) Å, respectively; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene).[8] The similarity between the NH tautomer and the NHC ligands[9] is also revealed by the $^{13}C\{^1H\}$ NMR spectra of **3** and **4**, which show the Os−C resonances at about 191 ppm.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with *trans*-phosphines (P−Os−P = 170.06(6)°) and *cis*-chlorines (Cl(1)−Os−Cl(2) = 86.07(6)°). The planar heterocycle lies in the plane determined by the metal and the chlorine ligands with the NH hydrogen toward Cl(2). The separation between them (2.05(7) Å) is shorter than the sum of the van der Waals radii of hydrogen and chlorine,[10] suggesting that there is an intramolecular Cl···H−N hydrogen bond, as a result of the electrostatic interaction of the electronegative chlorine and the acidic NH hydrogen.[11] The Cl···H−N hydrogen bond is also supported by the IR spectra, which show the NH stretching frequencies at 3106 (**3**) and 3130 (**4**) cm^{-1}, shifted about 200 cm^{-1} to lower wavenumber with regard to those expected,[10] and by the ^1H NMR spectra in CD_2Cl_2 where the NH resonances appear at unusually low field, 14.36 (**3**) and 14.43 (**4**) ppm. The Cl···H−N interaction certainly plays a significant role in the stabilization of the NH tautomer (Chart 1). DFT calculations on the model system $OsH_2Cl_2(C_9H_7N)(PH_3)_2$ indicate that the additional stabilization corresponding to the Cl···H−N interaction is of 8.0 kcal·mol^{-1}. While the species resulting from the coordination of the NH tautomer with the NH hydrogen toward the elongated dihydrogen (**B**) only lies 2.2 kcal·mol^{-1} under that resulting from the coordination of the CH tautomer (**A**), the latter is 10.2

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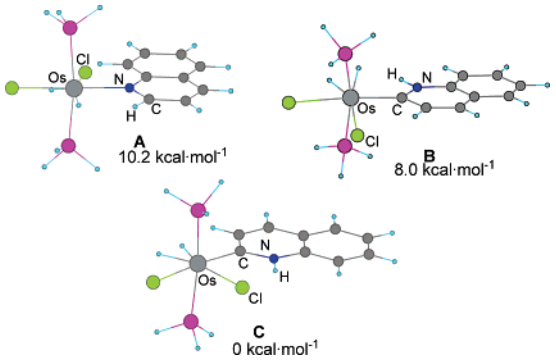
Chart 1



kcal·mol^{-1} less stable than the species containing the NH tautomer with the NH hydrogen toward a chlorine (**C**).

The elongated dihydrogen ligands of **3** and **4** give rise to triplets at −10.09 (J_{H-P} = 10.8 Hz; **3**) and −10.05 (J_{H-P} = 11.1 Hz; **4**) ppm in the ^{1}H NMR spectra. At 300 MHz, a T_1(min) value of 27 ± 1 ms was obtained for both compounds. Assuming slow spinning, it corresponds to a H−H separation of about 1.2 Å, which is consistent with the J_{H-D} values of 12.6 (**3**) and 12.3 (**4**) Hz.[12]

Ruthenium is a poorer π-back-bonder than osmium because the osmium valence orbitals have better overlap with the ligand orbitals. Thus, the Ru(η^2-H$_2$) bond is weaker than the Os(η^2-H$_2$) one,[13] and the dihydrogen ligand is lost during the reaction of **2** with quinoline and 8-methylquinoline. Treatment of toluene solutions of **2** with both heterocycles at 85 °C affords the five-coordinate derivatives **5** and **6** in 70% yield. Under hydrogen atmosphere, these compounds are in equilibrium with the corresponding dihydrogen derivatives **7** and **8** (Scheme 1).

Complex **6** has been characterized by X-ray diffraction analysis. The geometry around the ruthenium atom can be described as a square pyramid with the NH tautomer of the heterocycle located at the apex, *trans*-phosphines (P−Ru−P = 162.66(3)°) and *trans*-chlorines (Cl(1)−P−Cl(2) = 171.23(2)°). The Ru−C(1) bond length of 1.925(3) Å is about 0.08 Å shorter than that of **4**. This is consistent with the position of the RuC resonances in the ^{13}C{^{1}H} NMR spectra of **5** and **6**, which appear at about 218 ppm, shifted ca. 30 ppm to lower field with regard to the osmium compounds. Like in **4**, the separation between the NH hydrogen atom and Cl(2) is short (2.30(4) Å), in agreement with a Cl···H−N interaction.

The dihydrogen character of the RuH$_2$ units of **7** and **8** is supported by the ^{1}H NMR spectra of these compounds in CD_2Cl_2, which show the dihydrogen resonances at −12.47 (J_{P-H} = 8.4 Hz; **7**) and −12.52 (J_{P-H} = 8.1 Hz; **8**) ppm. In this case, a T_1(min) value of 19 ± 1 ms for both compounds and J_{H-D} constants of 30.5 (**7**) and 30.6 (**8**) Hz were observed. These values are consistent with a H−H separation of 0.91 Å.[12]

In conclusion, osmium− and ruthenium−chloro−phosphine complexes promote the tautomerization of quinoline and 8-methylquinoline to NH tautomers, which lie about 44 kcal·mol^{-1} above the usual CH tautomers. The NH tautomers are stabilized by coordination of the carbon atom at the 2-position of the heterocycle to the metal center and by means of a Cl···HN interaction between the NH hydrogen and a chlorine of the metal fragment.

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Supporting Information Available: Experimental details for the synthesis of the new complexes as well as X-ray crystallographic data (bond distances, bond angles, and anisotropic parameters) for **4** and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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