

Facile Nucleophilic Addition to Salophen Coordinated to Nitridoosmium(VI)

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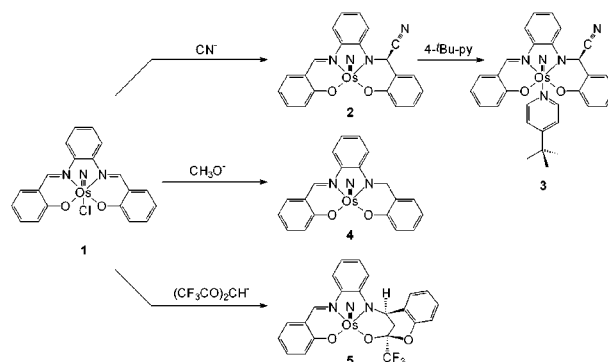
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Metal complexes of salen (ethylenediamine bridged) and related ligands such as salophen (*o*-phenylenediamine-bridged) have occupied a central role in the development of coordination chemistry for over half a century. The catalytic chemistry of these complexes is of particular importance in recent years, especially in the area of catalytic oxidation. The ability of salen to stabilize high oxidation states and the ease of systematic variation of its steric and electronic properties have led to the development of catalysts that are particularly effective for the epoxidation of several important classes of olefins.^{1–3} The aziridination of alkenes is another important reaction effected by nitridomanganese(V) salen complexes.⁴ Although coordinated salen and salophen are susceptible to hydrolysis, the reactions are usually slow unless under strongly acidic or basic conditions. It is generally believed that the hydrolysis is initiated by nucleophilic attack at the imine function; however, no such intermediates have been isolated and characterized.^{5,6} We report here the first structurally characterized complexes formed from remarkable nucleophilic addition of CN[−] (**2**, **3**), H[−] (**4**), and CF₃C(O)CH₂[−] (**5**) to a salophen ligand coordinated to nitridoosmium(VI). Our results suggest that nucleophilic attack at salen and salophen coordinated to a high-valent metal center could be very facile.

The syntheses of compounds **2–5** are outlined in Scheme 1.⁷ They are all stable to air and water and have been characterized by ¹H NMR, IR, elemental analysis, and electrospray mass spectrometry (ESMS). Compounds **3–5** have also been character-

Scheme 1



ized by X-ray crystallography, and they are all found to be racemic mixtures. The orange complex **2** is formed within minutes at room temperature by treatment of **1** with a few equivalents of KCN in CH₃OH. In the ¹H NMR the two equivalent H–C=N– protons in **1** resonate as a singlet at δ 9.87 ppm, while in **2** this becomes two singlets at 9.81 and 6.96 ppm, which are assigned to the H–C=N– proton and the H–C(CN)–N– proton, respectively. Treatment of **2** with 4-*tert*-butylpyridine in CH₃OH/CH₂Cl₂ produced the orange-red adduct **3**, and the X-ray structure is shown in Figure 1.⁸ It indicates the addition of a CN[−] to one of the imine carbons of the salophen ligand. Notably the reaction is stereospecific, the cyano group is added *syn* to the nitrido ligand. This suggests that the electrophilic nitrido ligand may play a role in directing the attack of the cyanide. In the ¹H NMR of **3**, the C(14)–H proton resonates as a singlet at 6.97 ppm, consistent with the presence of a single stereoisomer. The resulting cyano-salophen ligand is trianionic with N(3) bearing a formal negative charge. This is evidenced by an Os–N(3) distance of 1.965 Å shorter than the Os–N(2) distance of 2.029 Å. That the carbon bearing the cyano group, C(14), becomes sp³ is evidenced by the N(3)–C(14)–C(15) bond angle of 115.6° as compared with the N(2)–C(7)–C(6) angle of 126.5°. The C(14)–N(3) bond length of 1.447 Å is also of single-bond nature and is substantially longer than the C(7)–N(2) imine bond length of 1.302 Å. The Os≡N bond is rather short (1.622 Å), but the Os–N(4-*tert*-butylpyridine) bond is rather long (2.544 Å), indicating a large *trans* influence of the nitrido ligand.⁹

1 reacts rapidly with 1 equiv of KOH in methanol or 2-propanol at room temperature to produce **4** as dark red crystals in 63% yield, and the X-ray structure is shown in Figure 2.¹⁰ It reveals a five-coordinate osmium nitrido complex resulting from the addition of a hydride to an imine carbon, C(27), of the salophen ligand of **1**. The resulting ligand becomes trianionic with N(5) bearing a formal negative charge, as evidenced by an Os–N(5) bond length of 1.938 Å shorter than the Os–N(6) bond length of 2.025 Å. C(27) becomes sp³, with a N(5)–C(27)–C(26) bond angle of 117.2° and a N(5)–C(27) bond length of 1.445 Å compared with the N(6)–C(34)–C(35) angle of 125.3° and the N(6)–C(34) of 1.308 Å. In the ¹H NMR the two inequivalent protons of C(27) resonate as a doublet of doublets at 4.90 and 5.14 ppm. When 2-propanol was used as the solvent to prepare

