Conversion of Osmacyclopentatriene to Osmahexatriene by a 1,2-Hydrogen Shift

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Though the first metal carbene complex was reported[2] almost three decades ago, research on this important class of compounds has continued and remains active today.[3] Quite recently, two types of metallacyclopentatriene complexes have been synthesized, as shown below; they differ in that one, represented by an osmium complex, is planar,[4] while the two examples of the other type are not,[5] even though both types have the biscarbene functionality incorporated into a five-membered metallacycle. Metallacycle

complexes have been shown to be key intermediates in many metal-catalyzed reactions.[6] An intramolecular reaction of a carbene and a metallacycle has been reported recently.[7] Our synthesis of osmacyclopentatriene complexes[4] makes it possible to study the chemistry of a metal carbene in a new situation. Herein we report on one aspect of the reactivity of a metallacyclopentatriene: the base-catalyzed 1,2-hydrogen shift within one of the two carbene moieties.

When a solution of the osmacyclopentatriene complex [Os-(en)$_2$(C$_4$Me$_4$)](CF$_3$SO$_3$)$_2$ (en = ethylenediamine, 1; 0.17 mmol, 0.89 mM) in neat t-BuNH$_2$ is heated under N$_2$ at 39 °C for 24 h, there is no apparent change in the dark green color. However, upon removal of t-BuNH$_2$ by evaporation, a new complex, the triflate (CF$_3$SO$_3^-$) salt of 2, is obtained in ~79% yield by recrystallization from acetone and ether.[8] In a more concentrated solution, formation of other products besides 2 is observed. 2 is a conjugated osmahexatriene complex having the terminal alkene double bond coordinated to the metal center. The ^{1}H NMR spectrum of 2 shows two doublets at δ 4.38 (J = 9.6 Hz) and 2.45 (J = 9.0 Hz) and a triplet at δ 4.09 (J = 9.5 Hz) for the vinyl protons of the coordinated double bond and three singlets at δ 2.12, 1.86, and 1.79 for the remaining three methyl groups. A singlet at δ 283.5 and two singlets at δ 177.3 and 161.6 in the ^{13}C{^{1}H} NMR spectrum are assigned to the carbene carbon and the two uncoordinated sp^2 carbons, respectively. We conclude that one

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(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapters 9 and 18.
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(8) The reaction of complex 1 with less steric hindered amine, e.g., propylamine, takes place rapidly even at room temperature to form 2 and a mixture of other unidentified products.
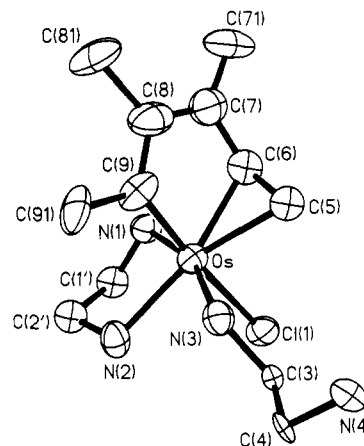
Figure 1. Structure and labeling scheme for the cation in 3 (the bidentate ethylenediamine has a disorder, of which one component is shown here): Os–C(5) 2.135 (13), Os–C(6) 2.124 (14), Os–C(9) 1.895 (11), Os–Cl(1) 2.576 (2), C(5)–C(6) 1.459 (17), C(6)–C(7) 1.405 (16), C(7)–C(8) 1.372 (22), C(8)–C(9) 1.434 (21) Å; N(1)–Os–C(9) 91.4 (4), N(1)–Os–C(6) 77.6 (4), N(1)–Os–C(5) 116.2 (4), N(1)–Os–Cl(1) 83.8 (2), N(1)–Os–N(2) 78.8 (3), N(1)–Os–N(3) 162.3 (4), C(5)–Os–C(6) 40.15 (5), C(5)–C(6)–C(7) 120.9 (11), C(6)–C(7)–C(8) 111.3 (13), C(7)–C(8)–C(9) 117.6 (12), C(8)–C(9)–Os 116.6 (10), Os–C(6)–C(7) 113.3 (10)°.

of the carbene ligands of the metallacyclopentatriene has isomerized, yielding a coordinated alkene, while the other remains intact. In deuterated water, the protons of the amino groups and the carbene methyl group of 2 exchange with deuterium, as has been reported for 1.[4] However, no hydrogen–deuterium exchange is observed for the three vinyl protons in 2.

