

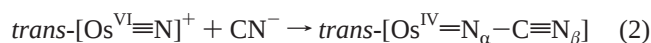
The Cyanoimido Ligand as an Oxo Analogue. Novel Approaches to the Preparations of Cyano(imino)-aza-phosphorus(V) and *N*-Cyanoaziridine

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We recently described a novel preparation of the cyanoimido ligand by coordination sphere assembly in the reactions between cyanide ion and the Os(VI)–nitrido complexes, *mer*-[Os^{VI}(bpy)-(Cl)₃(N)] (*mer*-[Os^{VI}≡N]) (bpy = 2,2′-bipyridine) and *trans*-[Os^{VI}-(tpy)(Cl)₂(N)]⁺ (*trans*-[Os^{VI}≡N]⁺) (tpy = 2,2′:6′,2″-terpyridine), eqs 1 and 2.¹

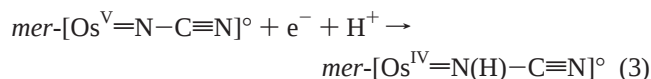


The reaction with CN[−] is one of a number of examples involving formal N[−]-transfer from Os^{VI}≡N to nucleophiles.^{2,3}

There are at least formal electronic relationships between the Os(IV)–cyanoimido products and analogous high oxidation Ru and Os-oxo complexes. These include multiple bonding to the metal, the ability to undergo multiple electron transfer, and the availability of nonbonding electron pairs for donation. In the N_α-C≡N_β^{2−} ligand, there are accessible electron pairs at both the N_α and the N_β positions.

We describe here results which demonstrate that Os(VI)–, Os(V)–, and Os(IV)–cyanoimido complexes have thermodynamic and reactivity properties reminiscent of Ru and Os-oxo analogues. This similarity may create the basis for a new family of multielectron redox reagents.

In 1:1 (v/v) CH₃CN:H₂O (1.0 M in KNO₃ and/or NH₄PF₆), the lower oxidation state couples (Os(V/IV), Os(IV/III), and Os(III/II)) are pH-dependent. The results are summarized in the *E*_{1/2}–pH diagram in Figure 1. The results of the pH-dependent electrochemical study are extended only to pH 8 because a reversible chemical change or changes occur in the complex at higher pH's. Proton contents are indicated on the diagram with Os^V=N–C≡N⁰/Os^{IV}=N(H)–C≡N⁰ as an abbreviation for the couple in eq 3.

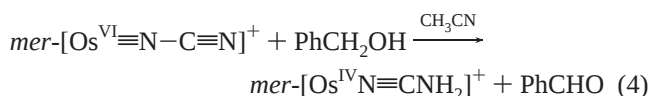


For purposes of comparison, the *E*_{1/2}–pH diagram for *cis*-[Os^{VI}-(bpy)₂(O)₂]²⁺ in H₂O (*μ* = 1.0 M at 25 ± 2 °C) is also shown in Figure 1.⁴ In these diagrams, breaks in the *E*_{1/2}–pH curves occur where there are proton changes (at the p*K*_a for one of the participating oxidation states).

There is a remarkable similarity between the two *E*_{1/2}–pH diagrams both in the appearance of accessible couples from Os(VI/V) to Os(III/II) and in the potential ranges over which they occur. However, the extensive multiple oxidation state chemistry found for the Os–cyanoimido complex is supported by a single

ligand set (N–C≡N^{2−}/N–(H)C≡N[−]/N≡C–NH₂⁰) rather than by two as in the di-oxo case.

The oxo-like behavior extends to reactions with a variety of organic reducing agents in net multielectron-transfer reactions. When benzyl alcohol (PhCH₂OH) is added to *mer*-[Os^{VI}≡N–C≡N]⁺ (generated by electrolysis of *mer*-[Os^{IV}=N–C≡N][−] in 0.1 M Bu₄NPF₆/CH₃CN with *n* = 2 at *E*_{app} = 2.05 V, V versus SSCE), a rapid reaction occurs with quantitative formation of *mer*-[Os^{IV}–N≡C–NH₂]⁺ as shown by spectral monitoring (*λ*_{max} = 430 nm with *ε* = 5.15 × 10³ M^{−1} cm^{−1} for the *mer*-[Os^{IV}–N≡C–NH₂]⁺ product¹). The results of a kinetics study with PhCH₂OH in pseudo first-order excess and stopped-flow spectrophotometric monitoring show that the rate law is first order in each reagent with *k*(CH₃CN, 25.0 ± 0.1 °C) = (8.6 ± 0.2) × 10² M^{−1} s^{−1}, eq 4.

