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Direct Aziridination of Alkenes by a Cationic (Salen)ruthenium(VI) Nitrido Complex

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The transfer of atoms or groups, multiply bonded to a transition metal, to an alkene is an important class of reactions.[1] Although the transfer of oxygen atoms from metal−oxo species to alkenes to give epoxides[2] and 1,2-diols[3] as well as the transfer of carbenes from metal carbenes to give cyclopropanes[4] have been extensively studied, less is known about the reactions of metal−nitrogen multiple bonds with alkenes. Nitrido complexes of manganese(V) porphyrin,[5] manganese(V) salen,[6] and ruthenium(VI) porphyrin[7] have been used as reagents for the aziridination of alkenes; however, these complexes need to be activated with an electrophile such as trifluoroacetic anhydride to produce imido complexes as the active species. Although a wide variety of transition metal−nitrido complexes are known, none of them has been found to effect direct aziridination of alkenes. The cationic species *cis*-$[(\mathrm{terpy})\mathrm{Os(N)Cl}_2]^+$ reacts directly with aryl-substituted alkenes; however, unusual η^2-azaallenium complexes, in which the nitrogen atom inserts between the two carbons of the alkene, are formed rather than aziridines.[8] This osmium complex also undergoes a [4 + 1] cycloaddition reaction with cyclohexadienes to produce bicyclic osmium amido complexes.[9]

We recently reported the synthesis and reactivities of a highly electrophilic, cationic ruthenium(VI) nitrido complex containing the cyclohexylene-bridged salen ligand, *N,N′*-bis(salicylidene)*o*-cyclohexyldiamine dianion (salchda).[10] We report herein that this ruthenium(VI) nitrido species undergoes direct nitrogen atom transfer to alkenes at room temperature to produce (salen)ruthenium aziridine complexes.

No reaction occurs between $[\mathrm{Ru^{VI}(N)(salchda)(CH_3OH)}]\mathrm{PF_6}$ (**1**) (0.16 mmol) and 2,3-dimethyl-2-butene (8.4 mmol) in $\mathrm{CH_2Cl_2}$ (5 mL) for over 24 h at room temperature. However, upon addition of a nitrogen donor ligand (2.5 mmol) such as pyridine (py) or 1-methylimidazole (1-MeIm), **1** reacts readily with 2,3-dimethyl-2-butene to give a blue solution, which then gradually changes to green after ca. 3 h at room temperature.[11] $[\mathrm{Ru^{IV}(Az^1{}_{(-H)})(salchda)(py)}]\mathrm{PF_6}$ (**2**, $\mathrm{Az^1}$ = 2,2,3,3-tetramethylaziridine)[12] and $[\mathrm{Ru^{III}(Az^1)(salchda)(py)}]\mathrm{PF_6}$ (**3**)[13] have been isolated from the blue and green solutions, respectively.[14] Compound **2** is formulated as a $\mathrm{Ru^{IV}}$ complex with a deprotonated aziridine ligand. The electrospray ionization mass spectrometry (ESI-MS) of **2** in $\mathrm{CH_2Cl_2}$ (+ve mode) shows peaks at $m/z = 599$ and 520, which are assigned to the parent ion $[\mathrm{Ru^{IV}(Az^1{}_{(-H)})(salchda)(py)}]^+$ and $[\mathrm{Ru^{IV}(Az^1{}_{(-H)})(salchda)}]^+$ respectively. **2** is diamagnetic, consistent with its formulation as a d^4 $\mathrm{Ru^{IV}}$ complex.[10] Solutions of **2** in various solvents such as $\mathrm{ClCH_2CH_2Cl}$, $\mathrm{CH_3CN}$, or $\mathrm{CH_3OH}$ are found to be converted to **3** within hours at room temperature.