On treatment of the triflate salt of 2 with 0.2 M hydrochloric acid for ~12 h, after removal of HCl and water under vacuum, a new complex, the triflate salt of 3, is isolated. 3 has a ^{1}H NMR spectrum in acetone-d_6 similar to that of 2. The three proton signals of the coordinated double bond have shifted to δ 4.63 (d, J = 9.9 Hz), 3.74 (t, J = 9.2 Hz), and 2.55 (d, J = 9.0 Hz), and the three methyl groups are observed at δ 2.12, 1.71, and 1.69. Its ^{13}C{^{1}H} NMR spectrum consists of a singlet at δ 274.4, corresponding to the carbene carbon.
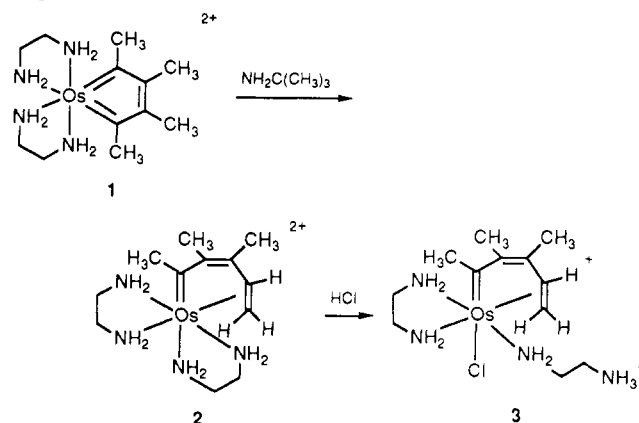

A single crystal of the chloride salt of 3[9] has been obtained, and the X-ray analysis has established the structure (Figure 1).[10] In 3, a chloride ion has replaced the amine group trans to the carbene carbon in 2, and the dissociated amine group is protonated by acid. As is true of 1, the five-membered ring [Os–C(6)–C-(7)–C(8)–C(9)] of 3 is also planar, in this case within the maximum deviation of 0.1022 Å [C(9)]. On isomerization of a carbene function in 1, C(5) moves out of the plane: the dihedral angle between the Os–C(5)–C(6) plane and the Os–C(6)–C(7)–C-(8)–C(9) plane is 73.3°, which is consistent with the angle of 16.3°

(9) The chloride salt is obtained by eluting 3 with 0.2 M hydrochloric acid solution through ion-exchange resin, followed by vacuum removal of volatiles.

between the planes of Os–C(5)–C(6) and Os–N(1)–N(2)–N(3) (mean deviation is 0.0098 Å). The remaining carbene double bond [Os–C(9)] distance of 1.895 (11) Å is slightly shorter than those observed in **1** [1.940 (8) and 1.931 (8) Å] and a previously reported osmium carbene complex [Os(=CHPh), 1.94 (1) Å].[11]

In an earlier study of the reaction scheme represented by A, a mechanism involving initial deprotonation of the carbene ligand followed by protonation of the metal–carbon bond was proposed.[12]
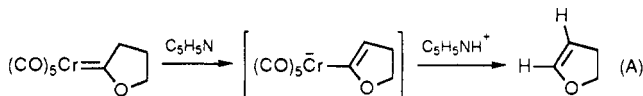

A similar mechanism, i.e., the formation of an α-substituent-deprotonated metallacycle intermediate **4**, can also account for the osmacyclopentatriene isomerization we have observed. Protonation of the Os–C single bond of intermediate **4**, followed by the coordination of the resulting double bond to the metal center, will generate **2**. Only recently has any work on the chemistry of substituents on metallacycles been reported.[13] The isomerization described here, involving activation of an α-substituent by a carbene, is a new reaction mode of a metallacycle.