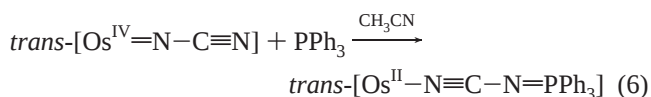


The organic benzaldehyde product was extracted from the reaction solution with hexane and identified by GC-MS. These results are consistent with the rate law and stoichiometry in eqs 4 and 5.

$$\text{rate} = k_{\text{benzyl}}[\text{mer-Os}^{\text{VI}}\equiv\text{N-C}\equiv\text{N}^+][\text{PhCH}_2\text{OH}] \quad (5)$$

There are a series of interesting mechanistic questions about the redox step for this reaction that remain to be answered. One is the possible magnitude of the α,α′-CH/CD kinetic isotope effect which could be large given the isotope effects found for related oxo reactions.⁵

We also investigated the formal NCN-group transfer reactivity of the cyanoimido ligand by analogy with the well-established O-atom transfer reactivity of the oxo ligand.⁶ The reaction between *trans*-[Os^{IV}=N–C≡N] and PPh₃ in eq 6 is also first order in each reagent and occurs with *k*_{PPh₃}(DMF, 25.0 ± 0.1 °C) = 4.06 ± 0.02 M^{−1} s^{−1}. The nitrilic, N-bound Os(II)–(N-cyano)iminophosphorano product, *trans*-[Os^{II}(tpy)(Cl)₂(NCNPPH₃)] (*trans*-[Os^{II}–N≡C–N=PPh₃]), was isolated in 95% yield and characterized by elemental analysis, cyclic voltammetry, and infrared, ¹H and ³¹P NMR, and UV–visible spectroscopies.^{7a} In CH₃CN under N₂ at 45 °C for 24 h, *trans*-[Os^{II}–N≡C–N=PPh₃] undergoes solvolysis to form the solvento complex, *trans*-[Os^{II}(tpy)(Cl)₂(CH₃CN)]₂,^{2b} and (N-cyano)-iminophosphorane (N_α≡C–N_β=PPh₃), which was identified by GC-MS and ³¹P NMR (*δ*, DMSO-*d*₆ = 25.7 ppm) spectroscopy.⁸ Direct evidence for N_β-attack and *trans*-[Os^{II}–N≡C–N=PPh₃] as the product comes from ¹⁵N-labeling and IR measurements in Nujol mulls.⁹



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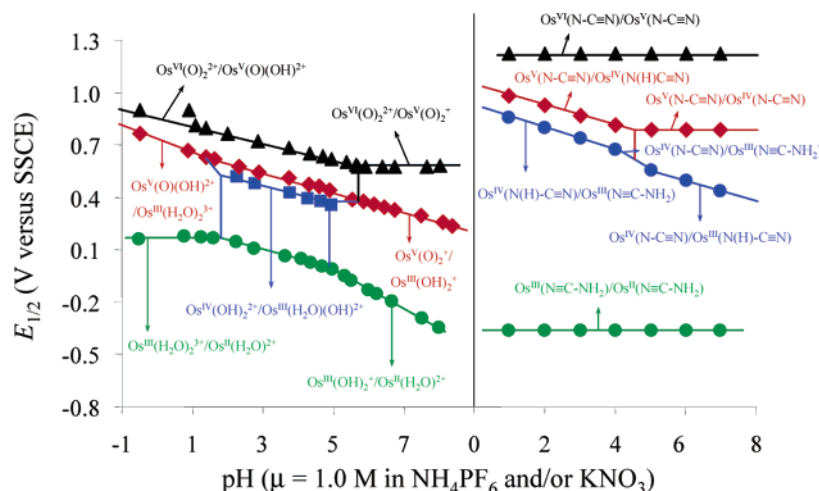
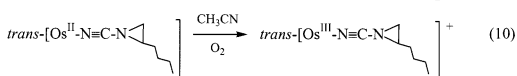
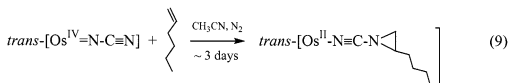
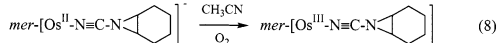
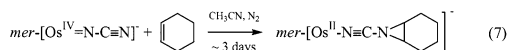


