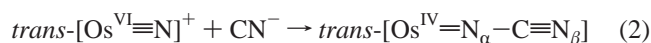# The Cyanoimido Ligand as an Oxo Analogue. Novel Approaches to the Preparations of Cyano(imino)-aza-phosphorus(V) and *N*-Cyanoaziridine

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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]

$$mer\text{-}[Os^{VI}\equiv N] + CN^- \rightarrow mer\text{-}[Os^{IV}=N_\alpha-C\equiv N_\beta]^- \quad (1)$$

$$trans\text{-}[Os^{VI}\equiv N]^+ + CN^- \rightarrow trans\text{-}[Os^{IV}=N_\alpha-C\equiv N_\beta] \quad (2)$$

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$_\alpha$−C≡N$_\beta^{2-}$ ligand, there are accessible electron pairs at both the N$_\alpha$ and the N$_\beta$ 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) CH$_3$CN:H$_2$O (1.0 M in KNO$_3$ and/or NH$_4$PF$_6$), 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≡N°/Os^{IV}=N(H)−C≡N° as an abbreviation for the couple in eq 3.
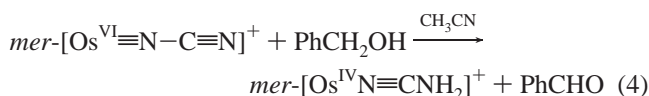
$$mer\text{-}[Os^V=N-C\equiv N]° + e^- + H^+ \rightarrow$$
$$mer\text{-}[Os^{IV}=N(H)-C\equiv N]° \quad (3)$$
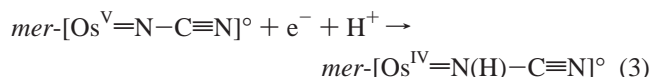
For purposes of comparison, the $E_{1/2}$−pH diagram for *cis*-[Os^{VI}-(bpy)$_2$(O)$_2$]$^{2+}$ in H$_2$O (μ = 1.0 M at 25 ± 2 °C) is also shown in Figure 1.[4] In these diagrams, breaks in the $E_{1/2}$−pH curves occur where there are proton changes (at the pK_a for one of the participating oxidation 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−NH$_2$°) 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 (PhCH$_2$OH) is added to *mer*-[Os^{VI}≡N−C≡N]$^+$ (generated by electrolysis of *mer*-[Os^{IV}=N−C≡N]$^-$ in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN 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−NH$_2$]$^+$ as shown by spectral monitoring (λ_{max} = 430 nm with ϵ = 5.15 × 10^3 M^{-1} cm^{-1} for the *mer*-[Os^{IV}−N≡C−NH$_2$]$^+$ product[1]). The results of a kinetics study with PhCH$_2$OH in pseudo first-order excess and stopped-flow spectrophotometric monitoring show that the rate law is first order in each reagent with k(CH$_3$CN, 25.0 ± 0.1 °C) = (8.6 ± 0.2) × 10^2 M^{-1} s^{-1}, eq 4.

$$mer\text{-}[Os^{VI}\equiv N-C\equiv N]^+ + PhCH_2OH \xrightarrow{CH_3CN}$$
$$mer\text{-}[Os^{IV}N\equiv CNH_2]^+ + PhCHO \quad (4)$$

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.

$$rate = k_{benzyl}[mer\text{-}Os^{VI}\equiv N-C\equiv N^+][PhCH_2OH] \quad (5)$$

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 PPh$_3$ 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)$_2$(NCNPPh$_3$)] (*trans*-[Os^{II}−N≡C−N=PPh$_3$]), was isolated in 95% yield and characterized by elemental analysis, cyclic voltammetry, and infrared, ^{1}H and ^{31}P NMR, and UV−visible spectroscopies.[7a] In CH$_3$CN under N$_2$ at 45 °C for 24 h, *trans*-[Os^{II}−N≡C−N=PPh$_3$] undergoes solvolysis to form the solvento complex, *trans*-[Os^{II}(tpy)(Cl)$_2$(CH$_3$CN)],[2b] and (*N*-cyano)-iminophosphorane (N$_\alpha$≡C−N$_\beta$=PPh$_3$), which was identified by GC-MS and ^{31}P NMR (δ, DMSO-d_6 = 25.7 ppm) spectroscopy.[8] Direct evidence for N$_\beta$-attack and *trans*-[Os^{II}−N≡C−N=PPh$_3$] as the product comes from ^{15}N-labeling and IR measurements in Nujol mulls.[9]

