Tetrahedron Letters 49 (2008) 6800–6803

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and reactivity of an unprecedented osmium(VIII) alkylidene

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ARTICLE INFO

Article history:
Received 10 September 2008
Accepted 11 September 2008
Available online 17 September 2008

ABSTRACT

The synthesis of a family of Os(VIII) alkylidene complexes, the highest oxidation state alkylidenes known to date, and their reactivity toward small organic molecules are reported.

Since the pioneering discoveries of Fischer and Schrock,[1,2] an extraordinary number of transition metal carbene complexes have been synthesized.[3] These compounds play important roles as reagents or as catalysts for carbonyl olefination,[4] olefin metathesis,[5] cyclopropanation,[6] C–H, N–H and O–H insertion,[6,7] ylide formation,[8] and diazoalkane dimerization reactions.[9] However, after more than four decades of research, high oxidation state carbene compounds remain limited to the early and middle transition metals (groups 4–7). To the best of our knowledge, Re(VII) alkylidenes remain the highest oxidation state species containing a M=C bond reported to date.[10]

Inspired by the versatility of Os(VIII) reagents, and by their ability to perform dihydroxylation,[11] aminohydroxylation,[12,13] and diamination reactions,[13] we hypothesized that an Os(VIII) alkylidene species such as **1** might function as a useful reagent for the vicinal carbohydroxylation of alkenes (Fig. 1). During the course of our synthetic investigation, this hypothesis received theoretical backing when Houthausen, Frenking and co-workers reported a DFT study, indicating that the [3+2] reaction between alkylidene **1** and ethylene was an energetically favorable pathway, with a barrier of just 2.3 kcal/mol.[14]

In this Letter, we report the synthesis of an Os(VIII) alkylidene species, and describe its reactivity with a variety of small organic molecules.

The use of diazoalkanes as alkylidene-transfer reagents has been well documented in transition metal chemistry.[15] Thus, our initial attempts to synthesize an Os(VIII) alkylidene species revolved around the reaction of Schrock's trisimido Os(VI) complex **2** with a variety of diazoalkanes (Scheme 1).[16] The major product obtained in these reactions arose from the dimerization of the diazoalkane. However, high-resolution mass spectrometry (+ESI) of the reaction mixture indicated that a species with mass 934.5833 was present, providing the first evidence that the desired alkylidene species had been formed.[17] Although no further

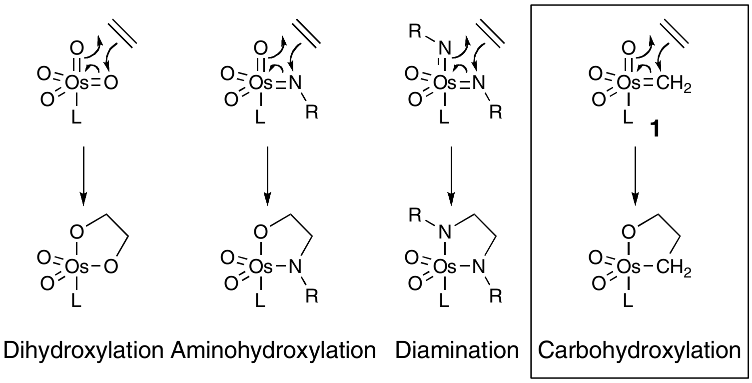

Figure 1. Osmium(VIII) complexes are versatile reagents for organic synthesis.

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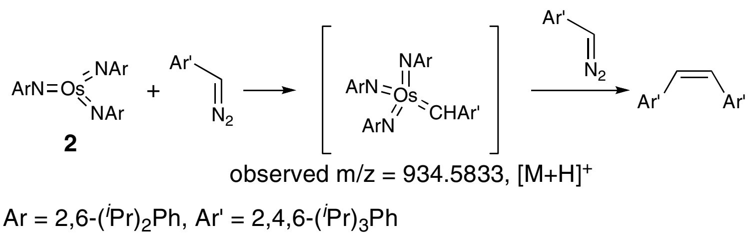
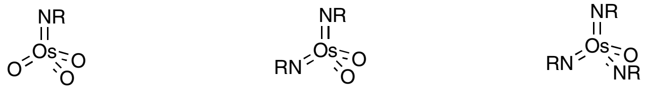
doi:10.1016/j.tetlet.2008.09.064



Scheme 1. Reaction of trisarylimidoosmium(VI) complex **2** with 2,4,6-triisopropylphenyldiazomethane.



