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Reactivity of Nitrido Complexes of Ruthenium(VI), Osmium(VI), and Manganese(V) Bearing Schiff Base and Simple Anionic Ligands

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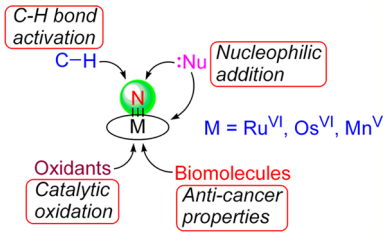
CONSPECTUS

Nitrido complexes (M≡N) may be key intermediates in chemical and biological nitrogen fixation and serve as useful reagents for nitrogenation of organic compounds. Osmium(VI) nitrido complexes bearing 2,2′:6′,2″-terpyridine (terpy), 2,2′-bipyridine (bpy), or hydrotris(1-pyrazolyl)-borate anion (Tp) ligands are highly electrophilic: they can react with a variety of nucleophiles to generate novel osmium(IV)/(V) complexes.



This Account describes our recent results studying the reactivity of nitrido complexes of ruthenium(VI), osmium(VI), and manganese(V) that bear Schiff bases and other simple anionic ligands. We demonstrate that these nitrido complexes exhibit rich chemical reactivity. They react with various nucleophiles, activate C−H bonds, undergo N···N coupling, catalyze the oxidation of organic compounds, and show anticancer activities. Ruthenium(VI) nitrido complexes bearing Schiff base ligands, such as $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ (salchda = *N,N*-bis(salicylidene)*o*-cyclohexyldiamine dianion), are highly electrophilic. This complex reacts readily at ambient conditions with a variety of nucleophiles at rates that are much faster than similar reactions using Os^{VI}≡N. This complex also carries out unique reactions, including the direct aziridination of alkenes, C−H bond activation of alkanes and C−N bond cleavage of anilines. The addition of ligands such as pyridine can enhance the reactivity of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$. Therefore researchers can tune the reactivity of Ru≡N by adding a ligand L *trans* to nitride: L−Ru≡N. Moreover, the addition of various nucleophiles (Nu) to Ru^{VI}≡N initially generate the ruthenium(IV) imido species Ru^{IV}−N(Nu), a new class of hydrogen-atom transfer (HAT) reagents.

Nucleophiles also readily add to coordinated Schiff base ligands in Os^{VI}≡N and Ru^{VI}≡N complexes. These additions are often stereospecific, suggesting that the nitrido ligand has a directing effect on the incoming nucleophile. M≡N is also a potential platform for the design of new oxidation catalysts. For example, $[Os^{VI}(N)Cl_4]^-$ catalyzes the oxidation of alkanes by a variety of oxidants, and the addition of Lewis acids greatly accelerates these reactions. $[Mn^{V}(N)(CN)_4]_2^-$ is another highly efficient oxidation catalyst, which facilitates the epoxidation of alkenes and the oxidation of alcohols to carbonyl compounds using H_2O_2. Finally, M≡N can potentially bind to and exert various effects on biomolecules. For example, a number of Os^{VI}≡N complexes exhibit novel anticancer properties, which may be related to their ability to bind to DNA or other biomolecules.

1. Introduction

The chemistry of transition metal nitrido complexes has attracted much interest in recent years.[1−6] Nitrido complexes (M≡N) are believed to be one of the key intermediates in chemical and biological nitrogen fixation.[3,4] They are also useful reagents for nitrogenation of organic compounds.[7,8] Extensive work by Meyer,[9−14] Mayer,[15,16] and Brown[17,18] also demonstrates that osmium(VI) nitrido complexes bearing terpy, bpy, or Tp ligands are highly electrophilic, and they react with a variety of nucleophiles to generate novel osmium(IV)/(V) products. Although the corresponding ruthenium(VI) nitrido complexes are expected to be much more reactive, there are few examples of electrophilic ruthenium nitrido complexes reported in the literature.[19−21]

In this Account, we describe our results on the reactivity of nitrido complexes of ruthenium(VI), osmium(VI), and manganese(V). We demonstrate that these complexes

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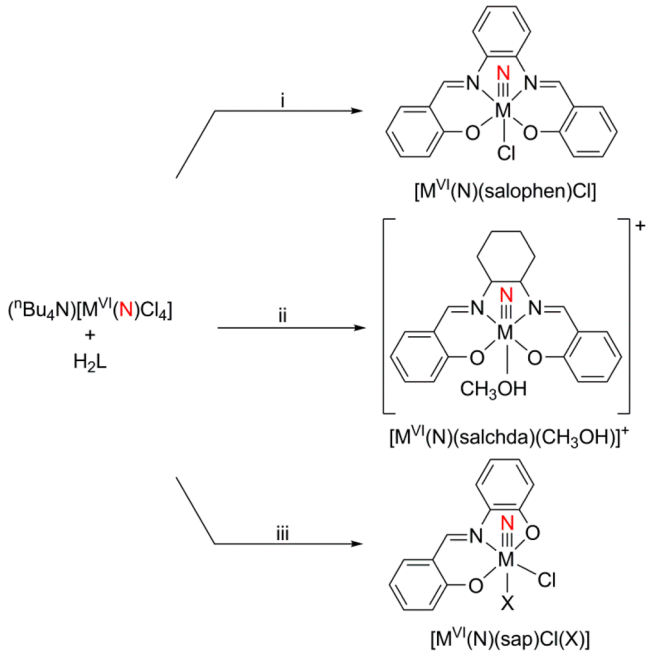
SCHEME 1. Synthesis of Salen Nitrido Complexes of Osmium(VI) and Ruthenium(VI)[a]



[a]Reagents and conditions: (i) M = Os, CH_3CN, 2,6-lutidine, 40 °C; M = Ru, CH_2Cl_2, 2,6-lutidine, 23 °C; (ii) M = Os or Ru, CH_3OH, 23 °C; (iii) M = Os, X = OH_2, refluxing CH_3OH; M = Ru, X = nil, CH_3OH, 23 °C.

possess novel chemical properties, including reaction with various nucleophiles, coupling of the nitrido ligands, C−H bond activation of alkanes, C−N bond cleavage of anilines, catalytic oxidation, and anticancer properties. The main ancillary ligands that we employ in these complexes are Schiff base ligands, although other simple ligands such as Cl^- and CN^- are also used.

2. Synthesis and Characterization of Nitrido Complexes of Ruthenium(VI) and Osmium(VI) Bearing Schiff Base Ligands

Schiff-base ligands have occupied a central role in the development of coordination chemistry. They are able to stabilize metal centers in high oxidation states, for example, Mn^V(salen)(N)[22,23] and Os^{VI}(salen)$(O)_2$.[24] They are also easily prepared, and steric and electronic effects can be readily tuned by using various substituents. We have synthesized a series of nitrido complexes of osmium(VI) and ruthenium(VI) bearing various Schiff base ligands (Scheme 1). These are d^2 diamagnetic compounds, as evidenced by well-resolved NMR signals in the normal region. In the IR, the medium ν(M≡N) band is located at 1036−1098 cm^{-1}, which has been confirmed by using ^{15}N-labeling. X-ray structures of some of these compounds have been determined (Figure 1). They are all octahedral complexes except Ru^{VI}(N)(sap)Cl, which has a square pyramidal geometry. The Os≡N distances are around 1.66 Å, while the Ru≡N distances are around 1.59 Å. These compounds exhibit electrophilic properties, and their reactions with various nucleophiles will be discussed below.