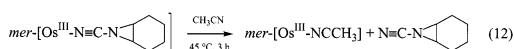
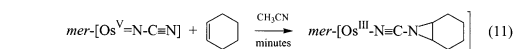
Figure 1. $E_{1/2}$ versus pH (Pourbaix) diagram for $mer\text{-}[\text{Os}^{\text{IV}}(\text{bpy})(\text{Cl})_3(\text{NCN})]^-$ in 1.0 M KNO_3 and/or NH_4PF_6 1:1 (v/v) $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (V versus SSCE) as compared to that for $cis\text{-}[\text{Os}^{\text{VI}}(\text{bpy})_2(\text{O})_2]^{2+}$ in H_2O .

Examples of Pd and Pt complexes containing nitrilic N-bound $\text{N}\equiv\text{C}-\text{N}=\text{PPh}_3$ ⁸ have been reported but were prepared by completely different synthetic routes. For example, $[\text{Pt}(\text{C}-\text{P})(\text{PPh}_3)(\text{NCCH}_3)]\text{ClO}_4$ ($\text{C}-\text{P} = o\text{-CH}_2\text{C}_6\text{H}_4\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_2$) undergoes substitution with the preformed $\text{N}\equiv\text{C}-\text{N}=\text{PPh}_3$ ligand to give $[\text{Pt}(\text{C}-\text{P})(\text{PPh}_3)(\text{N}\equiv\text{C}-\text{N}=\text{PPh}_3)]\text{ClO}_4$.⁸

The Os^{IV} -cyanoimido complex is also capable of effecting aziridination of alkenes, the analogue of epoxidation, as shown in eqs 7 and 8. A related reactivity exists for 1-hexene, eqs 9 and 10.^{7c}



The versatility of this new family of oxidants was demonstrated by studying the analogous reaction with the Os^{V} -cyanoimido analogue, $mer\text{-}[\text{Os}^{\text{V}}(\text{bpy})(\text{Cl})_3(\text{NCN})]$ ($mer\text{-}[\text{Os}^{\text{V}}=\text{N}-\text{C}\equiv\text{N}]$). When cyclohexene in CH_3CN is added to electrochemically generated $mer\text{-}[\text{Os}^{\text{V}}=\text{N}-\text{C}\equiv\text{N}]$ (in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ with $n = 1$ at $E_{\text{app}} = 1.6$ V, V versus SSCE), a rapid reaction occurs to give $mer\text{-}[\text{Os}^{\text{III}}\text{-N}\equiv\text{C}-\text{NC}_6\text{H}_{10}]$, eq 11.^{7d} After 3 h at 45 °C under N_2 , this product undergoes solvolysis to give $mer\text{-}[\text{Os}^{\text{III}}(\text{bpy})(\text{Cl})_3(\text{NCCH}_3)]$ ($mer\text{-}[\text{Os}^{\text{III}}\text{-N}\equiv\text{C}-\text{CH}_3]$)¹⁰ and the organic N -cyanoaziridine $\text{N}\equiv\text{C}-\text{NC}_6\text{H}_{10}$.



