Metallaheterobicycles

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Aromatic Osmacyclopropenefuran Bicycles and Their Relevance for the Metal-Mediated Hydration of Functionalized Allenes

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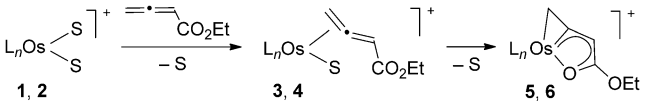
In memory of José Barluenga (1940–2016)

Abstract: *The aromatic osmacyclopropenefuran bicycles [OsTp{κ³-C¹,C²,O-(C¹H₂C²CHC(OEt)O)}(P^{i}Pr₃)]BF₄ (Tp = hydridotris(1-pyrazolyl)borate) and [OsH{κ³-C¹,C²,O-(C¹H₂-C²CHC(OEt)O)}(CO)(P^{i}Pr₃)₂]BF₄, with the metal fragment in a common vertex between the fused three- and five-membered rings, have been prepared via the π-allene intermediates [OsTp(η²-CH₂=CCHCO₂Et)(OCMe₂)(P^{i}Pr₃)]BF₄ and [OsH(η²-CH₂=CCHCO₂Et)(CO)(OH₂)(P^{i}Pr₃)₂]BF₄, and their aromaticity analyzed by DFT calculations. The bicycle containing the [OsH(CO)(P^{i}Pr₃)₂]⁺ metal fragment is a key intermediate in the [OsH(CO)(OH₂)₂(P^{i}Pr₃)₂]BF₄-catalyzed regioselective anti-Markovnikov hydration of ethyl buta-2,3-dienoate to ethyl 4-hydroxycrotonate.*

Heteroatom-containing metallapolycycles are a class of compounds essential to the understanding of aromaticity.[1] π-Aromaticity refers to π-electron conjugation in unsaturated rings, whereas σ-aromaticity is due to σ-electron delocalization in saturated rings.[2] σ-Aromaticity, which was initially proposed to explain the unexpected stability of cyclopropane,[3] has been extended to many other systems with σ-electron delocalization, such as hydrogen clusters,[4] saturated inorganic rings,[5] metal-hydride clusters,[6] hydrocarbon-protected metal clusters,[7] all-metal molecules,[8] and metal–carbonyl clusters.[9] Recently, Xia, Zhu, and co-workers reported σ-aromaticity in an unsaturated metallacyclopropene unit of cyclopropaosmapentalene complexes.[10] Herein, we present the first examples of metallacyclopropenefuran bicycles (Scheme 1), which show significant σ-aromaticity of the three-membered ring and can play a major role in the metal-mediated hydration of functionalized allenes, depending upon the L_nM unit of the bicycle.

One of the solvent molecules of the bis(solvento) complexes [OsTp(OCMe₂)₂(P^{i}Pr₃)]BF₄ (**1**) and [OsH(CO)-(OH₂)₂(P^{i}Pr₃)₂]BF₄ (**2**) was displaced by the sterically less hindered double bond of ethyl buta-2,3-dienoate to form the



L$_n$Os = OsTp(P^{i}Pr$_3$) (**1**, **3**, **5**), OsH(CO)(P^{i}Pr$_3$)$_2$ (**2**, **4**, **6**)
S = Me$_2$CO (**1**, **3**), H$_2$O (**2**, **4**)

Scheme 1. Formation of the osmacyclopropenefuran bicycles **5** and **6**.

η²-allene complexes [OsTp(η²-CH₂=CCHCO₂Et)(OCMe₂)-(P^{i}Pr₃)]BF₄ (**3**) and [OsH(η²-CH₂=CCHCO₂Et)(CO)(OH₂)-(P^{i}Pr₃)₂]BF₄ (**4**), respectively. The aqua complex **4** was characterized by X-ray diffraction analysis (Figure 1).[11] The coordination geometry around the osmium atom can be