3. N···N Coupling Reaction

Coupling of two terminal nitrides to give N_2 is of fundamental interest because it can provide insights into the reverse N≡N cleavage process. Ware and Taube first reported that coupling of $Os^{VI}(N)Cl_3(py)_2$ occurs at 100 °C in pyridine to give N_2 and $Os^{III}Cl_3(py)_3$.[25] Heterocoupling of $Os^{VI}(Tp)(N)Cl_2$ and $Mo^{VI}(N)(Et_2NCS)_3$ at 50 °C was reported by Brown.[26] Rapid N···N coupling reactions of $Os^{VI}N-Os^{V}N$/$Os^{V}N-Os^{V}N$ bearing ammine, terpy, or bpy ancillary ligands can be achieved at room conditions; however, at least one Os^{VI} center has to be reduced to Os^V by either photochemical, electrochemical, or chemical means.[27−29]

On the other hand, coupling of $Os^{VI}N-Os^{VI}N$ containing salen ancillary ligand occurs smoothly at room temperature (within 1−2 d) in the presence of a N-heterocyclic ligand (X). Coordination of X onto $[(salchda)Os^{VI}{\equiv}N]^+$ activates the complex toward N···N coupling to give initially $[(X)(salchda)Os^{III}N{\equiv}NOs^{III}(salchda)(X)]^{2+}$, which is then reduced to the more stable mixed-valence species $[(X)(salchda)Os^{III}N{\equiv}NOs^{II}(salchda)(X)]^+$ (eqs 1−3, L = salchda ligand and X represents a N-heterocyclic ligand).[30]

$$[Os^{VI}(N)(L)(MeOH)]^+ + X \rightleftharpoons [Os^{VI}(N)(L)(X)]^+ + MeOH \quad (1)$$

$$2[Os^{VI}(N)(L)(X)]^+ \rightarrow [(X)(L)Os^{III}N{\equiv}NOs^{III}(L)(X)]^{2+} \quad (2)$$

$$[(X)(L)Os^{III}N{\equiv}NOs^{III}(L)(X)]^{2+} + e^- \rightarrow [(X)(L)Os^{III}N{\equiv}NOs^{II}(L)(X)]^+ \quad (3)$$

X-ray crystallography of the $[Os-N_2-Os]^{5/6+}$ species resulting from 4-Mepy or 4-^{t}Bupy activated N···N coupling shows that the salchda ligands have isomerized to a *cis*-β configuration, which would prevent the N-heterocyclic and N_2 ligands from competing for the same dπ electrons of the osmium centers (Figure 2).

The corresponding ruthenium nitrido species undergoes similar ligand-induced N···N coupling, but at a much more rapid rate (within minutes at room temp). For example, when $[Ru^{VI}(salchda)N]^+$ is dissolved in DMF, it rapidly turns green to give the corresponding $[Ru^{III}(salchda)(DMF)_2]^+$ and N_2. The rather negative reduction potential of $Ru^{VI/V}$ (E_{pc} = −0.67 V vs $Cp_2Fe^{+/0}$) in CH_3CN suggests that the coupling

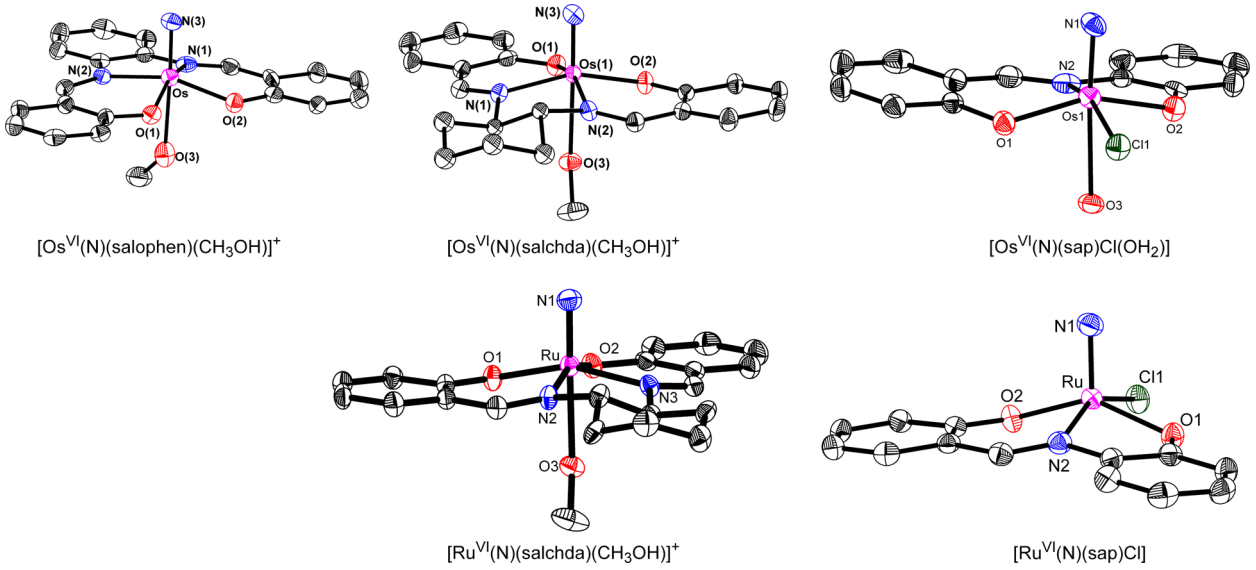


FIGURE 1. X-ray structures of osmium(VI) and ruthenium(VI) nitrido complexes bearing Schiff base ligands.

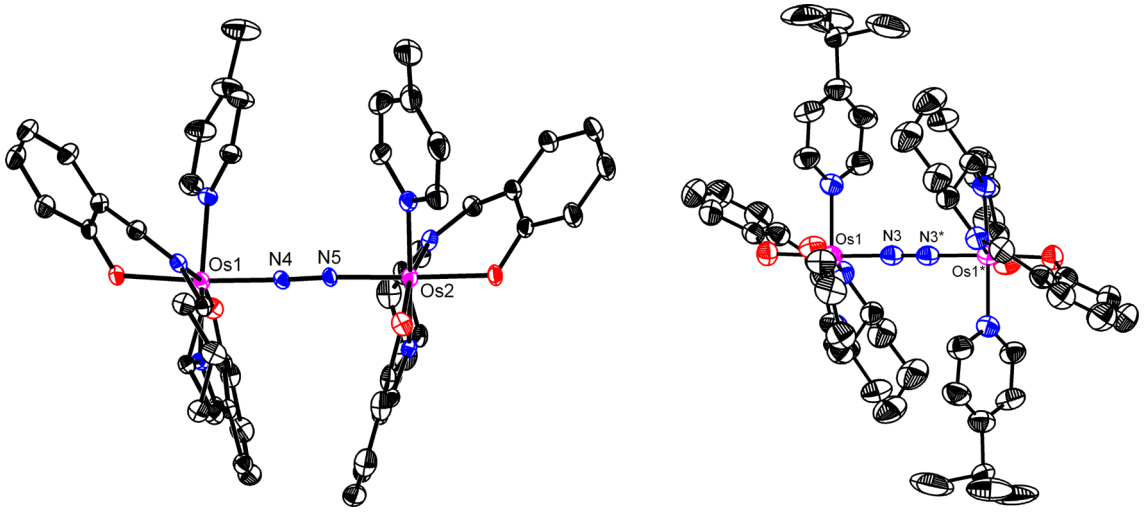


FIGURE 2. Molecular structures of $\{[Os(salchda)(4\text{-}Mepy)]_2(\mu\text{-}N_2)\}^{+}$ (left) and $\{[Os(salchda)(4\text{-}^{t}Bupy)]_2(\mu\text{-}N_2)\}^{2+}$ (right).

reaction should occur with $Ru^{VI}-Ru^{VI}$, as shown in eqs 4 and 5 (L = salchda ligand).[31,32]

$$2[Ru^{VI}(N)(L)]^{+} + 2DMF \rightarrow [(DMF)(L)Ru^{III}N{\equiv}NRu^{III}(L)(DMF)]^{2+} \quad (4)$$

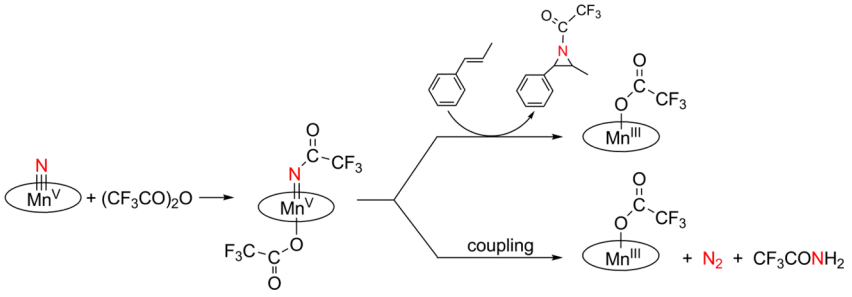
$$[(DMF)(L)Ru^{III}N{\equiv}NRu^{III}(L)(DMF)]^{2+} + 2DMF \rightarrow 2[Ru^{III}(L)(DMF)_2]^{+} + N_2 \quad (5)$$

Manganese(V) nitrido complexes containing porphyrin or salen ligands have been used as amination reagents.[7,8,22] In the presence of electrophiles such as trifluoroacetic anhydride (TFAA) or trifluoroacetic acid (TFA), these nitrido complexes are converted to the corresponding imido species, which can then transfer the imido groups to electron-rich alkenes.[23] We found that in the absence of alkenes, these imido species readily undergo N···N coupling reaction (Scheme 2).[33] Mechanistic studies suggest that the (imido)manganese(V) complexes undergo coupling to give initially manganese(III) μ-diazene species, which then undergo rapid decomposition to give Mn(III) and N_2.

