

The Chemistry of Pentaammineosmium(II) Complexes

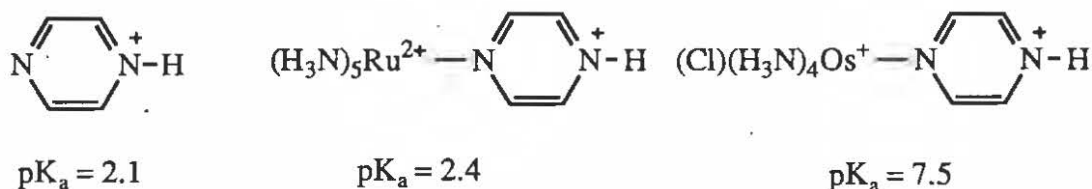
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The field of coordination chemistry can be subdivided into two primary areas of interest, traditional Werner and organometallic chemistry. Werner chemistry generally involves metals in a high oxidation state with saturated ligands. Organometallic chemistry usually involves metals in a low oxidation state with unsaturated ligands [1]. Compared to the extensive work in these two areas, relatively little work has focused on the interface with combinations of saturated and unsaturated ligands. Historically, copper(I) bridged this boundary, reflecting its affinity for π -acceptor ligands. However, these complexes tend to be labile limiting the systematic study of their chemistry. Platinum(II) complexes have and continue to provide an extensive amount of information concerning the behavior of saturated and unsaturated ligands [2].

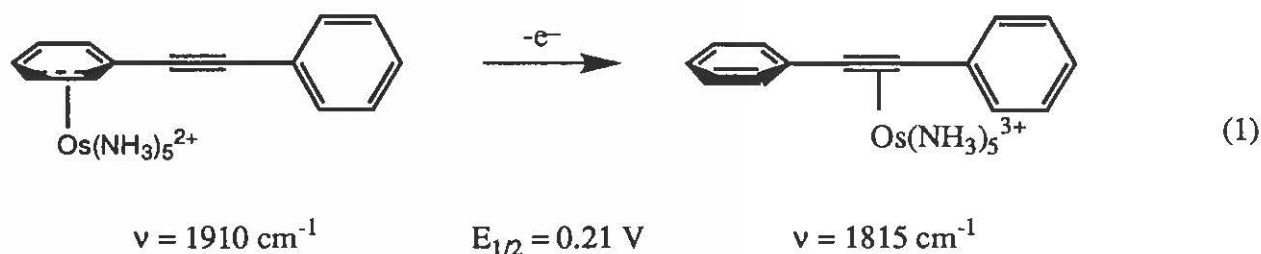
Since the preparation of the first stable dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ [3], the organometallic chemistry of ruthenium ammines has developed into an interfacial area. Later work has shown the analogous ethylene and acetylene complexes of $[\text{Ru}(\text{NH}_3)_5]^{2+}$ are also stable [4]. This stability has been attributed to the strong π -donor properties of the $[\text{Ru}(\text{NH}_3)_5]^{2+}$ unit. More dramatic results have followed from the analogous osmium ammine systems which reveal an even greater tendency for back-bonding to unsaturated ligands. Comparison of the $[\text{Ru}(\text{NH}_3)_5]^{2+}$ and $[\text{Os}(\text{NH}_3)_4(\text{Cl})]^+$ coordinated to the pyrazinium ion reveals this trend [5]:



The increased pK_a for the $[\text{Os}(\text{NH}_3)_5]^{2+}$ bound pyrazinium complex requires a large transfer of electron density to the ligand's π -system, increasing the basicity of the nitrogen by a factor of 10^5 .