(8) Crystal data for **3**, OsO₃N₅C₃₄H₃₇ (3·OEt₂): mol wt 753.89, triclinic, *P*-1, *a* = 11.1267(11) Å, *b* = 12.353(2) Å, *c* = 12.685(2) Å, α = 104.483(13)°, β = 95.217(13)°, γ = 105.799(11)°, *V* = 1600.5(4) Å³, *T* = 295(2) K, *Z* = 2, μ(Mo Kα) = 40.25 cm^{−1}, *D*_{calc} = 1.564 g/cm³, 5626 unique reflections, final *R*_F = 2.7%, GOF = 1.055.

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(10) Crystal data for **4**, OsO_{2.5}N₃C_{20.5}H₁₇ (4·(CH₃OH)_{0.5}): mol wt 535.07, triclinic, *P*-1, *a* = 12.537(4) Å, *b* = 16.768(3) Å, *c* = 9.287(4) Å, α = 104.58(2)°, β = 110.54(3)°, γ = 91.18(2)°, *V* = 1756(1) Å³, *T* = 301 K, *Z* = 4, μ(Mo Kα) = 72.80 cm^{−1}, *D*_{calc} = 2.023 g/cm^{−1}, 6175 unique reflections, final *R*_F = 3.3%, GOF = 1.59.

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(7) Detailed syntheses and characterizations of these complexes are given in the Supporting Information.

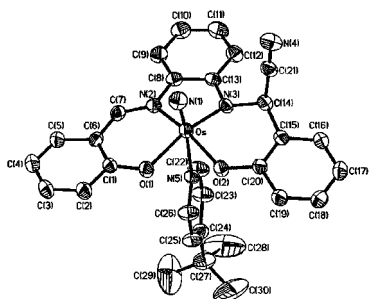


Figure 1. ORTEP diagram of **3**. Selected bond lengths (Å) and bond angles (deg): Os–O(1) 2.017(3), Os–O(2) 1.971(3), Os–N(1) 1.622(4), Os–N(2) 2.029(3), Os–N(3) 1.965(3), Os–N(5) 2.544(4), C(14)–N(3) 1.447(5), C(7)–N(2) 1.302(5), N(3)–C(14)–C(15) 115.6(3), N(2)–C(7)–C(6) 126.5(4).

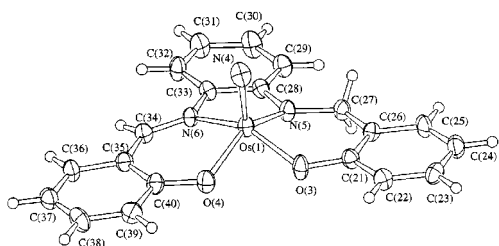


Figure 2. ORTEP diagram of **4**. Selected bond lengths (Å) and bond angles (deg): Os–O(3) 1.960(6), Os–O(4) 2.000(5), Os–N(4) 1.630(7), Os–N(5) 1.938(6), Os–N(6) 2.025(6), N(5)–C(27) 1.445(9), N(6)–C(34) 1.308(10), N(5)–C(27)–C(26) 117.2(6), N(6)–C(34)–C(35) 125.3(8).

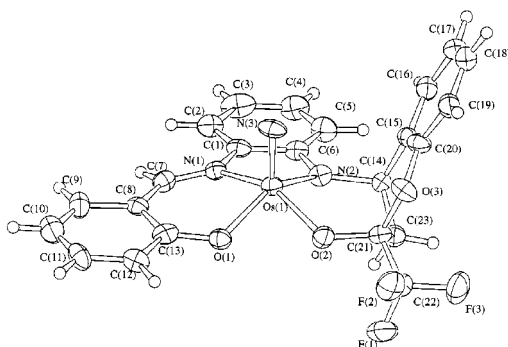
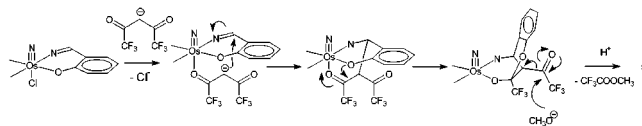


Figure 3. ORTEP diagram of **5**. Selected bond lengths (Å) and bond angles (deg) Os(1)–O(1) 2.004(6), Os(1)–O(2) 1.991(5), Os(1)–N(1) 2.045(6), Os(1)–N(2) 1.957(7), Os(1)–N(3) 1.648(7), N(1)–C(7) 1.299(10), N(2)–C(14) 1.50(1), N(1)–C(7)–C(8) 127.5(8), N(2)–C(14)–C(15) 110.5(7).