Compound **3** has a room-temperature magnetic moment of $\mu_{\mathrm{eff}} = 1.99\ \mu_{\mathrm{B}}$ (Gouy method), consistent with its formulation as a d^5 $\mathrm{Ru^{III}}$ complex. The ESI-mass spectrum (+ve mode) of **3** in $\mathrm{CH_2Cl_2}$ shows a single peak at $m/z = 600$, which is assigned to the parent ion $[\mathrm{Ru^{III}(Az^1)(salchda)(py)}]^+$. The N−H stretch of the aziridine, however, is not observed in the IR. The structure of **3** has been determined by X-ray crystallography (Figure 1). The Ru−N(aziridine) distance of 2.1049(19) Å is similar to the Ru−N(py) distance of 2.1068(19) Å, consistent with a neutral aziridine ligand. The C−C (1.513 Å) and C−N (1.506, 1.511 Å) distances in the aziridine ligand are all indicative of single bonds. There are a few examples of aziridine complexes, including that of Rh,[15] W,[16] Mn,[16] and Co;[17] these are all prepared by direct ligation of the aziridine to the metal center.

1 also reacts at room temperature with a variety of aryl-substituted alkenes including styrene and *trans*-β-methylstyrene in the presence of py or 1-MeIm to give the corresponding ruthenium(III) aziridine complexes, which are air-stable dark-green crystalline solids. For these substrates, however, the orange solution of **1** is changed directly to green upon addition of the alkene without going through a blue intermediate. This suggests that the intermediate $\mathrm{Ru^{IV}(Az_{(-H)})}$ species for these substrates are highly unstable and are reduced rapidly to the corresponding $\mathrm{Ru^{III}(Az)}$ species. The structure of the complex obtained from *trans*-β-methylstyrene, $[\mathrm{Ru^{III}(Az^2)(salchda)(1\text{-}MeIm)}]\mathrm{PF_6}$ (**4**, $\mathrm{Az^2}$ = *trans*-2-methyl-3-phenylaziridine),[18] has been determined by X-ray crystallography (Figure S1, Supporting Information). The aziridine ligand is in the *trans* configuration, indicating that no isomerization has occurred. The Ru−N(aziridine) distance (2.097 Å) is similar to that in **3**.

The free aziridines (Az) can be liberated in 90−95% yield (GC) from the ruthenium(III) aziridine complexes, $[\mathrm{Ru^{III}(Az)(salchda)(L)}]\mathrm{PF_6}$ (Az = 2,2,3,3-tetramethylaziridine, 2-phenylaziridine or *trans*-2-methyl-3-phenylaziridine; L = py or 1-MeIm) by reduction of Ru(III) to Ru(II) with zinc amalgam in acetonitrile in the presence of 10 equiv of $\mathrm{PPh_3}$ (Supporting Information).

The kinetics of the reaction of **1** with 2,3-dimethyl-2-butene in the presence of pyridine under argon have been studied by UV−vis spectrophotometric methods. The UV−vis spectral changes in 1,2-dichloroethane at 298.0 K show that this reaction consists of two well-separated consecutive steps (Figure S2). The final spectra for the first and second steps are very similar to those of **2** and **3**, respectively; hence, the reaction scheme is **1** → **2** → **3**. The kinetics of the first step were studied under pseudo-first-order conditions ($[\mathrm{Ru^{VI}}] = 1.0 \times 10^{-3} - 1.0 \times 10^{-4}$ M, [alkene] = 1.0−1.8 M, [py] = 0.02−1.0 M), the growth of **2** at 642 nm followed first-order kinetics for over three half-lives. The pseudo-first-order rate constant, k_{obs}, is independent of $[\mathrm{Ru^{VI}}]$, depends linearly on [alkene], but exhibits saturation behavior on [py] (Figure S3). The rate law of the reaction is shown in eq 1.

$$\frac{-\mathrm{d}[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{N})]}{\mathrm{d}t} = k_2[\mathrm{Ru}^{\mathrm{VI}}(\mathrm{N})][alkene]\left(\frac{K[\mathrm{py}]}{1+K[\mathrm{py}]}\right) \qquad (1)$$