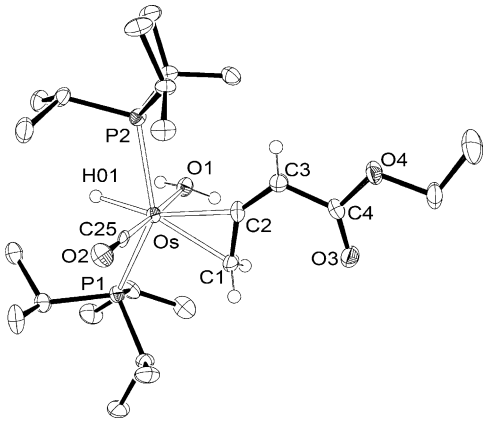


Figure 1. Molecular diagram of the cation **4** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Os–H01 1.62(4), Os–C1 2.193(5), Os–C2 2.129(5), Os–C25 1.825(5), Os–O1 2.162(3), Os–P1 2.4192(13), Os–P2 2.4292(13), C25–O2 1.169(5), C1–C2 1.393(6), C2–C3 1.337(6); P1-Os-P2 145.58(4), H01-Os-C1 154.9(15), H01-Os-C2 161.3(15), O1-Os-C25 178.22(17), C1-C2-C3 138.5(5), Os-C2-C3 147.8(4).

described as a highly distorted octahedron with pseudo-*trans* phosphine ligands (P1-Os-P2 145.58(4)°) at opposite sides of an ideal coordination plane defined by the carbonyl ligand disposed *trans* to the water molecule (O1-Os-C25 178.22-(17)°) and the hydride ligand disposed *trans* to the C1–C2 double bond of the allene, which is oriented almost parallel to the P1-Os-P2 direction. The Os–C1 (2.193(5) Å), Os–C2

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(2.129(5) Å), and C1–C2 (1.393(6) Å) distances as well as the angles C1-C2-C3 (138.5(5)°) and Os-C2-C3 (147.8(4)°) are in agreement with those reported for other osmium–η²-allene complexes.[12] Consistent with the presence of inequivalent phosphines, the $^{31}P\{^1H\}$ NMR spectrum in [D$_8$]THF at 213 K shows an AB spin system centered at $\delta = 24.8$ ppm and defined by $\Delta\nu = 1026$ Hz and $J_{AB} = 126$ Hz. In the ^1H NMR spectrum, the hydride ligand displays a double doublet ($J_{H-P} = J_{H-P'} = 28.1$ Hz) at $\delta = -2.21$ ppm, whereas the resonances corresponding to the coordinated C1 and C2 atoms appear at $\delta = 166.6$ and 15.7 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectrum.

Complexes **3** and **4** evolved into the heterometallabicycle derivatives [OsTp{κ³-*C*¹,*C*²,*O*-(C¹H$_2$C²CHC(OEt)O)}-(P^{i}Pr$_3$)]BF$_4$ (**5**) and [OsH{κ³-*C*¹,*C*²,*O*-(C¹H$_2$C²CHC(OEt)O)}-(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**6**) as a consequence of the displacement of the second solvent molecule by the carbonyl group of the allene. Complex **5** was characterized by a single-crystal X-ray diffraction analysis. Its structure (Figure 2) proves the formation of the heterometallabicycle, which can be regarded as a cyclopropene ring fused to a furan, in which a common vertex has been replaced by an [OsTp(P^{i}Pr$_3$)]$^+$ metal fragment. The coordination polyhedron around the osmium atom can be rationalized as the typical osmium(IV) pentagonal bipyramid with the phosphine and a pyrazolyl group in the axial positions (P1-Os-N5 175.37(15)°), whereas the bicycle and the other two pyrazolyl groups lie at the equatorial plane. The bicycle is planar. The maximum deviation from the best plane through the atoms Os, O1, C1, C2, C3, and C4 is 0.032(4) Å and involves O1. The Os–O1 (2.102(5) Å), O–C1 (1.261(9) Å), C1–C2 (1.437(12) Å), C2–C3 (1.348(11) Å), and C3–Os (1.995(7) Å) bond lengths compare well with those reported for single osmafuran derivatives,[12a,c,g,13] whereas this last bond length (C3–Os) along with the C3–C4 (1.356(11) Å), and C4–Os (2.196(7) Å) distances, which are almost identical to the related Os–C(sp²), C(sp²)–C(sp³), and Os–C(sp³) bond lengths reported for the cyclopropaosmapentalene complexes prepared by Xia, Zhu, and coworkers (1.996(5), 1.376(8), and 2.272(5) Å, and 1.997(4), 1.396(6), and 2.368(4) Å),[10a] support the osmacyclopropene nature of the three-membered ring.[14] Although for an adequate description of the metallabicycle, the resonance structures **I**–**IV** could be taken into account as contributors to the cation **5**, the bond lengths suggest that the contributions from **I** and **IV** are less important than those from **II** and **III**. In agreement with this conclusion, the $^{13}C\{^1H\}$ NMR spectrum of **5** revealed significant carbene character of the Os–C3 bond, as strongly supported by the chemical shift of the C3 resonance, $\delta = 232.0$ ppm, which is characteristic for aromatic osmacycles[10a,12a,c,g,13] and is shifted 65.7 ppm toward lower field with regard to the resonance of the analogous carbon atom of its η²-allene precursor **3** ($\delta = 166.3$ ppm). In accordance with that of **5**, the $^{13}C\{^1H\}$ NMR spectrum of **6** contains the resonance due to the common carbon atom of the bicycle at $\delta = 223.9$ ppm, shifted by 57.3 ppm toward lower field with regard to the resonance corresponding to the C2 atom of **4**. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at $\delta = 19.8$ ppm in accordance with two coplanar fused rings.