$$trans\text{-}[Os^{IV}=N-C\equiv N] + PPh_3 \xrightarrow{CH_3CN}$$
$$trans\text{-}[Os^{II}-N\equiv C-N=PPh_3] \quad (6)$$
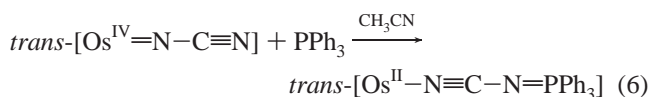
† The Associate Director for Strategic Research.
‡ Dynamic Experimentation Division.
§ Chemistry Division.
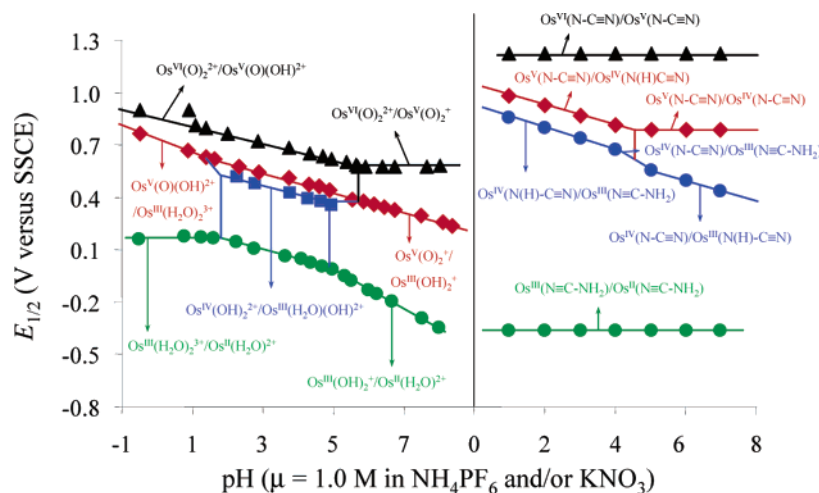
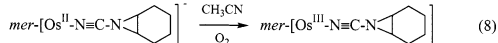**Figure 1.** $E_{1/2}$ versus pH (Pourbaix) diagram for *mer*-[Os^{IV}(bpy)(Cl)$_3$(NCN)]$^-$ in 1.0 M KNO$_3$ and/or NH$_4$PF$_6$ 1:1 (v/v) CH$_3$CN:H$_2$O (V versus SSCE) as compared to that for *cis*-[Os^{VI}(bpy)$_2$(O)$_2$]$^{2+}$ in H$_2$O.

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

$$mer\text{-}[Os^{IV}\text{-}N\text{-}C≡N]^- + \bigcirc \xrightarrow[\sim 3\ days]{CH_3CN,\ N_2} mer\text{-}[Os^{II}\text{-}N≡C\text{-}N\bigcirc]^- \quad (7)$$

$$mer\text{-}[Os^{II}\text{-}N≡C\text{-}N\bigcirc]^- \xrightarrow[O_2]{CH_3CN} mer\text{-}[Os^{III}\text{-}N≡C\text{-}N\bigcirc] \quad (8)$$

$$trans\text{-}[Os^{IV}\text{=}N\text{-}C≡N] + \big\rangle \xrightarrow[\sim 3\ days]{CH_3CN,\ N_2} trans\text{-}[Os^{II}\text{-}N≡C\text{-}N\triangleleft] \quad (9)$$

$$trans\text{-}[Os^{II}\text{-}N≡C\text{-}N\triangleleft] \xrightarrow[O_2]{CH_3CN} trans\text{-}[Os^{III}\text{-}N≡C\text{-}N\triangleleft]^+ \quad (10)$$
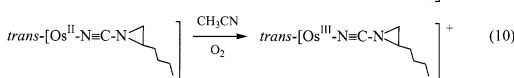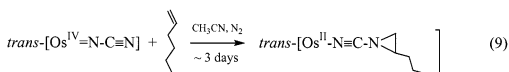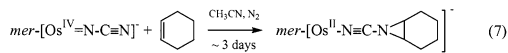
The versatility of this new family of oxidants was demonstrated by studying the analogous reaction with the Os(V)−cyanoimido analogue, *mer*-[Os^V(bpy)(Cl)$_3$(NCN)] (*mer*-[Os^V=N−C≡N]). When cyclohexene in CH$_3$CN is added to electrochemically generated *mer*-[Os^V=N−C≡N] (in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN with $n = 1$ at $E_{app} = 1.6$ V, V versus SSCE), a rapid reaction occurs to give *mer*-[Os^{III}−N≡C−NC$_6$H$_{10}$], eq 11.[7d] After 3 h at 45 °C under N$_2$, this product undergoes solvolysis to give *mer*-[Os^{III}(bpy)(Cl)$_3$(NCCH$_3$)] (*mer*-[Os^{III}−N≡C−CH$_3$])[10] and the organic *N*-cyanoaziridine N≡C−NC$_6$H$_{10}$.