3a, R=^{t}Bu
3b, R = 2,6-(^{i}Pr)$_2$Ph

4a, R=^{t}Bu
4b, R = 2,6-(^{i}Pr)$_2$Ph

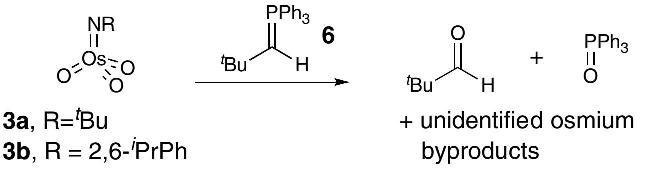
5a, R=^{t}Bu
5b, R = 2,6-(^{i}Pr)$_2$Ph

Figure 2. Osmium(VIII) imido complexes for alkylidene synthesis.

spectroscopic evidence for the alkylidene could be obtained, these preliminary results suggested that the alkylidene may be an intermediate in the dimerization process.

A survey of known high-oxidation state alkylidene complexes indicated that both sterically demanding imido ligands and electron-withdrawing perfluoroalkoxide ligands are often used in combination to stabilize the reactive alkylidene species.[3] In order to apply these design criteria to the problem of an Os(VIII) alkylidene, we synthesized Os(VIII) complexes **3**–**5** containing one, two, and three bulky imido ligands, respectively (Fig. 2).[18] In these complexes, we envisaged that the oxo ligands would fulfill the electron-withdrawing role played by the perfluoroalkoxide ligands in high oxidation state group 6 and 7 alkylidene complexes. In this approach, phosphorous ylides were employed as alkylidene-transfer reagents.

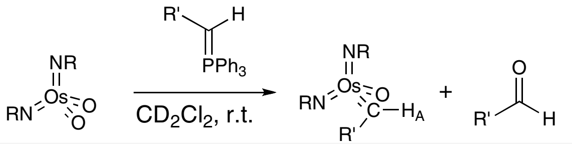
Monoimido complex **3a** proved to be too reactive, and immediately oxidized phosphorous ylide **6**, providing the corresponding aldehyde in quantitative yield (Eq. 1). The osmium byproducts of these reactions could not be identified.



(1)

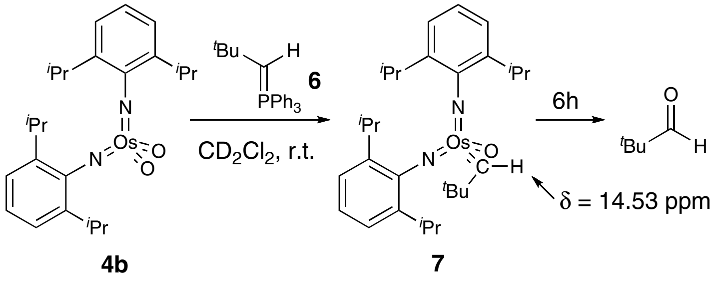
However, when bisoxobisimido-Os(VIII) complex **4b** was treated with phosphorous ylide **6**, we were delighted to observe the formation of Os(VIII) alkylidene **7** (Scheme 2). The alkylidene could be clearly identified by HRMS (–ESI, 611.3048 [M−OH]$^-$), ^{1}H NMR with the alkylidene hydrogen appearing characteristically downfield at 14.53 ppm (in CD_2Cl_2) and by ^{13}C NMR (δ = 286.1, Os=CH^t-Bu).[10b,19] Although transition metal alkylidenes are not reported to give rise to characteristic absorptions in the infrared region, we do observe loss of strong absorption signals at 874 and 885 cm^{-1} (symmetric and anti-symmetric Os=O, in an MO_2 system) and a new weak signal at 991 cm^{-1} (Os=O). The shift in the Os=O stretching frequency is consistent with the replacement of a weak π-donor ligand with a strong π-acceptor alkylidene ligand. The alkylidene is observed as the major component of the reaction mixture by ^{1}H NMR. However, it decays over the course of several hours to produce pivaldehyde. The osmium byproducts of this