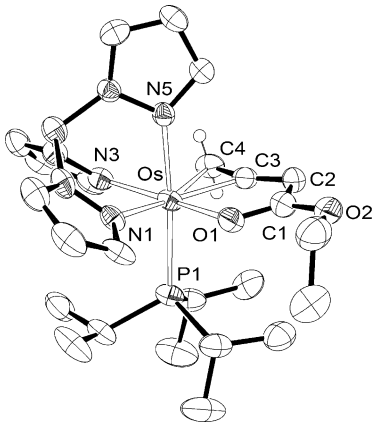
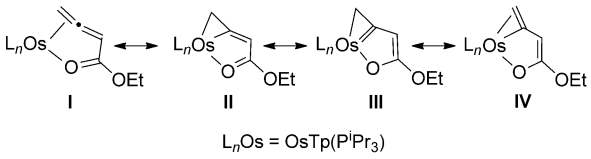
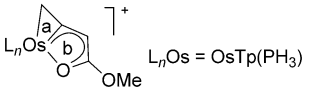


Figure 2. Molecular diagram of the cation **5** (50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Os–C3 1.995(7), Os–C4 2.196(7), Os–O1 2.102(5), C3–C4 1.356(11), C2–C3 1.348(11), C1–C2 1.437(12), C1–O1 1.261(9), C1–O2 1.342(9); C3-Os-O1 74.9(3), C3-Os-C4 37.4(3), C2-C3-C4 158.7(8), C2-C3-Os 121.5(6), P1-Os-N5 175.37(15).

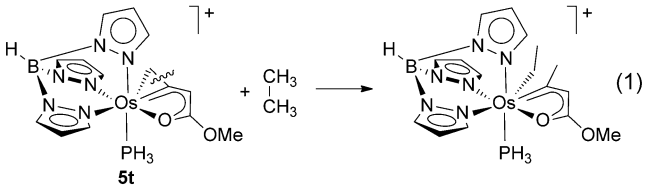


The Wiberg bond indices calculated on the optimized structure of the model cation [OsTp{κ³-*C*¹,*C*²,*O*-(C¹H$_2$C²-CHC(OMe)O)}(PH$_3$)]$^+$ (**5t**) for the Os–C4, Os–C3, and Os–O1 bonds of 0.61 (0.55 in **5**), 0.71 (0.72 in **5**), and 0.52 (0.51 in **5**), respectively, also reveal that the Os–C3 interaction has greater double-bond character than the Os–C4 and Os–O1 interactions, which is consistent with the mainly sp³ hybridization calculated for the carbon atom of the Os–C4 bond (88% p orbital component). Negative nucleus-independent chemical shift (NICS)[1f,15] values were calculated for **5t**. These values, along with structural and spectroscopic data, support the aromatic character of the bicycle. Table 1 collects the isotropic NICS(0) and NICS(1) values, calculated at the center of the rings and at 1 Å above this point, respectively, as well as the dissected NICS(1)$_{zz}$ values, which account for the contributions arising from the *zz* vector component of the

Table 1: Computed NICS values for the two fused rings in the model cation **5t**.