These Os - N -cyanoaziridino complexes are the first well-characterized examples of transition metal complexes containing the cyanoaziridino ligand. Our results demonstrate a remarkable versatility in redox behavior for the cyanoimido $\text{N}_\alpha\text{-C}\equiv\text{N}\beta^{2-}$ ligand. The existence of multiple oxidation states with different proton contents and reactivities based on Os^{VI} , Os^{V} , and Os^{IV} offers a new family of oxidants for a variety of organic reactions which have access to multiple pathways. Our results also provide novel

approaches to the preparations of (N -cyano)iminophosphoranes ($\text{N}\equiv\text{C}-\text{N}=\text{PR}_3$) and N -cyanoaziridines ($\text{N}\equiv\text{C}-\text{NR}_2$). These stepwise assembly methods offer a potentially general route to (cyano)imino-aza-phosphorus(V) compounds¹¹ and families of biologically active agents such as cyanoaziridine and azimexone.¹²

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Supporting Information Available: Text containing characterizations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Detailed preparation and characterization data are provided in the Supporting Information: (a) for $trans\text{-}[\text{Os}^{\text{II}}(\text{tpy})(\text{Cl})_2(\text{NCNPPH}_3)]$, (b) for $mer\text{-}\text{Et}_4\text{N}[\text{Os}^{\text{II}}(\text{bpy})(\text{Cl})_3(\text{NCNC}_6\text{H}_{10})]$, (c) for $trans\text{-}[\text{Os}^{\text{III}}(\text{tpy})(\text{Cl})_2(\text{NCNC}_6\text{H}_{10})]$, and (d) for $mer\text{-}[\text{Os}^{\text{III}}(\text{bpy})(\text{Cl})_3(\text{NCNC}_6\text{H}_{10})]$.
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- $\nu(\text{C}\equiv^{14}\text{N}_\beta)$ for the cyanoimido ligand in $trans\text{-}[\text{Os}^{\text{IV}}\text{-}^{14}\text{N}_\alpha\text{-C}\equiv^{14}\text{N}_\beta]$ and in the ^{15}N Os^{IV} -analogue, $trans\text{-}[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})_2(^{15}\text{N}_\alpha\text{C}\equiv^{14}\text{N}_\beta)]$ ($trans\text{-}[\text{Os}^{\text{IV}}\text{-}^{15}\text{N}_\alpha\text{-C}\equiv^{14}\text{N}_\beta]$), appears at $1939 \pm 1 \text{ cm}^{-1}$. $\nu(^{14}\text{N}_\alpha\equiv\text{C})$ and $\nu(^{14}\text{N}_\beta\equiv\text{P})$ for $^{14}\text{N}_\alpha\equiv\text{C}-^{14}\text{N}_\beta=\text{PPh}_3$ in $trans\text{-}[\text{Os}^{\text{II}}\text{-}^{14}\text{N}_\alpha\equiv\text{C}-^{14}\text{N}_\beta=\text{PPh}_3]$ appear at 2235 ± 1 and $1116 \pm 1 \text{ cm}^{-1}$, respectively. $\nu(^{15}\text{N}_\alpha\equiv\text{C})$ and $\nu(^{14}\text{N}_\beta\equiv\text{P})$ for $^{15}\text{N}_\alpha\equiv\text{C}-^{14}\text{N}_\beta=\text{PPh}_3$ in $trans\text{-}[\text{Os}^{\text{II}}\text{-}^{15}\text{N}_\alpha\equiv\text{C}-^{14}\text{N}_\beta=\text{PPh}_3]$ appear at 2205 ± 1 and $1116 \pm 1 \text{ cm}^{-1}$, respectively.
- At ambient temperature under N_2 , $mer\text{-}[\text{Os}^{\text{III}}\text{-N}\equiv\text{C}-\text{NC}_6\text{H}_{10}]$ undergoes reversible one-electron reduction in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{DMF}$ with $n = 1$ at $E_{\text{app}} = -1.3$ V (V versus SSCE) to give the corresponding $mer\text{-}[\text{Os}^{\text{II}}\text{-N}\equiv\text{C}-\text{NC}_6\text{H}_{10}]^-$ form in eq 7 quantitatively as shown by cyclic voltammetry and UV-visible spectroscopy. $E_{1/2}$ for the $\text{Os}^{\text{III}}/\text{II}$ couple is -0.91 V in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{DMF}$, V versus SSCE.
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