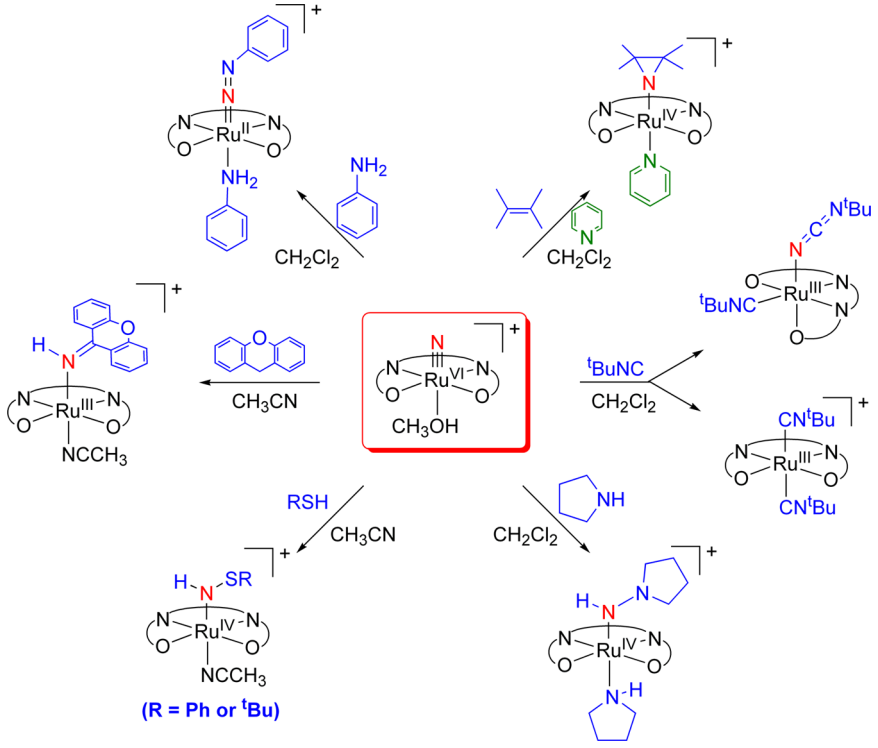
4. Electrophilic Reactivity of (Salen)ruthenium(VI) Nitrido Complexes

We found that the ruthenium(VI) nitrido complex $[Ru^{VI}(N)(salchda)(CH_3OH)]^{+}$ is much more reactive toward various nucleophiles than osmium(VI) nitrido complexes. Although it undergoes a facile N···N coupling reaction, as described in the previous section, it reacts more rapidly (especially in

SCHEME 2. N···N Coupling vs Aziridination of Alkene by (Salen)manganese(V) Nitrido Species in the Presence of TFAA



SCHEME 3. Reaction of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ with Various Nucleophiles



dilute solutions) with a variety of nucleophiles such as amines, isocyanides, thiols, and alkenes to produce novel ruthenium species in lower oxidation states, as summarized in Scheme 3.[34−38]

4.1. Reaction with Aliphatic Amines. $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ reacts rapidly with secondary amines such as pyrrolidine (HNC_4H_8) to produce a ruthenium(IV) hydrazido(1−) species, $[Ru^{IV}(N\{H\}NC_4H_8)(salchda)(HNC_4H_8)]^+$. The presence of the hydrazido(1−) ligand is evidenced by IR (ν(N−H) = 3217 and 3276 cm^{-1}) and ^1H NMR (N−H = 13.3 ppm in CD_3CN) spectroscopy. The X-ray structure of the PF_6^- salt shows a Ru−N(hydrazido) distance of 1.940 (5) Å and an acute Ru−N−N angle of 129.4(4)° (Figure 3).[31]

Kinetic studies on the reaction of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ with morpholine indicate that the reaction is first order in Ru^{VI} concentration and second order in morpholine concentration, consistent with the mechanism shown in Scheme 4. The third-order rate constant, $k_3 = (2.08 \pm 0.07) \times 10^6\ M^{-2}\ s^{-1}$ in CH_3CN at 298 K is over 4 orders of magnitude larger than that of the reaction of *trans*-$[Os^{VI}(N)(tpy)Cl_2]^+$ with morpholine, which has a similar rate law with $k_3 = 58.1 \pm 1.2\ M^{-2}\ s^{-1}$.[11]

4.2. Reaction with Anilines: C−N Bond Cleavage. Although osmium(VI) nitrido complexes react readily with aliphatic amines, their reaction with anilines (which are weaker nucleophiles) has not been reported. We found that

$[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ reacts readily with anilines in CH_2Cl_2 at room temperature to produce initially a ruthenium(IV) hydrazido complex, $[Ru^{IV}(N{-}NH_2Ph)(salchda)(NH_2Ph)]^+$, which then undergoes rapid $2e^-/1H^+$ transfer to give the ruthenium(II) diazonium complex, $[Ru^{II}(salchda)(N_2Ph)(NH_2Ph)]^+$. The latter species then undergoes unimolecular decomposition to generate $[Ru^{III}(salchda)(NH_2Ph)]^+$, N_2, and C_6H_6. The proposed mechanism is shown in Scheme 5, which is supported by kinetic studies and DFT calculations. The overall result is the cleavage of the strong C–N bond of aniline (BDE = 103 kcal mol^{-1}) by $Ru^{VI}{\equiv}N$.[37]

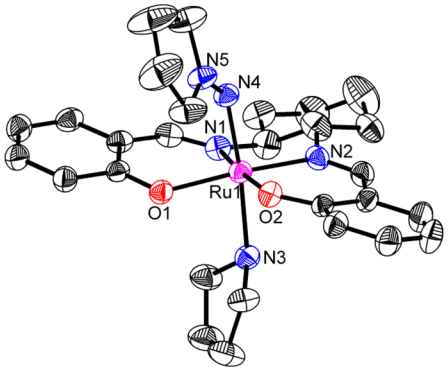
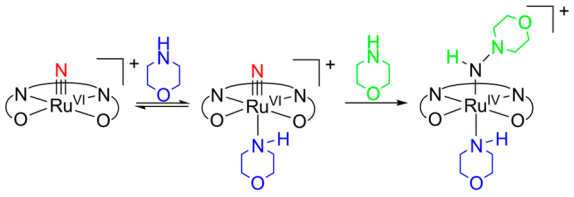