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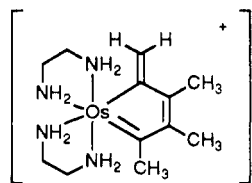
(10) Crystal data for **3** (120 K): $C_{12}H_{29}N_4Cl_3Os\cdot0.5C_2H_5OH$, triclinic, $P\bar{1}$; $a = 7.388$ (1) Å, $b = 8.756$ (1) Å, $c = 16.149$ (2) Å, $\alpha = 95.54$ (1)°, $\beta = 102.93$ (1)°, $\gamma = 90.31$ (1)°, $V = 1013.0$ (2) Å^3, $Z = 2$, $D_{calcd} = 1.805$ g cm^{-3}, $\mu = 15.643$ mm^{-1}. A green tabular plate (0.14 × 0.10 × 0.04 mm) was used for data collection (Siemens P4RA, 0.0° < 2θ < 108.5°, Cu Kα). Of 2702 reflections collected, 2473 were independent, and 2316 with $F_o > 6.0\sigma(F)$ were considered observed and were empirically corrected for absorption by using the XABS program (this program generates an absorption correction tensor based on F_o and F_c differences. Hope, H.; Moezzi, B. Chemistry Department, University of California at Davis). The atoms were located by Patterson methods and refined by full-matrix least-squares. Hydrogen atoms were calculated and refined by a riding model with fixed isotropic U: $R = 5.83\%$, $R_w = 6.62\%$ ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = \sum ||F_o| - |F_c|| w^{1/2} / \sum |F_o| w^{1/2}$), all data $R = 6.03\%$, GOF = 1.04. All computer programs and sources of scattering factors are contained in SHELXTL PLUS (G. M. Sheldrick, A program for crystal-structure determination, version 4.0, 1989, Siemans Analytical X-ray Instruments, Madison, WI).

The 1,2-hydrogen shift of alkyl carbene ligands can also occur in the absence of base. For example, Fischer observed a transient aryl–alkyl chromium carbene species formed at –40 °C which undergoes a 1,2-hydrogen shift to generate a stable alkene complex.[14] When a crystal of **1** under dynamic vacuum is heated at ~165 °C for 1.2 h, only very small amount of it decomposes. Among the products is that resulting from the 1,2-hydrogen shift, **2**, which is detected by ^{1}H NMR spectroscopy. The synthesis and isomerization of the osmacyclopentatriene complex represent an overall conversion of two dialkyl-substituted alkynes to a metal vinyl carbene species. This transformation may serve as a model

$$M + 2\,\text{—}\!\!\equiv\!\!\text{—} \rightarrow M\!\!=\!\!\text{—}\!\!=\!\!\text{—}\!\!=$$
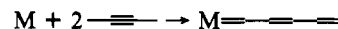
for the generation of a metal carbene catalyst in the polymerization of internal alkynes catalyzed by certain transition metal complexes.[15] A conjugated metallacyclohexatriene has also been proposed as an intermediate in carbene alkyne coupling reactions to form cyclic organic compounds.[3a] Research on the reactivity of the metallahexatriene complexes through introduction of alkene or alkyne molecules onto the metal center is in progress.

Supplementary Material Available: Listings of analytical and spectroscopic data for compounds **2** and **3** and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients (7 pages); table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Book Reviews[*]

Ions, Electrodes and Membranes. Second Edition. By J. Koryta (Czechoslovak Academy of Sciences). J. Wiley & Sons: New York. 1991. xiv + 198 pp. $74.95. ISBN 0-471-93079-2.

This little book introduces concepts about ionic solutions, electrochemistry, and membranes in a nonmathematical way to scientists from other disciplines, especially, from its content and approach, to those in biology. Crammed into 198 pages is a rather superficial treatment of many topics. For example, within the space of 4 pages, one can find a discussion of ionically and electronically conductive polymers, alkali metals in liquid ammonia, and high-temperature superconductors. Even cold fusion gets a paragraph. Reading this book reminds me very much of those tours that take you through eight countries in five days: there are lots of interesting things to see, but you never feel like you have seen enough. Nevertheless, this is a useful little book. It is full of interesting facts and information, and the personal and informal approach of the author makes it rather easy reading. I found a few small errors, e.g., Nafion is not "a perfluorostyrene sulphonate" (p 142) and the equation

on p 150 and the current axis and caption for Figure 94 on p 174 cannot be correct. It is hard to justify the high price of the hardback version, but a cheaper paperback version, if one were available, would be a nice way to introduce ionic solutions, electrochemistry, and membranes to a neophyte.

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Strategies and Tactics in Organic Synthesis. Volume 3. Edited by Thomas Lindberg (The Upjohn Company). Academic Press: San Diego. 1991. xx + 544 pp. $125.00. ISBN 0-12-450282-2.

Volume 3 of the well-known series *Strategies and Tactics in Organic Synthesis* maintains the same high standards of presentation and content that were set by the preceding volumes. Each of the thirteen chapters is written either by leading industrial or academic practitioners and focuses on material of current interest. The contributions are full of insights concerning the tribulations and triumphs associated with the research endeavor.

The book is very enjoyable to read, being both entertaining and highly educational. The style differs from that of the original literature in a

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