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Formation of Osmium- and Ruthenium-Cyclobutylidene Complexes by Ring Expansion of Alkylidenecyclopropanes

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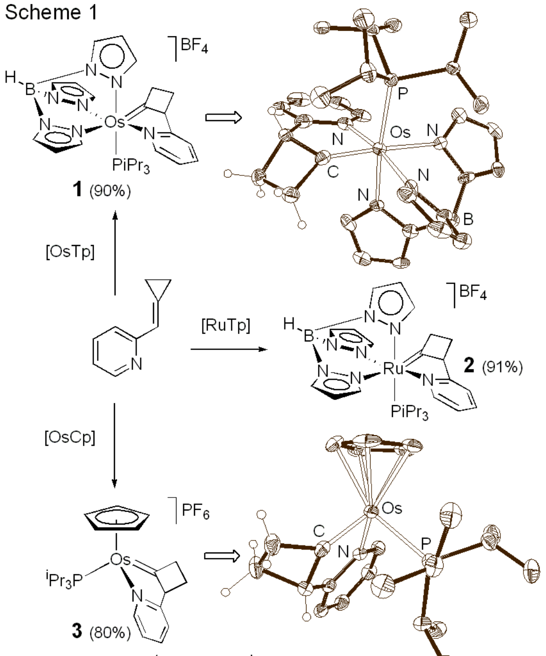
Alkylidenecyclopropanes are receiving much attention as useful building blocks in organic synthesis, due to the presence of an exocyclic C-C double bond and a strained three-membered carbocycle.[1] Thus, a variety of metal-catalyzed processes involving this type of substrates have been developed, [2] including cycloaddition reactions.[3] Several pathways have been proposed for these reactions. They include oxidative addition of the distal or proximal C-C bond of the three-membered ring and regioselective hydrometalation or carbometalation of the olefin moiety.[4] Recently, Fürstner[5] and Shi[6] have also speculated on the hypothetical participation of alkylidene species in Pt- and Pd-catalyzed ring enlargement reactions. It is proposed that they should be formed via cyclopropylmethyl zwitterionic intermediates.[5-7]

The transition metal complexes isolated from reactions involving alkylidenecyclopropanes are extremely scarce. They can be categorized in four groups: (i) η^2-methylenecyclopropanes and 1-3 diene derivatives formed via ring-opening isomerization,[8] (ii) alkylidenemetalacyclobutanes,[9] (iii) η^4-trimethylenemethanes,[10] and (iv) metalacyclopentanes resulting from the oxidative coupling of the C-C double bond with that of an usual olefin.[11] We have discovered a novel group of products (Scheme 1). These cyclobutylidene derivatives are formed as a result from a new reaction pattern between a transition metal complex and an alkylidenecyclopropane (Figure 1).

Treatment at room temperature of the bis-acetone complex $[OsTp(\kappa^1\text{-}OCMe_2)_2(P^iPr_3)]BF_4$ (Tp=hydridotris(pyrazolyl)borate) with 1.3 equiv of (2-pyridyl)methylenecyclopropane in CH_2Cl_2 leads to the cyclobutylidene derivative **1**, as a result from a ring expansion of the organic substrate. Complex **1** is isolated as a green solid in 90% yield. Its X-ray structure proves the ring expansion process and supports the presence of an Os-C double bond (1.847(9)Å).[12] In the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2, the OsC resonance appears at 298.0 ppm.

The $[RuTp(P^iPr_3)]^+$ metal fragment also stabilizes the pyridyl-cyclobutylidene ligand of **1**, despite of the differences previously observed between Os and Ru.[13] Thus, the bis-acetone complex $[RuTp(\kappa^1\text{-}OCMe_2)_2(P^iPr_3)]BF_4$ reacts with (2-pyridyl)methylenecyclopropane as its Os-counterpart, to give **2** as a pale pink solid in 91% yield. The presence of the cyclobutylidene unit in this complex is supported by its $^{13}C\{^1H\}$ NMR spectrum, which shows the RuC resonance at 359.6 ppm. In agreement with related Ru-compounds,[14] it appears shifted by about 60 ppm to lower field with regard to that of **1**.

Scheme 1



$[MTp] = [MTp(\kappa^1\text{-}OCMe_2)_2(P^iPr_3)]BF_4$ M = Os, Ru
$[OsCp] = [OsCp(NCMe)_2(P^iPr_3)]PF_6$

This ring expansion is also extensible to the cyclopentadienyl (Cp) chemistry. Despite of the differences in steric and electronic properties between Tp and Cp,[15] complex $[OsCp(NCCH_3)_2(P^iPr_3)]PF_6$ reacts as its Tp analog. Treatment of a CH_2Cl_2 solution of this compound with 1.5 equiv of (2-pyridyl)methylenecyclopropane affords the cyclobutylidene derivative **3** as a pale pink solid in 80% yield. Complex **3** has been characterized by X-ray diffraction analysis. In agreement with **1**, the Os-C double bond distance is 1.886(5)Å. In the $^{13}C\{^1H\}$ NMR spectrum the OsC resonance is observed at 279.2 ppm.