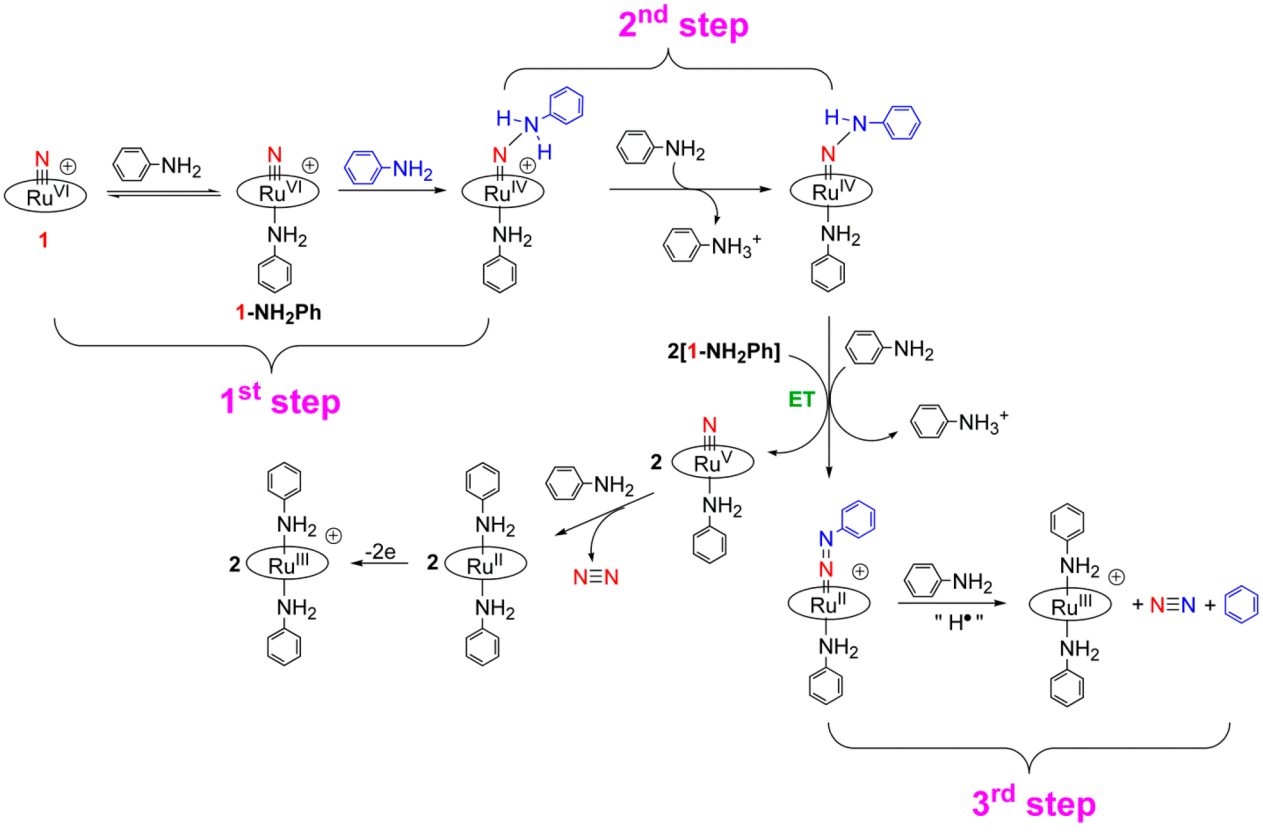
FIGURE 3. Molecular structure of a ruthenium(IV) hydrazido complex.

SCHEME 4. Proposed Mechanism for the Formation of Ru(IV) Hydrazido Complex



4.3. Reaction with Isocyanides. Although isocyanide is a good nucleophile, its reaction with nitrido complexes was not previously reported. We found that isocyanide (RNC, R = ^{t}Bu or Cy) readily undergoes nucleophilic attack at the nitrido ligand of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ to generate the carbodiimido complex $[Ru^{III}(NCNR)(salchda)(CNR)]$, presumably this reaction goes through a $[Ru^{IV}(NCNR)(salchda)(CNR)]^+$ intermediate, which is then reduced to the Ru^{III} product.[35] The bis-isocyanide complex, $[Ru^{III}(salchda)(CNR)_2]^+$, is also produced, which comes from RNC induced N···N coupling. The X-ray structure of $[Ru^{III}(NCN^tBu)(salchda)(CN^tBu)]^+$ is shown in Figure 4. The *tert*-butylcarbodiimido unit has a typical diazacumulene structure, and the salchda ligand has isomerized to a *cis*-β configuration from the usual planar geometry in the nitrido complex.

SCHEME 5. Proposed Mechanism for the C–N Cleavage of Aniline



4.4. Reaction with Thiols. Reaction of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ with a stoichiometric amount of RSH in CH_3CN gives the corresponding (salen)ruthenium(IV) sulfilamido species, $[Ru^{IV}(N\{H\}SR)(salchda)(NCCH_3)]^+$ (R = ^{t}Bu or Ph). This reaction occurs by initial nucleophilic attack of RSH at the nitrido ligand followed by proton shift.[36] This is in contrast to the reaction of *trans*- or *cis*-$[Os^{VI}(N)(terpy)Cl_2]^+$ with RSH, which produces the corresponding osmium(IV) sulfilimido species, *trans*- or *cis*-$[Os^{VI}(NS\{H\}R)(terpy)Cl_2]^+$ (R = Ph, 4-MePh, or 3,5-Me_2Ph), where the S atom is protonated instead of the N atom.[12] Moreover, although $[Os^{VI}(NS\{H\}R)(terpy)Cl_2]^+$ is relatively inert, $[Ru^{IV}(N\{H\}SR)(salchda)(NCCH_3)]^+$ is able to abstract a H-atom from another thiol or from hydrocarbons with relatively weak C–H bonds, as shown in Scheme 6.

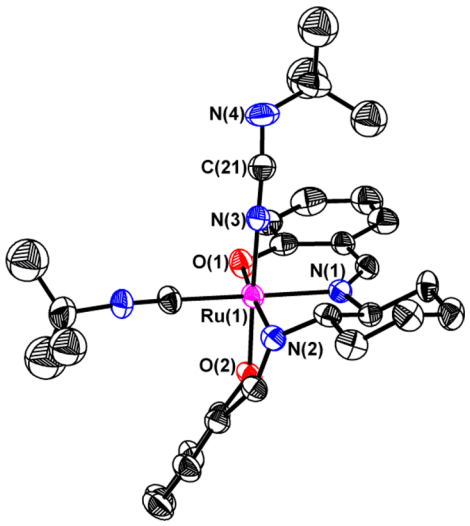
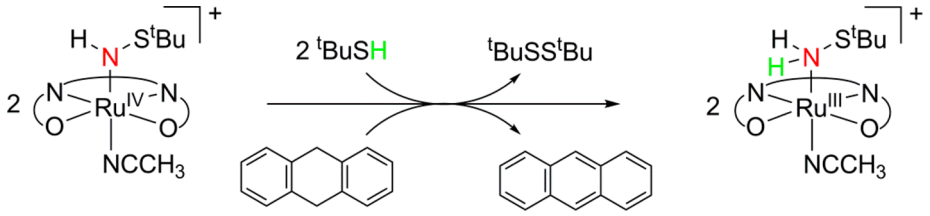


FIGURE 4. Molecular structure of ruthenium(III) carbodiimido complex.

The reaction of $[Ru^{IV}(N\{H\}S^tBu)]^+$ with ^{t}BuSH/^{t}BuSD occurs with a kinetic isotope effect (KIE) value of 3.2. On the other hand, much larger KIEs were observed in the oxidation of hydrocarbons; the KIE values for 9,10-dihydroanthracene (DHA), 1,4-cyclohexadiene (CHD), and fluorene are 51, 56, and 11, respectively. There is also a good linear correlation between log(rate constant) vs bond dissociation energies (BDEs) of hydrocarbons (Figure 5), except for the more bulky hydrocarbons diphenylmethane and triphenylmethane, which react much more slowly than expected from their BDEs, most likely due to the substantial steric hindrance for HAT.

