Facile Nucleophilic Addition to Salophen Coordinated to Nitridoosmium(VI)

Sze-Man Chiu,[†] Tsz-Wing Wong,[†] Wai-Lun Man,[†] Wing-Tak Wong,[‡] Shie-Ming Peng,[§] and Tai-Chu Lau*[,†]

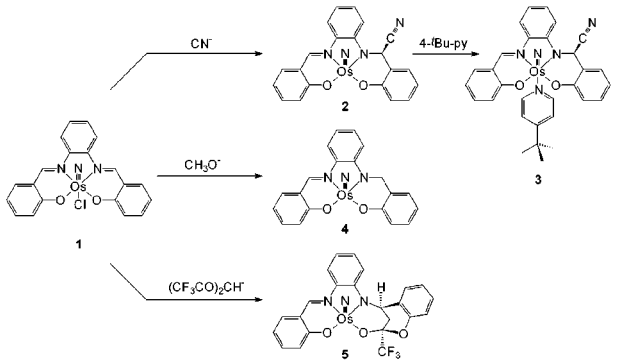
Department of Biology and Chemistry City University of Hong Kong, Tat Chee Avenue Kowloon Tong, Hong Kong, P. R. China
Department of Chemistry, University of Hong Kong Pokfulam Road, Hong Kong, P. R. China
Department of Chemistry, National Taiwan University Taipei 106, Taiwan

Received May 9, 2001

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 $CF_3C(O)CH_2^-$ (**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 ^{1}H NMR, IR, elemental analysis, and electrospray mass spectrometry (ESMS). Compounds **3**−**5** have also been characterized 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 CH_3OH. In the ^{1}H 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 CH_3OH/CH_2Cl_2 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 ^{1}H 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 sp^3 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]

Scheme 1



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 sp^3, 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 ^{1}H 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

* Author for correspondence. Email: bhtclau@cityu.edu.hk. Fax: (852)2788 7406.
† City University of Hong Kong.
‡ The University of Hong Kong.
§ National Taiwan University.

(1) (a) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis;* Ojima, I., Ed.; VCH: New York 1993; pp 159−202. (b) Jacobson, E. N. In *Comprehensive Organometallic Chemistry II.;* Hegedus, L. S., Ed.; Elsevier: New York 1995; pp 1097−1135. (c) Jacobson, E. N.; Wu, M. H. In *Comprehensive Asymmetric catalysis II;* Jacobson, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin 1999; pp 649−674.

(2) (a) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189. (b) Katsuki, T. *J. Mol. Catal.* **1996**, *113*, 87.

(3) (a) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (b) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.

(4) (a) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, *2*, 1517. (b) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915. (c) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M.; Day, M. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1645. (d) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364. (e) Minakata, S.; Ando, T.; Nishimura, M.; Ryu, I.; Komatsu, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3392. (f) Ho, C. M.; Lau, T. C.; Kwong, H. L.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1999**, 2411.

(5) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 84.

(6) There are some reports on the formation of metal amides from metal aldimines. These reactions are most likely initiated by addition of water to the neutral imine ligand. See, for example: Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.*, **1997**, *36*, 1095. Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.*, **1995**, *34*, 3310.

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

(8) Crystal data for **3**, $OsO_3N_5C_{34}H_{37}$ (**3**·OEt_2): 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) Å^3, T = 295(2) K, Z = 2, μ(Mo Kα) = 40.25 cm^{-1}, D_{calc} = 1.564 g/cm^3, 5626 unique reflections, final R_f = 2.7%, GOF = 1.055.

(9) Wong, T. W.; Lau, T. C.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 6181.

(10) Crystal data for **4**, $OsO_{2.5}N_3C_{20.5}H_{17}$ (**4**·$(CH_3OH)_{0.5}$): 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) Å^3, 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.

10.1021/ja011152c CCC: $20.00
Published on Web 11/27/2001

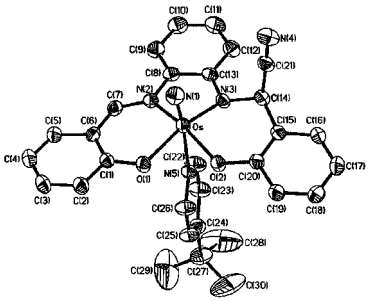


Figure 1. ORTEP diagram of **3**. Selected bond lengths (Å) and bond angles (deg): Os−O(1) 2.017(3), Os−O(2) 1.971(3), Os−N(1) 1.622(4), Os−N(2) 2.029(3), Os−N(3) 1.965(3), Os−N(5) 2.544(4), C(14)−N(3) 1.447(5), C(7)−N(2) 1.302(5), N(3)−C(14)−C(15) 115.6(3), N(2)−C(7)−C(6) 126.5(4).