The ring expansion has been analyzed by DFT(B3PW91/Lanl2dz) calculations for both OsTp- and OsCp-precursors. Figure 1 shows the energy profiles. Starting from η^2-methylenecyclopropane species stabilized by N-atom coordination, the oxidation of the metal center promotes sp^2 to sp^3 rehybridizations of the nitrogen atom and the $C(sp^2)$-atom of the three-membered ring to afford 1-osma-2-azacyclopent-3-ene intermediates.[16] Related complexes resulting from the bidentate coordination of α-β-unsaturated ketones and aldehydes to osmium and ruthenium have been reported.[17] Then the CH_2 group *cis*-disposed to pyridyl in the free substrate undergoes concerted shift from position *5* to position *4* of the five-membered ring. The ring expansion is accompained with the reduction of the metal center and the sp^3 to sp^2 retrohybridization of the initially

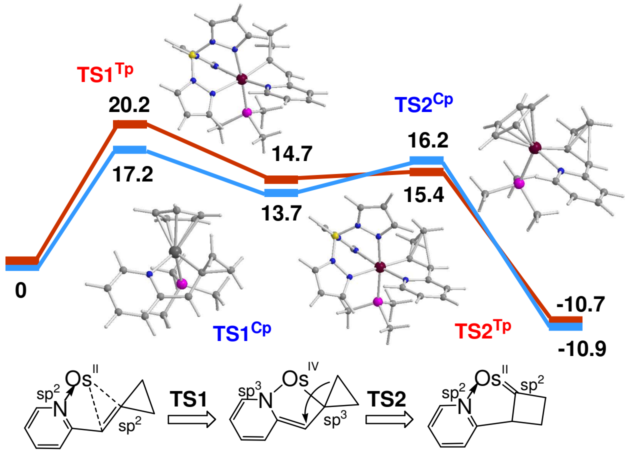


Figure 1. Energy profile for the ring expansion (E, kcal·mol^{-1}).

rehybridized atoms. The formation of the osmaazacyclopentene intermediate is the rate determining step. The Cp ligand imposes less geometrical restrictions than Tp, favoring higher oxidation states.[15] Thus, the replacement of Tp by Cp produces a decrease of the activation barrier for the formation of the osmium (IV) intermediate. Olefin to alkylidene rearrangements by 1,2-hydrogen shift are well documented.[18] In contrast to the CH$_2$ group, the hydrogen atom migrates via the metal center.

The presence of a chelation assistant containing a rehybridizable donor atom, which allows the oxidation of the metal center, appears to be necessary for the ring expansion. While ethyl 2-cyclopropylideneacetate containing ester instead of pyridyl also affords a cyclobutylidene ligand (Scheme 2), benzylidenecyclopropane and phenylmethylenecyclopropane do not undergo ring expansion. Treatment of [OsTp(κ^1-OCMe$_2$)$_2$(P^{i}Pr$_3$)]BF$_4$ with 1.0 equiv of ethyl 2-cyclopropylideneacetate in fluorobenzene leads to **5**, via the η^2-alkylidenecyclopropane intermediate **4**. The latter is detected in solution when the reaction is carried out in CD$_2$Cl$_2$. Its most noticeable spectroscopic feature is the presence of a singlet at 61.0 ppm and a doublet ($J_{C\text{-}P}$ = 6 Hz) at 31.1 ppm, in the $^{13}C\{^1H\}$ NMR spectrum, corresponding to the coordinated atoms of the olefinic moiety. Complex **5** is isolated as a green solid in 67% yield. In agreement with **1** and **3**, its $^{13}C\{^1H\}$ NMR spectrum shows the OsC resonance at 260.2 ppm. The DFT analysis (see supporting information) reveals that the oxidation-rehybridization and the carbon-migration steps have activation barriers higher than those of (2-pyridyl)methylenecyclopropane. Like for the latter, the activation energy of the first step is higher than that of the second one.

In conclusion, alkylidenecyclopropanes containing a chelation assistant at the terminal carbon atom of the olefinic moiety undergo ring expansion promoted by transition metal complexes, to afford cyclobutylidene derivatives. The process is a concerted 1,2- migration of a CH$_2$ group of the three membered ring from an olefinic carbon atom to the other one. It takes place, without direct participation of the metal, on a metallaheterocyclopentene intermediate which is generated from an η^2-methylenecyclopropane species stabilized by coordination of the chelation assistant.

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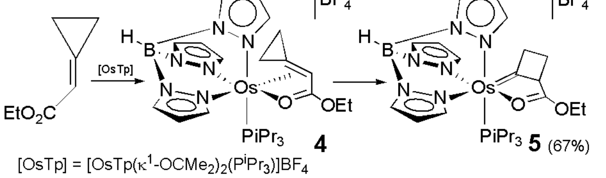
Scheme 2



[OsTp] = [OsTp(κ^1-OCMe$_2$)$_2$(P^{i}Pr$_3$)]BF$_4$

Supporting Information Available: Experimental details for the synthesis, characterization and crystallographic data for **1** and **3**, 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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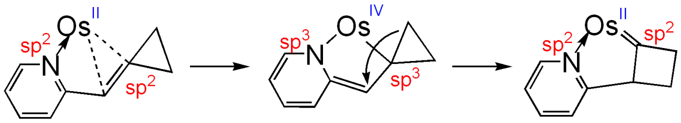

Alkylidenecyclopropanes containing a chelation assistant at the terminal carbon atom of the olefinic moiety undergo an Os or Ru-promoted ring expansion reaction to afford metal cyclobutylidene derivatives. The process occurs through a novel mechanism that implies a 1,2- migration of a CH_2 group of the three membered ring from an olefinic carbon atom to the other one. It takes place, without direct participation of the metal, on a metallaheterocyclopentene intermediate which is generated from an η^2- methylenecyclopropane species stabilized by coordination of the chelation assistant.