4.5. Reaction with Alkenes. Aziridination of alkenes has been reported using nitrido complexes of (salen)manganese(V) or (porphyrin)ruthenium(VI).[7,8,22,23] However, these complexes need to be activated with an electrophile such as TFAA to produce imido complexes as the active species. The osmium(VI) nitride, *cis*-$[Os^{VI}(N)(tpy)Cl_2]^+$, reacts with aryl-substituted alkenes

SCHEME 6. H-Atom Abstraction by Ru(IV) Sulfilamido Species



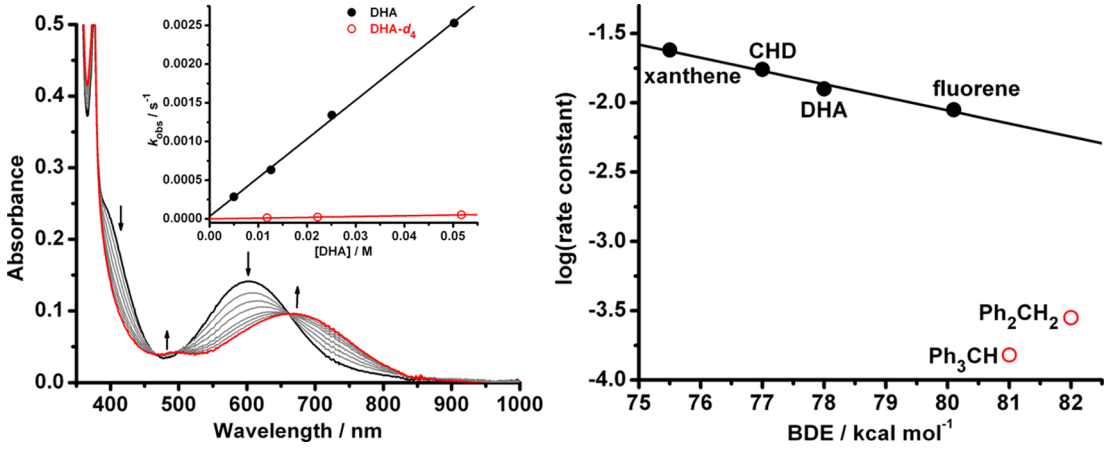


FIGURE 5. (left) Spectrophotometric changes at 1200 s intervals for the reaction of $[Ru^{IV}(N\{H\}S^tBu)(salchda)(NCCH_3)]^+$ (4.0×10^{-5} M) with DHA (3.1×10^{-2} M) at 298.0 K in CH_3CN. Inset shows the plot of k_{obs} vs [DHA] (●) and [DHA-d_4] (○). (right) Plot of log(rate constant) vs BDE of hydrocarbons.

at 60 °C in CH_3CN to produce unusual η^2-azaallenium complexes.[18] It also undergoes a [4 + 1] cycloaddition reaction with 1,4-cyclohexadienes at 65 °C to produce bicyclic osmium amido complexes.[17] On the other hand, $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ can undergo direct N-atom transfer to a variety of alkenes at room temperature in the presence of N-donor ligands such as pyridine or 1-methylimidazole (1-MeIm), to produce ruthenium(III) aziridine complexes.[34] The parent aziridine can be released from the ruthenium center by treatment with PPh_3. These reactions probably go through the initial formation of ruthenium(IV) azirido complex, for example, $[Ru^{IV}(Az_{(-H)})(salchda)(py)]^+$, which is then reduced to $[Ru^{III}(Az)(salchda)(py)]^+$. However, the source of the H-atom is uncertain. When 2,3-dimethyl-2-butene was used as substrate, the ruthenium(IV) species $[Ru^{IV}(Az_{(-H)})(salchda)(py)]^+$ (Az = 2,2,3,3-tetramethylaziridine) could be isolated as a blue diamagetic PF_6^- salt, which is then gradually reduced to the green paramagnetic ruthenium(III) complex, $[Ru^{III}(Az)(salchda)(py)]^+$. The X-ray structure of the latter complex (PF_6^- salt) is shown in Figure 6. Results from kinetic studies (Figure 7) are consistent with the mechanism shown in Scheme 7. A similar ligand-accelerated reaction has also been observed in the epoxidation of alkenes by $[Cr^V(salen)(O)]^+$.[39]

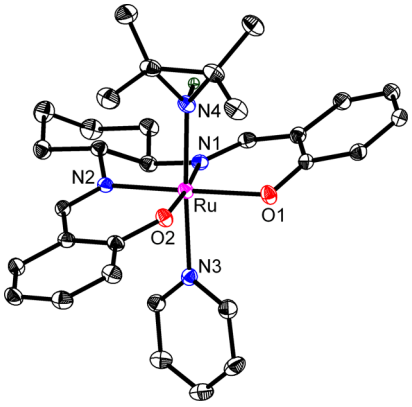


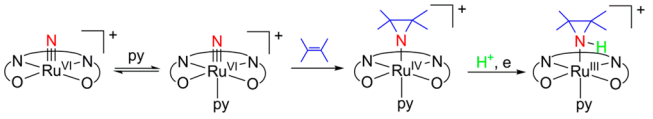
FIGURE 6. Molecular structure of $[Ru^{III}(Az)(salchda)(py)]^+$ (Az = 2,2,3,3-tetramethylaziridine).

5. C−H Bond Activation of Alkanes by Ru^{VI}≡N

Highly active nitrido species have been generated *in situ* by thermolysis, photolysis, or electrospray ionization; these species can undergo intramolecular C−H bond activation.[40−43] On the other hand, the stable and readily isolated nitrido complex $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ can undergo intermolecular C−H bond activation at room temperature. It reacts readily with xanthene or DHA in CH_3CN to produce $[Ru^{III}(N\{H\}=xanthene_{(-2H)})(salchda)(NCCH_3)]^+$ and $[Ru^{III}(N\{H\}=DHA_{(-2H)})(salchda)(NCCH_3)]^+$, respectively, as detected by ESI/MS.[38] The X-ray structure of $[Ru^{III}(N\{H\}=xanthene_{(-2H)})(salchda)(NCCH_3)]PF_6$ (Figure 8) shows the presence of the imine ligand ($N\{H\}=xanthene_{(-2H)}$) that is derived formally from insertion of the nitrido ligand into an alkyl C−H bond of xanthene, together with the loss of a H atom from the α-carbon center. This is consistent with a mechanism that involves an initial HAT from xanthene to Ru^{VI}≡N followed by N-rebound. The resulting $[Ru^{IV}(N\{H\}=xanthene_{(-H)})(salchda)(NCCH_3)]^+$ species then loses another H atom (presumably to another Ru^{VI}≡N) to give the $[Ru^{III}(N\{H\}=xanthene_{(-2H)})(salchda)(NCCH_3)]^+$ product. A KIE value of 3.3 ± 0.3 was obtained for DHA/d_4-DHA.

$[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ alone does not react with hydrocarbons with larger C−H BDEs than DHA (78.0 kcal mol^{-1}).

SCHEME 7. Proposed Mechanism for Aziridination of Alkene by Ru^{VI}≡N



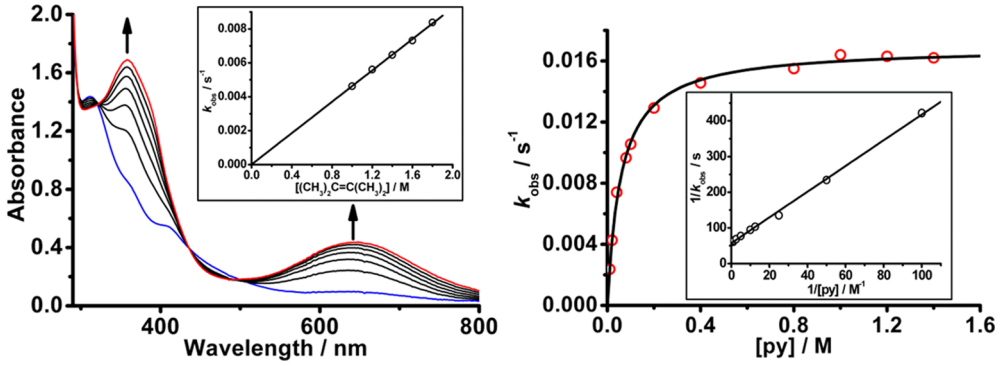


FIGURE 7. (left) Spectrophotometric changes at 144 s intervals during the reaction of 2,3-dimethyl-2-butene (1.0 M) with $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ (9.04×10^{-4} M) in the presence of pyridine (1.0 M) at 298.0 K in 1,2-dichloroethane. Inset shows the plot of k_{obs} vs $[(CH_3)_2C{=}C(CH_3)_2]$. (right) Plot of k_{obs} vs [py]. Inset shows the corresponding plot of $1/k_{obs}$ vs 1/[py].