	Ring a	Ring b
NICS(0)	−50.2	−4.3
NICS(1) *syn* to pz	−11.0	−2.5
NICS(1) *syn* to PH$_3$	−16.8	−4.0
NICS(1)$_{zz}$ *syn* to pz	−26.0	−5.4
NICS(1)$_{zz}$ *syn* to PH$_3$	−28.2	−4.2

shielding tensor. In agreement with the asymmetry of the molecule, two different values of NICS(1) and NICS(1)$_{zz}$ are given for each ring, *syn* to the pyrazolyl (pz) group of the Tp ligand and *syn* to the phosphine ligand. The computed NICS values for the three-membered ring were found to be more negative than those of the five-membered ring. The highly positive computed electronic energy of 28.7 kcal mol^{-1} for the isodesmic reaction shown in Equation (1), involving the cleavage of the C–C bond of the three-membered ring, agrees well with values previously reported for related reactions of the cyclopropaosmapentalene described by Xia, Zhu, and co-workers[10] and is additional evidence in favor of the aromatic character of the three-membered ring.



5t

To elucidate the nature of the aromaticity in this ring, we also performed canonical molecular orbital (CMO) NICS calculations. The total contribution to the NICS(0) value of the three-membered ring from the key occupied π molecular orbitals is −0.02 ppm, whereas the contribution from the key occupied σ orbitals is −37.38 ppm (see Figures S2 and S3 in the Supporting Information), which indicates σ-aromaticity. The σ-aromaticity of the three-membered ring was further supported by anisotropy of the induced current density (AICD) analysis.[16] As shown in Figure 3, the diatropic ring currents in this ring only appear in the σ system.

The bis(phosphine) complex **6** reacts with water [Eq. (2)], in contrast to its Tp counterpart **5**, even though the optimized structures and NICS values suggest a similar bonding situation in both compounds (see Figure S1 and Table S1 in the Supporting Information). Thus, complex **6** can only be isolated as a pure white solid in 73% yield, starting from the bis(acetone) solvento precursor [OsH(CO)(OCMe$_2$)$_2$-(P^{i}Pr$_3$)$_2$]BF$_4$ (**2a**), under strict exclusion of water. The reaction with water, which shows a rate comparable to the formation of **6** from **4**, leads to the complex [OsH{κ^3-*C*,*C*,*O*-CH-(CO$_2$Et)=CHCH$_2$OH}(CO)(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**), containing a chelating ethyl 4-hydroxycrotonate ligand, which results from the addition of the water molecule to the three-membered ring of the bicycle.[17] The formation of the allylic alcohol is strongly supported by the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the new compound. The ^{1}H NMR spectrum shows a broad signal at $\delta = 4.20$ ppm corresponding to the OH hydrogen atom, whereas the olefinic resonances are observed at $\delta = 4.81$ and 4.14 ppm. In agreement with the *trans* disposition of the coordinated C–C double bond with respect to the hydride, the spectrum shows a double doublet ($J_{H-P} = 27.7$ Hz, $J_{H-P'} = 27.2$ Hz) toward the lower end of the high-field region ($\delta = -3.63$ ppm). In the ^{13}C{^{1}H} NMR spectrum, the resonances due to the coordinated carbon atoms are observed at $\delta = 48.0$ and 43.9 ppm. The ^{31}P{^{1}H} NMR spectrum contains an AB spin system ($\Delta\nu = 962$ Hz, $J_{AB} = 131$ Hz) centered at $\delta = 25.2$ ppm. The difference in behavior between **5** and **6** may be attributed to the different nature of the OsTp and OsH(CO)(P^{i}Pr$_3$) metal fragments. The robustness of the Tp coordination prevents dissociation processes,[18] which are necessary for inner-sphere metal-mediated attack by water.