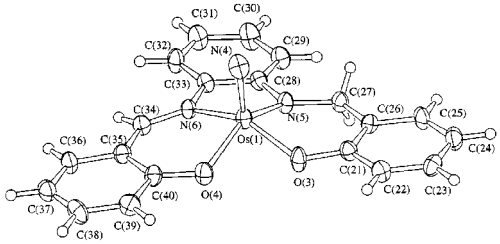


Figure 2. ORTEP diagram of **4**. Selected bond lengths (Å) and bond angles (deg): Os−O(3) 1.960(6), Os−O(4) 2.000(5), Os−N(4) 1.630(7), Os−N(5) 1.938(6), Os−N(6) 2.025(6), N(5)−C(27) 1.445(9), N(6)−C(34) 1.308(10), N(5)−C(27)−C(26) 117.2(6), N(6)−C(34)−C(35) 125.3(8).

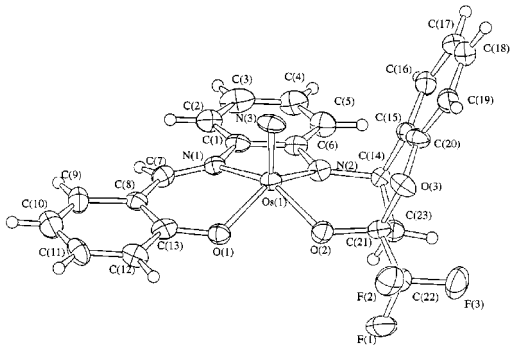
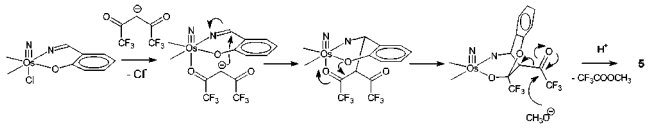


Figure 3. ORTEP diagram of **5**. Selected bond lengths (Å) and bond angles (deg) Os(1)−O(1) 2.004(6), Os(1)−O(2) 1.991(5), Os(1)−N(1) 2.045(6), Os(1)−N(2) 1.957(7), Os(1)−N(3) 1.648(7), N(1)−C(7) 1.299(10), N(2)−C(14) 1.50(1), N(1)−C(7)−C(8) 127.5(8), N(2)−C(14)−C(15) 110.5(7).

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 reduction[11]) or a free alkoxide.[12]

1 reacts with a few equivalents of Tb(hfacac)$_3$ (hfacac = $(CF_3CO)_2CH^-$) 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 salophen ligand modified by the net stereospecific addition of a $CF_3C(O)CH_2^-$ 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 sp^3 and the N(2)−C(14) bond length of 1.50 Å shows that it is a single bond. At the unattacked 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 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 CH_3O^- to produce CF_3COOCH_3. The presence of CF_3COOCH_3 in the reaction mixture was confirmed by GC−MS.

Scheme 2



The modified salophen complexes **2**−**5** readily decompose to the original salophen 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 $[Os(terpy)NCl_2]^+$ and $[TpOsNCl_2]$; in many cases redox reactions are initiated by nucleophilic attack at the nitrido ligand.[14,15] Although bulky nucleophiles such as PPh_3 readily attack the nitrido ligand of **1** ($k_2 = 2.53 \times 10^4$ M^{-1} s^{-1} at 25.0 °C in CH_3CN) to produce the corresponding osmium(IV) phosphoraniminato complex,[9] our studies here show that for less bulky nucleophiles attack at an imine carbon of the salophen 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 CD_3OD 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 $[Os^{VI}(tpy)(N)Cl_2]PF_6$ to produce $[Os^{IV}(tpy)(NCN)Cl_2]$ has recently been reported.[14a]

Our studies suggest that nucleophilic addition to salophen 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.

Acknowledgment. This work was substantially supported by the Research Grants council of Hong Kong (CityU 1117/00P), partially supported by the City University of Hong Kong, the University of Hong Kong, and the National Science Council of the Republic of China.

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

JA011152C

(11) Wilds, A. L. *Org. React.* **1944**, *2*, 178.

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

(13) Crystal data for **5**, $OsF_3O_4N_3C_{24}H_{20}$ (**5**·CH_3OH): mol wt 661.63, monoclinic, $P2_1/c$ (No. 14), $a = 9.862(3)$ Å, $b = 12.667(4)$ Å, $c = 18.125(3)$ Å, $\beta = 98.01(2)°$, $V = 2242(9)$ Å^3, $T = 301$ K, $Z = 4$, μ(Mo Kα) = 57.47 cm^{-1}, $D_{calc} = 1.957$ g/cm^3, 4145 unique reflections, final $R_f = 4.1\%$, GOF = 1.47.

(14) (a) Huynh, M. H. V.; White, P. S.; Carter, C. A.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3037. (b) Huynh, M. H. V.; El-Samanody, E.-S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 3075. (c) Huynh, M. H. V.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 2825. (d) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3610. (e) Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 838.

(15) (a) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.*, **2001,** *123*, 1059. (b) McCarthy, M. R.; Crevier, T. J.; Bennett, B. K.; Dehestani, A.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 12391. (c) Crevier, T. J.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 6607. (d) Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5595. (e) Crevier, T. J.; Mayer, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1891.