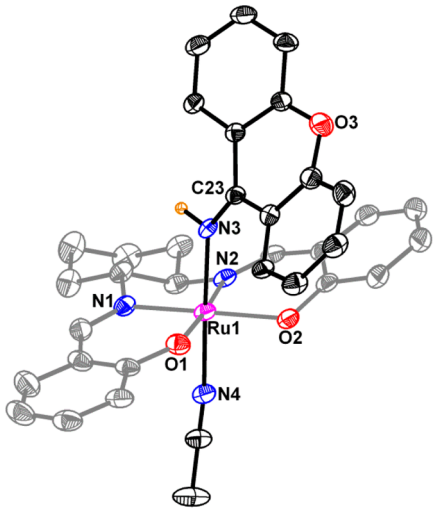


FIGURE 8. Molecular structure of $[Ru^{III}(xanthene_{(-2H)})(salchda)(NCCH_3)]^+$.

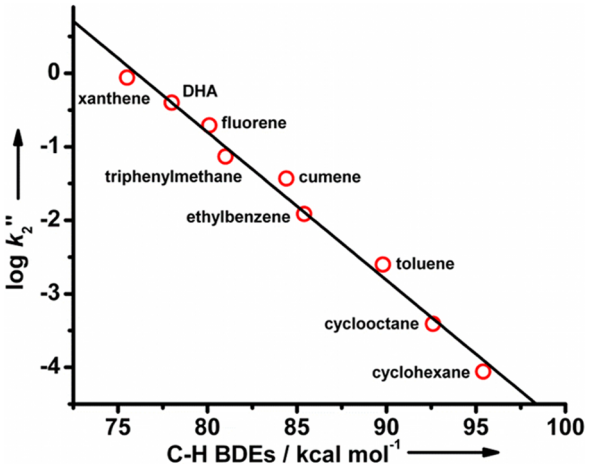


FIGURE 9. Plot of log k_2'' (second-order rate constants per active hydrogen in 0.1 M py) against C–H BDE of alkanes in CH_2ClCH_2Cl at 296.0 K.

However, the nitrido complex becomes much more reactive when pyridine is added; the resulting $[Ru^{VI}(N)(salchda)(py)]^+$ species can activate C–H bonds as strong as those in cyclohexane (95.4 kcal mol^{-1}). The reaction of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ with cyclohexane in the presence of excess pyridine in 1,2-dichloroethane has the following rate law (eq 6):

$$\frac{-d[Ru^{VI}(N)]}{dt} = k_{py}[Ru^{VI}(N)][alkane]\left(\frac{K[py]}{1+K[py]}\right) \quad (6)$$

This is consistent with initial equilibrium binding of $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ and pyridine to produce $[Ru^{VI}(N)(salchda)(py)]^+$, which then reacts with the alkane. The oxidation of cyclohexane-d_{12} occurs much more slowly with a KIE value of 8.4. A linear correlation between the log(rate constant) and the C–H BDE of alkanes was also obtained (Figure 9). These results are consistent with an initial rate-limiting HAT step to produce an alkyl radical, which can undergo a variety of reactions, including N-rebound in the case of cyclohexane and desaturation (further loss of another H-atom) in the case of cyclooctane. The proposed mechanism for the reaction of $[Ru^{VI}(N)(salchda)(py)]^+$ with alkanes is shown in Scheme 8.

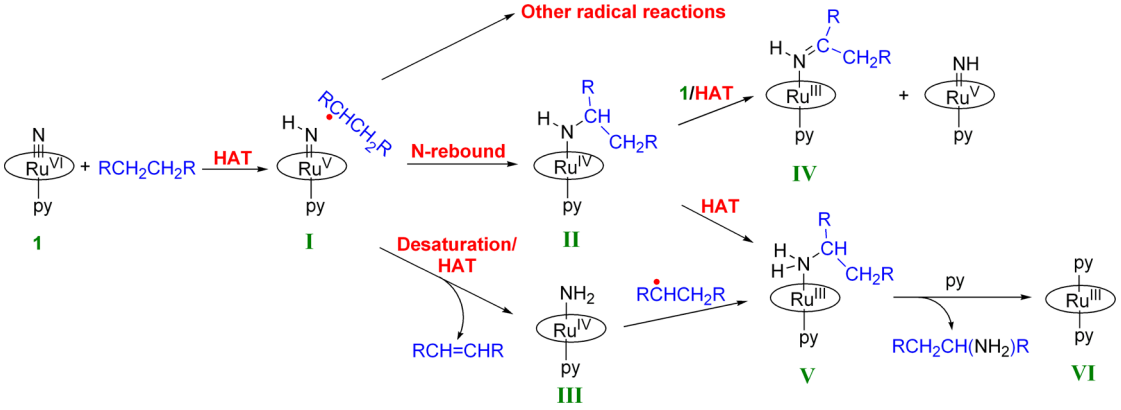
6. Nucleophilic Addition to Coordinated Schiff Base Ligands in Nitrido Complexes

In osmium(VI) and ruthenium(VI) nitrido complexes bearing Schiff base ligands, we found that in addition to the nitrido ligand, the coordinated Schiff base ligand can also be electrophilic. Nucleophilic addition to the coordinated ligand is often stereospecific, suggesting that the incoming nucleophile may have prior association with the nitrido ligand, M≡N···Nu. This reaction is apparently specific to high-valent metal complexes, since no products arising from addition to Schiff base ligands could be observed when manganese(III), ruthenium(III), or osmium(III) Schiff base complexes were treated by nucleophiles under similar conditions.

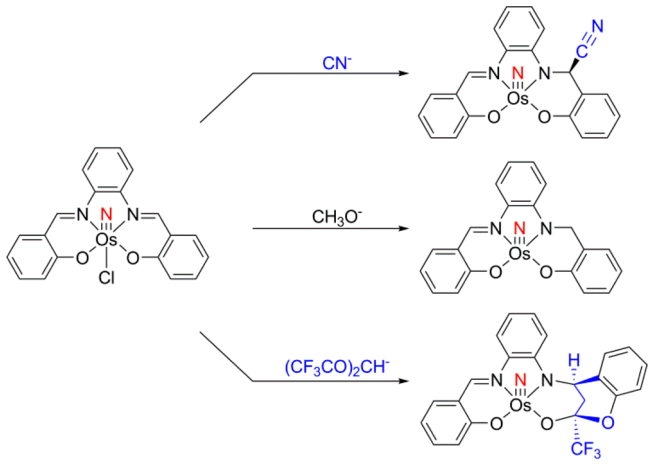
6.1. Nucleophilic Addition to Salophen Ligand Coordinated to Nitridoosmium(VI). Reaction of $[Os^{VI}(N)(salophen)Cl]$ with CN^- in CH_3OH results in addition of CN^- to one of the imine carbons of the salophen ligand within minutes at room temperature (Scheme 9).[44] The reaction is stereospecific, the cyano group is added *syn* to the nitrido ligand, as revealed by the X-ray structure (Figure 10). The formation of a single stereoisomer is also supported by ^1H NMR spectroscopy. The (H–C=N–) and (H–C(CN)–N–) resonances occur as two singlets at δ 9.81 and 6.96 ppm, respectively. $[Os^{VI}(N)(salophen)Cl]$ also reacts rapidly with 1 equiv of KOH in alcohol to afford a five-coordinate osmium(VI) nitride with a H^- added to the imine carbon of the salophen ligand. A mechanism involving H^- transfer from alkoxide (either coordinated or free) was proposed, as evidenced by the production of acetone when 2-propanol was used as solvent. $[Os^{VI}(N)(salophen)Cl]$ also reacts with $hfacac^-$ ($hfacac^- = (CF_3CO)_2CH^-$) to afford a five-coordinate osmium(VI) nitride. X-ray structure reveals stereospecific addition of $CF_3C(O)CH_2^-$ to one of the imine carbons and with the carbonyl group being inserted into an Os–O bond (Figure 10).[44]

6.2. Reaction of Cyanide with $[Os^{VI}(N)(sap)Cl(OH_2)]$. Reaction of $[Os^{VI}(N)(sap)Cl(OH_2)]$ with CN^- affords various products, depending on the solvent used (Scheme 10).[45] In CH_3CN, $[Os^{VI}(N)(sap)Cl(OH_2)]$ undergoes simple substitution of H_2O when 1 equiv of CN^- is added. When 3 equiv of CN^- is used, nucleophilic substitution as well as addition at the

SCHEME 8. Proposed Mechanism for the C−H Activation of Alkanes by $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$



SCHEME 9. Reaction of $[Os^{VI}(N)(salophen)Cl)]$ with Various Nucleophiles



imine function of the sap ligand occur to generate a dicyanoosmium(VI) nitride that bears a trianionic CN-sap ligand. X-ray structure reveals that the CN-sap ligand coordinates to the osmium center in a facial fashion, as opposed to meridional coordination in the original sap ligand. The Os≡N group remains unreacted even though the complex was refluxed with excess CN^- in CH_3CN.