$$mer\text{-}[Os^V\text{=}N\text{-}C≡N] + \bigcirc \xrightarrow[minutes]{CH_3CN} mer\text{-}[Os^{III}\text{-}N≡C\text{-}N\bigcirc] \quad (11)$$

$$mer\text{-}[Os^{III}\text{-}N≡C\text{-}N\bigcirc] \xrightarrow[45\ ^\circ C,\ 3\ h]{CH_3CN} mer\text{-}[Os^{III}\text{-}NCCH_3] + N≡C\text{-}N\bigcirc \quad (12)$$
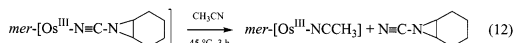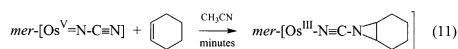
These Os−*N*-cyanoaziridino complexes are the first well-characterized examples of transition metal complexes containing the cyanoaziridino ligand. Our results demonstrate a remarkable versatility in redox behavior for the cyanoimido N$_\alpha$−C≡N$_\beta{}^{2-}$ ligand. The existence of multiple oxidation 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 (N≡C−N=PR$_3$) and *N*-cyanoaziridines (N≡C−NR$_2$). These stepwise assembly methods offer a potentially general route to (cyano)imino-aza-phosphorus(V) compounds[11] and families of biologically active agents such as cyanoaziridine and azimexone.[12]

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(7) Detailed preparation and characterization data are provided in the Supporting Information: (a) for *trans*-[Os^{II}(tpy)(Cl)$_2$(NCNPPh$_3$)], (b) for *mer*-Et$_4$N[Os^{II}(bpy)(Cl)$_3$(NCNC$_6$H$_{10}$)], (c) for *trans*-[Os^{III}(tpy)(Cl)$_2$-(NCNC$_6$H$_{11}$)], and (d) for *mer*-[Os^{III}(bpy)(Cl)$_3$(NCNC$_6$H$_{10}$)].

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(9) ν(C≡^{14}N$_\beta$) for the cyanoimido ligand in *trans*-[Os^{IV}=^{14}N$_\alpha$−C≡^{14}N$_\beta$] and in the ^{15}N Os(IV)-analogue, *trans*-[Os^{IV}(tpy)(Cl)$_2$(^{15}N$_\alpha$C≡^{14}N$_\beta$)] (*trans*-[Os^{IV}=^{15}N$_\alpha$−C≡^{14}N$_\beta$]), appears at 1939 ± 1 cm^{-1}. ν(^{14}N$_\alpha$≡C) and ν-(^{14}N$_\beta$=P) for ^{14}N$_\alpha$≡C−^{14}N$_\beta$=PPh$_3$ in *trans*-[Os^{II}−^{14}N$_\alpha$≡C−^{14}N$_\beta$=PPh$_3$] appear at 2235 ± 1 and 1116 ± 1 cm^{-1}, respectively. ν(^{15}N$_\alpha$≡C) and ν(^{14}N$_\beta$=P) for ^{15}N$_\alpha$−C≡^{14}N$_\beta$=PPh$_3$ in *trans*-[Os^{II}=^{15}N$_\alpha$−C≡^{14}N$_\beta$=PPh$_3$]) appear at 2205 ± 1 and 1116 ± 1 cm^{-1}, respectively.

(10) At ambient temperature under N$_2$, *mer*-[Os^{III}−N≡C−NC$_6$H$_{10}$] undergoes reversible one-electron reduction in 0.1 M Bu$_4$NPF$_6$/DMF with $n = 1$ at $E_{app} = -1.3$ V (V versus SSCE) to give the corresponding *mer*-[Os^{II}−N≡C−NC$_6$H$_{10}$]$^-$ form in eq 7 quantitatively as shown by cyclic voltammetry and UV−visible spectroscopy. $E_{1/2}$ for the Os(III/II) couple is −0.91 V in 0.1 M Bu$_4$NPF$_6$/DMF, V versus SSCE.

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