4, acetone was produced in 80% yield as analyzed by GC and GC–MS. This is consistent with a mechanism involving hydride transfer from either coordinated alkoxide (analogous to the Meerwein–Ponndorf–Verley reduction¹¹) or a free alkoxide.¹²

1 reacts with a few equivalents of Tb(hfacac)₃ (hfacac = (CF₃CO)₂CH[−]) at room temperature to produce **5** as dark red crystals in 75% yield. Tb(hfacac)₃ was used as a source of hfacac[−]; when Khfacac was used instead, the product was found to be a mixture of **4** and **5**. The X-ray structure (Figure 3)¹³ shows a five-coordinate osmium(VI) nitrido complex with the salen ligand modified by the net stereospecific addition of a CF₃C(O)CH₂[−] to one of the imine carbons and with the carbonyl group being inserted into an Os–O bond. The resulting ligand is also trianionic, as in **3** and **4**, with N(2) bearing a formal negative charge; the Os–N(2) bond length (1.957 Å) is shorter than the Os–N(1) bond length (2.045 Å), the N(2)–C(14)–C(23) bond angle of 110.5° indicates that C(14) is sp³ and the N(2)–C(14) bond length of 1.50 Å shows that it is a single bond. At the unattached side, the N(1)–C(7)–C(8) angle is 127.5° and N(1)–C(7) bond length is 1.299 Å. Notably the stereochemistry of

Scheme 2



addition is reversed compared to that of cyanide. This suggests a mechanism involving intramolecular attack by coordinated hfacac[−] (Scheme 2),¹² followed by insertion of a carbonyl group into an Os–O bond, and subsequent addition of CH₃O[−] to produce CF₃COOCH₃. The presence of CF₃COOCH₃ in the reaction mixture was confirmed by GC–MS.

The modified salen complexes **2–5** readily decompose to the original salen complex in the gas phase, as revealed by electrospray mass spectrometry (Supporting Information).

There is a rich redox chemistry of electrophilic osmium nitrido complexes such as [Os(terpy)NCl₂]⁺ and [TpOsNCl₂]; in many cases redox reactions are initiated by nucleophilic attack at the nitrido ligand.^{14,15} Although bulky nucleophiles such as PPh₃ readily attack the nitrido ligand of **1** (*k*₂ = 2.53 × 10⁴ M^{−1} s^{−1} at 25.0 °C in CH₃CN) to produce the corresponding osmium(IV) phosphoraninato complex,⁹ our studies here show that for less bulky nucleophiles attack at an imine carbon of the salen ligand is more facile. Nucleophilic addition to salen-type osmium(VI) nitrido complexes was also found to occur, although the reaction is slower and more complicated. A NMR study of the reaction of [Os(salchda)(N)Cl] (salchda = *N,N'*-bis(salicylidene)-*trans*-1,2-diaminocyclohexane dianion) with a few equivalents of KCN in CD₃OD at room temperature indicated an initial decrease in intensity of the imine protons peaks, consistent with nucleophilic attack of CN[−] at an imine carbon. However the NMR spectrum gradually became broader and more complicated, suggesting a parallel reaction involving the addition of CN[−] to the nitrido ligand of the diamagnetic osmium(VI) complex to produce a paramagnetic osmium(IV) cyanoimido complex. The facile reaction of CN[−] with [Os^{VI}(tpy)(N)Cl₂]PF₆ to produce [Os^{IV}-(tpy)(NCN)Cl₂] has recently been reported.^{14a}

Our studies suggest that nucleophilic addition to salen and salen coordinated to a high-valent metal center could be very facile. One of the reasons for the low turnovers of most (salen)-manganese epoxidation catalysts could be due to attack at the (salen)manganese(V) oxo intermediates by nucleophiles in the reaction mixture; hence, suitable modifications of the salen ligand to inhibit attack at the imine carbons could increase the lifetime of the epoxidation catalysts.

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Supporting Information Available: Experimental, spectroscopic, and crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) We thank one of the reviewers for making suggestions on the mechanisms.

(13) Crystal data for **5**, OsF₃O₂N₃C₂₄H₂₀ (5·CH₃OH): mol wt 661.63, monoclinic, *P*2₁/*c* (No. 14), *a* = 9.862(3) Å, *b* = 12.667(4) Å, *c* = 18.125(3) Å, β = 98.01(2)°, *V* = 2242(9) Å³, *T* = 301 K, *Z* = 4, μ(Mo Kα) = 57.47 cm^{−1}, *D*_{calc} = 1.957 g/cm³, 4145 unique reflections, final *R*_f = 4.1%, GOF = 1.47.

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