On the other hand, when CH_3OH was used as solvent, $[Os^{VI}(N)(sap)Cl(OH_2)]$ reacts with an excess amount of CN^- to generate an osmium(III) hydrogen cyanamide complex, which has been characterized by X-ray crystallography (Figure 11). The osmium center is coordinated by a N(H)CN-(1−) ligand, three meridional cyanides, and a bidentate 2-(2-hydroxyphenyl)benzoxazole(1−) ligand. The latter ligand is presumably formed by initial addition of CN^- to sap followed by oxidative cyclization.

6.3. Reaction of Cyanide with $[Ru^{VI}(N)(sap)Cl]$. $[Ru^{VI}(N)(sap)Cl]$ reacts with KCN in refluxing MeOH to afford the complex $[Ru^{III}(CN\text{-}sap)(CN)_3]^{2-}$. The X-ray crystal structure (Figure 12) shows the presence of a cyano group attached to the imine function of the sap ligand. In this case, a formal nucleophilic substitution of H^- by CN^- has occurred, as evidenced by the N(1)−C(10) bond distance of 1.277(3) Å, which is typical of C=N. This product is probably formed by initial additional of CN^- to the imine function of sap, followed by intramolecular redox reaction.

7. Nitrido Complexes as Oxidation Catalysts

Due to the large *trans* influence of the nitrido ligand, transition metal nitrido complexes often have square pyramidal geometry or octahedral geometry with a weakly bound ligand *trans* to nitride.[1] The presence of a vacant or weakly bound coordination site should facilitate binding of substrates or reactants to the metal center. Thus nitrido complexes can potentially act as catalysts for various organic transformations.

We found that the complexes $[Os^{VI}(N)Cl_4]^-$ and $[Mn^{V}(N)(CN)_4]^{2-}$ are highly efficient catalysts for the oxidation of organic substrates using various terminal oxidants, including the "green" oxidant hydrogen peroxide. Mechanistic studies suggest that the oxidant initially binds to the metal catalyst and the metal center either acts as a Lewis acid to activate the oxidant (XO) or can abstract an O-atom from XO to generate a M=O species as the active oxidant, as shown in eqs 7−10.

$$N{\equiv}M^n + XO \rightleftharpoons N{\equiv}M^n{-}OX \quad (7)$$

$$N{\equiv}M^n{-}OX \rightleftharpoons N{\equiv}M^{n+2}{=}O + X \quad (8)$$

$$N{\equiv}M^n{-}OX + S \rightleftharpoons N{\equiv}M^n + SO + X \quad (9)$$

$$N{\equiv}M^{n+2}{=}O + S \rightleftharpoons N{\equiv}M^n + SO \quad (10)$$

7.1. $[Os^{VI}(N)Cl_4]^-$ as Catalyst for Alkane Oxidation. $[Os^{VI}(N)Cl_4]^-$ can catalyze the oxidation of cyclohexane in

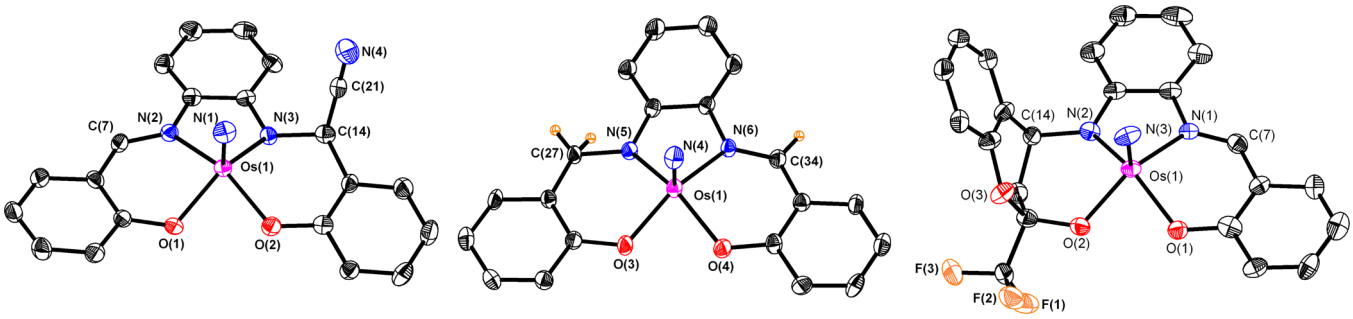
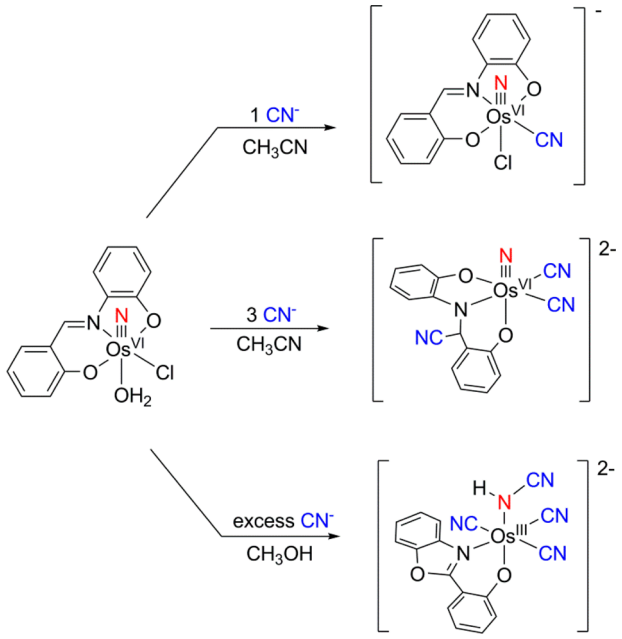


FIGURE 10. Molecular structures of some osmium(VI) nitrido complexes with salophen-derived ligands (see Scheme 9).

SCHEME 10. Reaction of $[Os^{VI}(N)(sap)Cl(OH_2)]$ with CN^- under Various Conditions



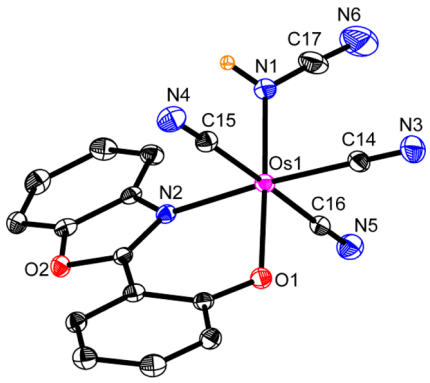


FIGURE 11. Molecular structure of osmium(III) hydrogen cyanamide complex.

CH_2Cl_2/CH_3COOH by ^tBuOOH or H_2O_2 with yields up to 48% at room temperature after 8 h. The catalytic oxidation is

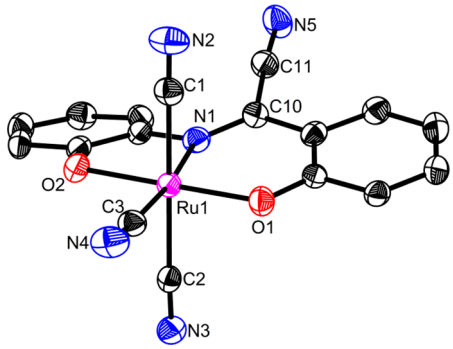
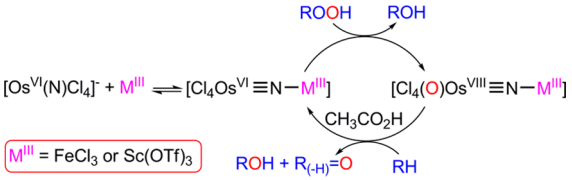


FIGURE 12. Molecular structure of $[Ru^{III}(CN\text{-}sap)(CN)_3]^{2-}$.