The observed saturation kinetics on varying [py] is consistent with

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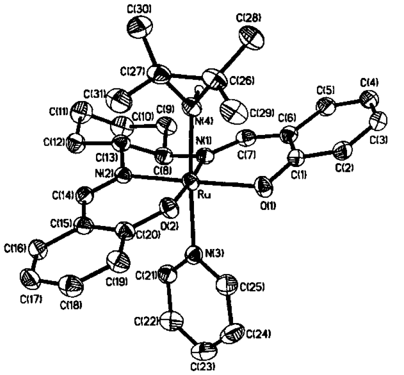
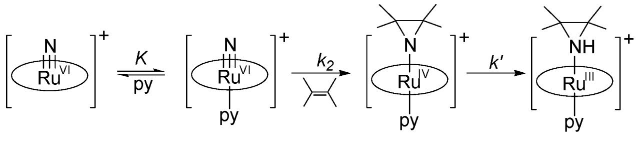


Figure 1. Molecular structure of the cation of **3**, thermal ellipsoids drawn at the 30% probability (H atoms are omitted except N(4)−H). Selected bond lengths (Å) and bond angles (deg): Ru−N(4) 2.1049(19), Ru−N(3) 2.1068(19), Ru−N(1) 2.009(2), Ru−N(2) 1.9844(19), Ru−O(1) 2.0047(16), Ru−O(2) 2.0098(16), C(26)−C(27) 1.513(4), N(4)−C(26) 1.506(3), N(4)−C(27) 1.511(3), N(3)−Ru−N(4) 177.03(7), Ru−N(4)−C(26) 131.67(16), Ru−N(4)−C(27) 133.76(15), C(26)−N(4)−C(27) 60.21(16), N(4)−C(26)−C(27) 60.04(15), N(4)−C(27)−C(26) 59.75(15)

Scheme 1



1 **2** **3**

the reversible binding of pyridine to ruthenium(VI) (Scheme 1), and the equilibrium constant K is (15.6 ± 1.1) M^{-1} at 298.0 K. k_2 (which represents the rate constant for the reaction between the pyridine-coordinated species, $[Ru^{VI}(N)(salchda)(py)]^+$, and the alkene) is found to be (4.61 ± 0.20) × 10^{-3} M^{-1} s^{-1} at 298.0 K.

The second step of the reaction, i.e., **2** → **3**, also follows first-order kinetics for over three half-lives. The first-order rate constant, k', is independent of $[Ru^{VI}]$, [alkene] or [py]. At 298.0 K, k' is found to be (6.2 ± 0.1) × 10^{-4} s^{-1}. The conversion of **2** to **3** was also independently studied using a pure sample of **2**; the rate constants in 1,2-dichloroethane and acetonitrile were found to be (9.0 ± 0.3) × 10^{-4} and (8.2 ± 0.3) × 10^{-4} s^{-1}, respectively, at 298.0 K. The reaction of **1** with 2,3-dimethyl-2-butene can be represented by Scheme 1.

A similar ligand-accelerated reaction has also been observed in the epoxidation of alkenes by $[Cr^V(salen)(O)]^+$.[19] In the five-coordinate complex the Cr atom is displaced 0.53 Å above the salen plane; however, it is pulled back to 0.26 Å upon axial ligation with pyridine *N*-oxide. This is accompanied by a weakening of the Cr═O bond. It is likely that similar geometrical changes occur upon coordination of pyridine to $Ru^{VI}≡N$, which would reduce the reorganization energy for atom transfer.

The conversion of $Ru^{IV}(Az_{(-H)})$ to $Ru^{III}(Az)$ species requires the addition of a H atom. In the reaction of **1** with excess styrene in py/CH_2Cl_2, in addition to the formation of the corresponding ruthenium(III) aziridine complex, PhC≡N was detected (GC) in the solution in 25% yield.[20] Also a close examination of the UV/vis spectral changes for **2** → **3** indicates that only 69 ± 2% of **3** is formed. These observations are consistent with a mechanism that involves an initial rate-limiting, aziridine ring-opening rearrangement of $Ru^{IV}(Az_{(-H)})$ to a species **RuX** which can transfer H atoms to $Ru^{IV}(Az_{(-H)})$. When the substrate is styrene, loss of H atoms from **RuX** results in the formation of PhC≡N, among other products. A possible candidate for **RuX** is an η^2-azaallenium complex that is similar to that formed between $[(terpy)Os(N)Cl_2]^+$ and aryl-substituted alkenes,[8] where the nitrogen atom of the aziridine is inserted between the carbon−carbon bond.

