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

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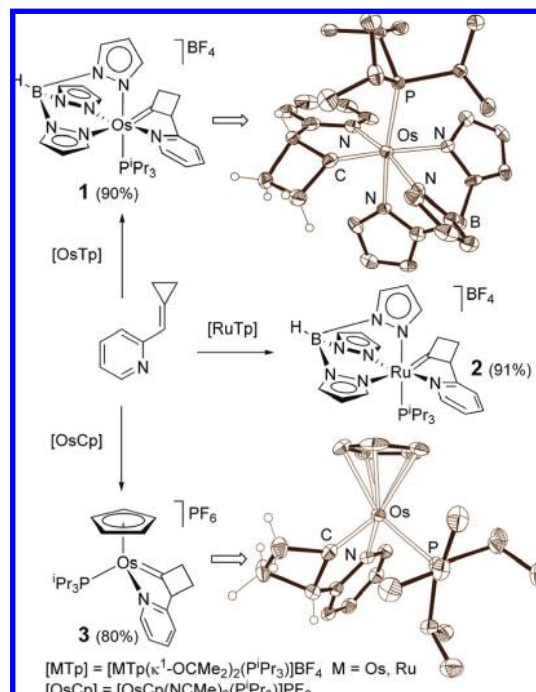
Alkylidenecyclopropanes are receiving much attention as useful building blocks in organic synthesis, due to the presence of an exocyclic C=C double bond and a strained three-membered carbocycle.¹ Thus, a variety of metal-catalyzed processes involving this type of substrates have been developed,² including 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 hydro-metalation or carbometalation of the olefin moiety.⁴ Recently, Fürstner⁵ and Shi⁶ 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 -methylene-cyclopropanes 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 a typical 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 $[\text{OsTp}(\kappa^1\text{-OCMe}_2)_2(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (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 of 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 , the OsC resonance appears at 298.0 ppm.

The $[\text{RuTp}(\text{P}^i\text{Pr}_3)]^+$ metal fragment also stabilizes the pyridyl-cyclobutylidene ligand of **1**, despite the differences previously observed between Os and Ru.¹³ Thus, the bis-acetone complex $[\text{RuTp}(\kappa^1\text{-OCMe}_2)_2(\text{P}^i\text{Pr}_3)]\text{BF}_4$ 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which shows the RuC resonance at 359.6 ppm. In agreement with related Ru-compounds,¹⁴ it appears shifted by ~60 ppm to lower field with regard to that of **1**.

Scheme 1



This ring expansion is also extensible to the cyclopentadienyl (Cp) chemistry. Despite the differences in steric and electronic properties between Tp and Cp,¹⁵ complex $[\text{OsCp}(\text{NCCH}_3)_2(\text{P}^i\text{Pr}_3)]\text{PF}_6$ reacts as

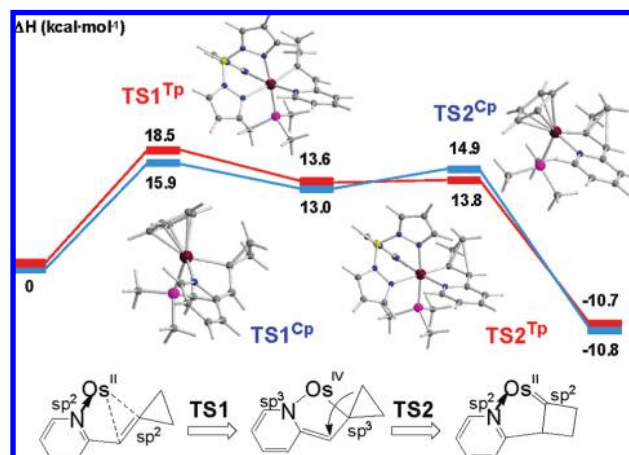


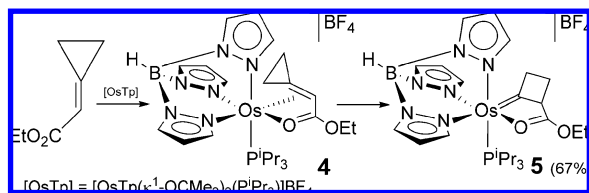
Figure 1. Energy profile for the ring expansion (ΔH , $\text{kcal}\cdot\text{mol}^{-1}$).

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Scheme 2



its Tp analogue. 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the OsC resonance is observed at 279.2 ppm.

The ring expansion has been analyzed by DFT(B3PW91/Lan12dz) 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 a concerted shift from position 5 to 4 of the five-membered ring. The ring expansion is accompanied by the reduction of the metal center and the sp^3 to sp^2 retrohybridization of the initially 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 a 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 $[\text{OsTp}(\kappa^1\text{-OCMe}_2)_2(\text{P}^i\text{Pr}_3)_2]\text{BF}_4$ 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_2Cl_2 . Its most noticeable spectroscopic feature is the presence of a singlet at 61.0 ppm and a doublet ($J_{\text{C-P}} = 6$ Hz) at 31.1 ppm, in the $^{13}\text{C}\{^1\text{H}\}$ 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 $^{13}\text{C}\{^1\text{H}\}$ 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. As in the case of 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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Supporting Information Available: Experimental details for the synthesis, characterization and crystallographic data for **1** and **3**, and the computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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