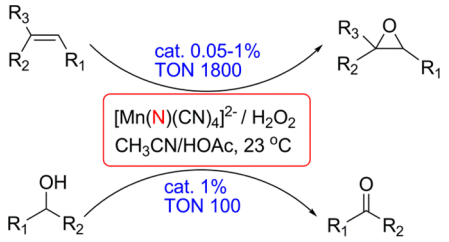
greatly accelerated (8 h to 5 min) by the presence of Lewis acids such as $FeCl_3$ or $Sc(OTf)_3$; excellent yields and turnover numbers (TON) of over 7500 and 1000 can be achieved in the oxidation of cyclohexane with ^tBuOOH and H_2O_2, respectively. Mechanistic studies by UV−vis, ESI/MS, and ^{18}O-labeled experiments suggest that the active intermediate is an Os^{VIII} nitrido oxo species, which is activated by Lewis acid to oxidize alkanes via a H-atom abstraction mechanism, as shown in Scheme 11.[47,48] Since $Os^{VI}{\equiv}N$ can be readily stabilized by a variety of ligands, our results suggest that this is potentially a new class of oxidation catalysts.

7.2. $[Mn^V(N)(CN)_4]^{2-}$ as Oxidation Catalyst for Alkenes and Alcohols. Manganese oxidation catalysts are usually in +2 or +3 oxidation states, and they are usually relatively unstable. The manganese(V) nitrido complex, $[Mn(N)(CN)_4]^{2-}$, prepared by Weighardt and co-workers, has a d^2 configuration and is relatively stable.[49] We found that it is a very active and selective catalyst for alkene epoxidation and alcohol oxidation by H_2O_2, with yields >90% (Scheme 12).[50] DFT calculations using ethene as substrate reveal that the active intermediate is a Mn−(HOOH) species, which is stabilized by hydrogen bonding with CN^- and acetic acid. The Mn^V catalyst functions as a Lewis acid to facilitate O-atom transfer from H_2O_2 to alkene. Since $Mn^V{\equiv}N$ maybe stabilized by a variety of

SCHEME 11. Proposed Mechanism for the Catalytic Oxidation of Alkanes by $[Os^{VI}(N)Cl_4]^-$/Lewis Acid (M^{III})/ROOH System



SCHEME 12. Catalytic Alkene Epoxidation and Alcohol Oxidation by $[Mn(N)(CN)_4]^{2-}/H_2O_2$



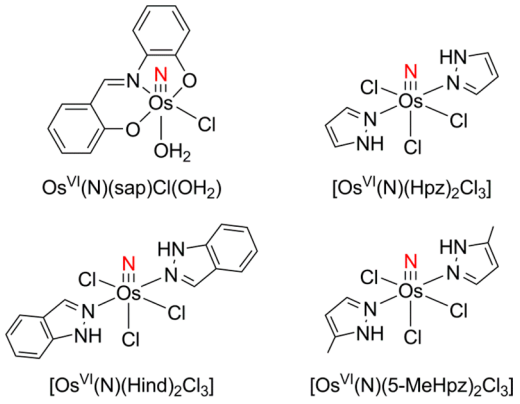


FIGURE 13. Structures of osmium nitrido complexes with anticancer activities.

anionic ligands,[7,8] our results suggest that this is potentially a new and efficient class of oxidation catalysts.

8. Anticancer Properties of Os(VI) Nitrido Complexes

As described in section 7, nitrido complexes usually have a vacant or labile coordination site; hence it is anticipated that they can be used to bind and exert certain effects on various biomolecules. We found that osmium(VI) nitrido complexes bearing a variety of ancillary ligands exhibit potent anticancer activities (Figure 13).[51,52] The cytotoxicity of various osmium nitrido complexes toward a number of cancer cell lines are shown in Table 1. $Os^{VI}(N)(sap)Cl(OH_2)$ also shows *in vivo* anticancer properties using nude mice models. It can bind to 5′-guanosine monophosphate (5′-GMP), a nucleotide

TABLE 1. Cytotoxicity of Nitridoosmium(VI) Complexes Towards Various Cancer Cell Lines

	$IC_{50}{}^a$, (μM)		
compound	HeLa	HepG2	K562
$Os^{VI}(N)(sap)Cl(OH_2)^b$	7.9 ± 0.3	11.4 ± 0.9	8.5 ± 0.1
$Os^{VI}(N)Cl_3(Hpz)_2{}^c$	24.0 ± 1.1	27.3 ± 1.2	12.4 ± 0.6
$Os^{VI}(N)Cl_3(Hind)_2{}^c$	11.6 ± 0.3	9.16 ± 1.5	25.7 ± 1.4
$Os^{VI}(N)Cl_3(5\text{-}MeHpz)_2{}^c$	40.8 ± 4.3	49.4 ± 3.4	28.8 ± 3.9
cisplatin^c	11.5 ± 3.2	4.4 ± 0.3	

[a] 50% inhibitory concentrations in the MTT assay. [b] Exposure time 24 h. [c] Exposure time 48 h.

of cellular nucleic acid, to form a stable adduct, [Os(N)(sap)-(5′-GMP)]$^-$, as monitored by UV−vis and ESI/MS. This suggests that $Os^{VI}(N)(sap)Cl(OH_2)$ should be able to bind to DNA, which may be partly responsible for its anticancer properties.[51] These results suggest that M≡N may be a promising platform for designing new anticancer drugs.

9. Concluding Remarks

We have demonstrated that nitrido complexes of Ru(VI), Os(VI), and Mn(V) bearing Schiff base and other simple anionic ligands possess novel chemical reactivity, including reaction with various nucleophiles, C−H and C−N bond activation, N···N coupling, catalytic oxidation of organic substrates, and anticancer activities.

Ruthenium(VI) nitrido complexes bearing Schiff base ligands such as $[Ru^{VI}(N)(salchda)(CH_3OH)]^+$ is shown to be highly electrophilic; it reacts readily at ambient conditions with a variety of nucleophiles. Many of these reactions are unique to this complex, including direct aziridination of alkenes, C−H bond activation of alkanes, and C−N cleavage of anilines. Hence ruthenium(VI) nitrido complexes are potentially useful reagents for various organic transformations, such as nitrogenation and C−H and C−N bond activation.

We also found that addition of a nucleophile (Nu) to Ru^{VI}≡N generates initially a ruthenium(IV) imido species, Ru^{IV}−N(Nu), which readily accepts a H-atom to give Ru^{III}−NH(Nu). Hence Ru^{IV}−N(Nu) is potentially a new class of HAT reagents.

M≡N is a potential platform for the design of new oxidation catalysts as well as anticancer reagents. For example, $[Os^{VI}(N)Cl_4]^-$ catalyzes the oxidation of alkanes by a variety of oxidants. The oxidants are activated through binding to Os^{VI}. The catalytic oxidation is greatly accelerated by the addition of Lewis acids. Thus it is possible to activate M≡N using Lewis acids E: M≡N→E. $[Mn^V(N)(CN)_4]^{2-}$ is another highly efficient oxidation catalyst; it can catalyze the epoxidation of alkenes and the oxidation of alcohols to carbonyl compounds using H_2O_2.

M≡N is potentially able to bind to and exert certain effects on biomolecules. A number of Os^{VI}≡N complexes

are found to exhibit novel anticancer properties, which are probably related to their ability to bind to DNA.

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ABBREVIATIONS

bpy, 2,2′-bipyridine; HAT, hydrogen atom transfer; HeLa, cervical epithelioid carcinoma cell line; HepG2, hepatocellular carcinoma cell line; K562, myelogenous leukemia cell line; py, pyridine; salchda, *N*,*N*′-bis(salicylidene)*o*-cyclohexyldiamine dianion; salophen, *N*,*N*′-bis(salicylidene)*o*-phenyldiamine dianion; sap, *N*-salicylidene-2-aminophenol dianion; terpy, 2,2′:6′,2″-terpyridine; TFAA, trifluoroacetic anhydride; Tp, hydrotris(1-pyrazolyl)borate anion; 4-Mepy, 4-methylpyridine; 4-^{t}Bupy, 4-*tert*-butylpyridine;

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FOOTNOTES

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The authors declare no competing financial interest.

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