Table 1
Synthesis of Osmium (VIII) alkylidene complexes

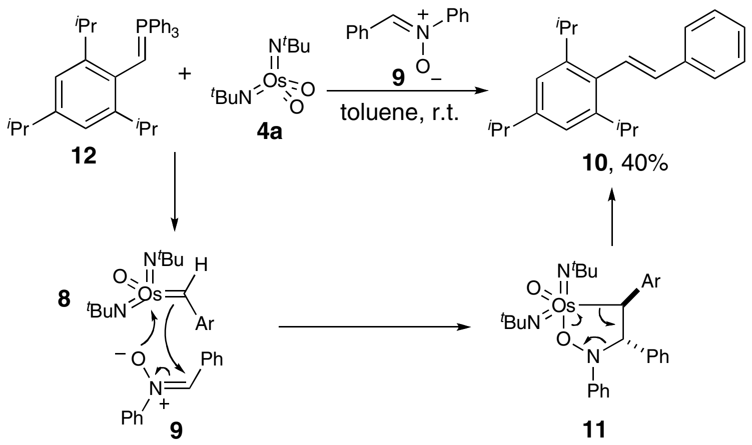


Entry	R	R′	δH_A (ppm)	Alkylidene:aldehyde[a]
1	^{t}Bu	2,4,6-^{i}Pr$_3$Ph	15.25	1:1.3
2	^{t}Bu	^{t}Bu	14.20	2.3:1
3	2,6-^{i}Pr$_2$Ph	2,4,6-^{i}Pr$_3$Ph	15.39	1.4:1
4	2,6-^{i}Pr$_2$Ph	^{t}Bu	14.53	4.0:1

[a] Initial ratio; measured by ^{1}H NMR immediately after phosphorous ylide is added to the bisoxobisimidoosmium(VIII) complex.



Scheme 2. Synthesis and decay of Os(VIII) alkylidene **7**.



Scheme 3. Proposed mechanism for Os(VIII) alkylidene reaction with a nitrone.

decomposition reaction have yet to be identified. To date, our attempts to purify alkylidene **7** have only accelerated the decay. The complex is sensitive to chromatography (even under inert conditions in a glove box), and the slow decay has prevented us from growing crystals for structural characterization.

Despite these limitations, we have explored the parameters that facilitate the formation of this unprecedented high-oxidation state alkylidene. Use of the sterically encumbered trisimidooxoosmium(VIII) complexes **5a** and **5b** severely retards the reaction with the phosphorous ylide, and no alkylidene formation is observed. At the other extreme, use of less sterically demanding substituents on the imido ligands in the bisimidobisoxo series, or on the phosphorous ylide itself leads to very rapid ylide oxidation. Again, no Os(VIII) alkylidene species are observed. To date, we have observed Os(VIII) alkylidene formation using sterically demanding bisimidobisoxoosmium(VIII) species reacting with sterically demanding phosphorous ylides, as outlined in Table 1. In all cases, the alkylidene is readily identified by ^{1}H NMR, and is accompanied by initial simultaneous formation of aldehyde, corresponding to the starting phosphorous ylide.

Despite our attempts to perform these reactions in a variety of solvents, at low temperature, and at a variety of concentrations, all the Os(VIII) alkylidenes decay to release the oxidized alkylidene as an aldehyde over a time frame of 1–6 h.

Having established conditions to synthesize a variety of Os(VIII) alkylidene complexes, our attention turned to investigating their reactivity profile. At the onset of this study, we outlined a potentially useful [3+2] reaction between the alkylidene complex and an olefin. However, our attempts to realize such a transformation have yet to meet with success. We have studied the reaction of alkylidene complexes **7** and **8** with a range of electronically and sterically diverse olefins, as well as with allenes and alkynes. In all cases, the alkylidene decay proved to be faster than reaction with the external reagent. To overcome the inherent instability of these complexes, we turned to highly reactive dipolar species as alkylidene traps. To our delight, reaction of the alkylidene **8** with nitrone **9** led to the rapid formation of olefin **10** in 40% yield (Scheme 3). Mechanistically, we propose that the alkylidene undergoes a [3+2] cycloaddition with the nitrone, and subsequent cycloreversion of the resulting osmacycle (**11**) leads to olefin formation, and concomitant reduction of the Os(VIII) to a more stable Os(VI) species. Control experiments show no reaction between nitrone **9** and ylide **12** in the absence of osmium complex **4a**, confirming the intermediacy of a reactive osmium species.

In conclusion, we have synthesized a series of unprecedented Os(VIII) alkylidene complexes. Despite theoretical studies indicating that these species may be useful for C–C bond formation via [3+2] reaction with olefins, we have yet to observe this experimentally. In our hands, alkylidene decay to release the corresponding aldehyde is too rapid. However, the alkylidenes do undergo [3+2] reaction with reactive nitrones, leading to C–C bond formation, and ultimately to olefin synthesis.

Acknowledgments

We thank Syed Hussaini for performing preliminary experimental investigations. We are grateful to Emory University College of Arts and Sciences for financial support.

Supplementary data

Synthetic procedures and spectral data for new compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.064.

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