This is the first example of direct nitrogen atom transfer from a metal nitride to alkenes. The remarkable steric and electronic tunability of salen will be utilized to probe the mechanism of the aziridination reaction and the reduction of $Ru^{IV}(Az_{(-H)})$ to $Ru^{III}(Az)$.

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Supporting Information Available: Experimental procedures and kinetics. X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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(11) Oxygen donor ligands such as DMSO and DMF can also induce the reaction of **1** with the alkene, but they are less effective.
(12) Preparation of **2**: Pyridine (0.2 mL) was slowly added with stirring to an orange suspension of **1** (100 mg, 0.16 mmol) in 2,3-dimethyl-2-butene (1 mL, 8.4 mmol) and CH_2Cl_2 (5 mL) at room temperature. The resulting deep-blue solution was stirred for 5 min. Addition of pentane gave a dark-blue microcrystalline solid which was recrystallized from dichloromethane/*n*-pentane at −20 °C. Yield: 50%. Anal. Calcd. for $C_{31}H_{37}N_4O_2PF_6Ru$: C, 50.07; H, 5.01; N, 7.53. Found: C, 49.87; H, 5.20; N, 7.72. UV−vis ($Cl_2CH_2CH_2Cl_2$): λ_{max} [nm] (ϵ [mol^{-1} dm^3 cm^{-1}]) 240 (28840), 362 (11560), 660 (2900). ^1H NMR (300 MHz, CD_3CN): δ 8.8 (s, 1H), 8.6 (s, 1H), 7.2−7.8 (m, 9H), 6.8−7.0 (m, 4H), 4.0−4.1 (t, 1H), 4.2−4.3 (t, 1H), 3.2−3.2 (d, 1H), 3.0−3.1 (d, 1H), 0.93 (s, 6H) and 0.91 (s, 6H).
(13) Preparation of **3**: The same procedure for the preparation of **2** was used except that the reaction time was 3 h. The resulting green solution was filtered and concentrated to ca. 2 mL. Addition of diethyl ether resulted in the precipitation of a green solid, which was dissolved in CH_2Cl_2 and loaded onto a silica gel column. Elution with CH_2Cl_2/acetone (30:1) followed by recrystallization from CH_2Cl_2/diethyl ether afforded **3** as dark-green crystals. Yield: 50 mg (41%). Anal. Calcd. for $C_{31}H_{38}N_4O_2PF_6Ru$: C, 50.00; H, 5.14; N, 7.52. Found: C, 49.84; H, 5.01; N, 7.69. UV−vis ($Cl_2CH_2CH_2Cl_2$): λ_{max} [nm] (ϵ [mol^{-1} dm^3 cm^{-1}]) 239 (30900), 378 (15300), 506 (1720), 712 (4480).
(14) Pyridine also induces N−N coupling of **1**. However, the reaction of 1 with the alkene is predominant when [RuN] < 1mM and [alkene] > 1 M.
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(18) **4** was prepared by a procedure similar to that for **3** using *trans-β*-methylstyrene. Yield: (30%). Anal. Calcd. for $C_{33}H_{37}N_5O_2PF_6Ru$: C, 50.70; H, 4.77; N, 8.96. Found: C, 49.97; H, 4.97; N, 9.05. ESI-MS in CH_2Cl_2: m/z = 636 (M^+).
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(20) PhC≡N was also observed when *trans-β*-methylstyrene was used as substrate. However, we have not been able to detect any organic products when 2,3-dimethyl-2-butene was used, presumably because the products could not be separated from other organics in the solution by GC.

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