Complexes **4**, **6**, and **7** are intermediates in the regioselective anti-Markovnikov hydration, mediated by **2**, of the unsubstituted C–C double bond of ethyl buta-2,3-dienoate to give ethyl 4-hydroxycrotonate [Eq. (3)]. In fluorobenzene at 80 °C with 5 mol% of the catalyst and a 1:5 allenoate/water molar ratio, the transformation is quantitative after 20 h. Allene hydration is of great interest from the point of view of organic synthesis.[19] However, as far as we know, only two

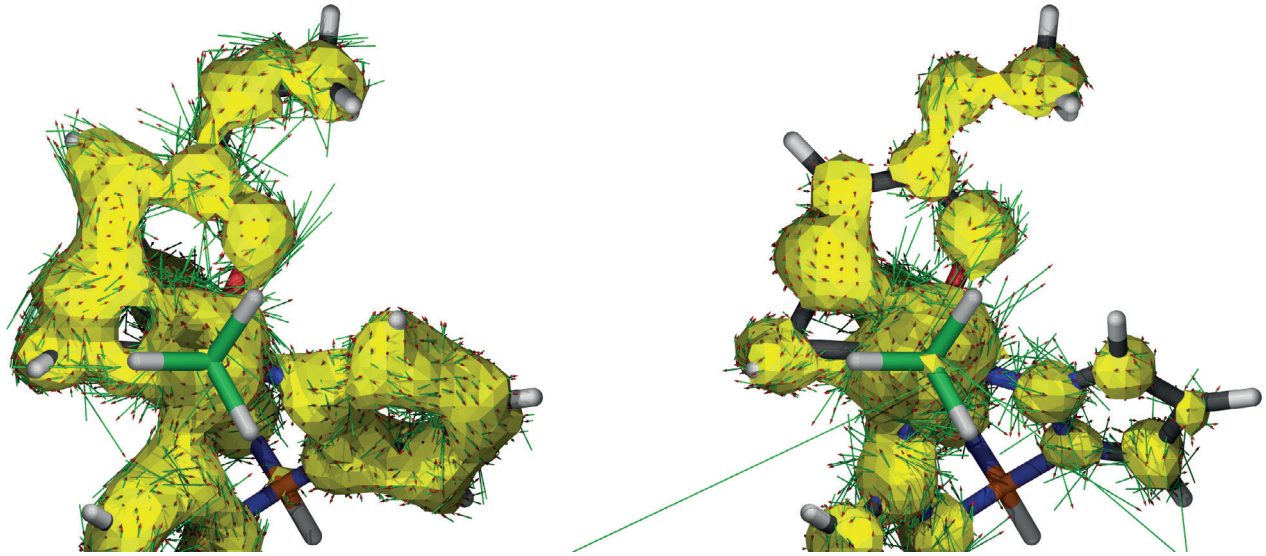
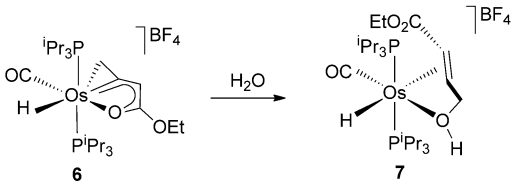
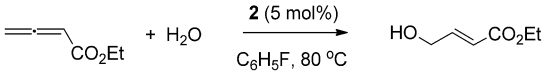


Figure 3. AICD plots of **5t** separated into the σ (left) and π contributions (right) with an isosurface value of 0.03. The magnetic-field vector is orthogonal with respect to the ring plane and points towards the viewer (clockwise currents are diatropic).



6 7 (2)

catalytic systems have been reported previously. Saito et al. described the use of $[Ru_3(CO)_{10}]$ to promote the formation of methyl and γ,δ-unsaturated ketones in the presence of trifluoroacetic acid,[20] whereas Widenhoefer and co-workers demonstrated the gold-mediated generation of allylic alcohols.[21]



(3)

In conclusion, metallacyclopropenefuran compounds have been discovered, isolated in the solid state, and characterized by X-ray diffraction analysis and their aromaticity analyzed by DFT calculations. It was also demonstrated that these novel species can be intermediates in the metal-mediated hydration of allenes to give allylic alcohols.

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Keywords: allenes · aromaticity · hydration · metallaheterobicycles · osmium

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