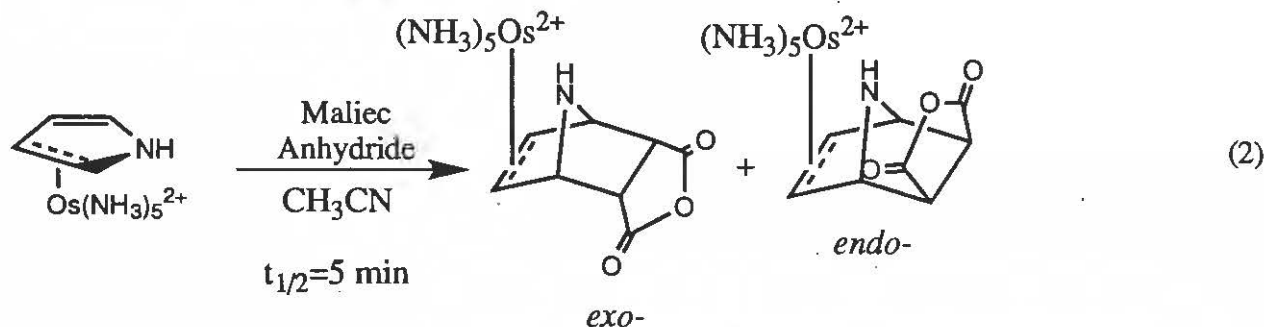
The organometallic chemistry of osmium ammines has been limited due to difficulty in the preparation of $[\text{Os}(\text{NH}_3)_5(\text{L})]^{3+}$ complexes [6]. $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ has proven to be an effective synthetic intermediate in the preparation of $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes [4] while the $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ analog [7] has not due to oxidation by water or ligand reduction. Since the preparation of $[\text{Os}(\text{NH}_3)_5(\text{OTf})]^{2+}$ [8], a variety of $[\text{Os}(\text{NH}_3)_5(\text{L})]^{2+}$ complexes where L = aldehydes, ketones, arenes, heterocycles, alkynes, and olefins have been reported. The uniqueness of these complexes is that η^2 -coordination is the preferred bonding mode [9-14]. In $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$ complexes, the strength of π -bonding by osmium(II) imparts a stability ranging from hours to days in solution. This kinetic stability has allowed for an extensive study of substituent effects, redox chemistry, and tautomerization of the arene ligand [11,14].

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$ complexes display a wide range of reactivity. This is illustrated by the linkage isomerization of diphenylacetylene on $\text{Os}(\text{NH}_3)_5^{2+}$ [12], as well as in N-heterocycles [14] and carbonyl complexes [9]. In eqn. 1, $[\text{Os}(\text{NH}_3)_5(2,3\text{-}\eta^2\text{-diphenylacetylene})]^{2+}$ migrates to the alkyne upon a 1 electron-oxidation. Reduction of the

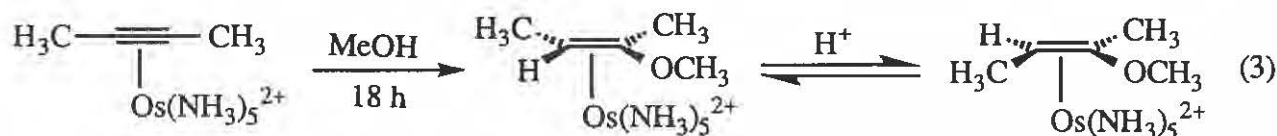


$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-diphenylacetylene})]^{3+}$ gives $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-diphenylacetylene})]^{2+}$ instead of the starting complex.

η^2 -complexation of $[\text{Os}(\text{NH}_3)_5]^{2+}$ to pyrrole has been shown to influence the chemistry of pyrrole toward 1,3-dipolar cycloadditions via an azomethine ylide intermediate [15]. Eqn. 2, $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-pyrrole})]^{2+}$, reacts with maleic anhydride quantitatively as evidenced by ^1H NMR. The resultant products correspond to the *exo*- and *endo*-isomers (4:1 ratio) with the metal moiety bound in the *exo* configuration for both species.



The addition of nucleophiles across unactivated alkynes represents an important method in alkyne functionalization [16]. $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-alkyne})]^{2+}$ reacts quantitatively with methanol or water via the formation of π -vinyl ether and π -enol complexes, eqn. 3 [17].



Oxidation of the π -enol or π -vinyl ether complexes liberates the organic ligand and $[\text{Os}(\text{NH}_3)_5(\text{solvent})]^{3+}$.

$[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$ complexes undergo selective hydrogenations by Pd/C to produce the respective cyclohexene complex, $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-C}_6\text{H}_{10})]^{2+}$, in quantitative yields [18]. Oxidation of the $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$ complex generates $[\text{Os}(\text{NH}_3)_5(\text{solvent})]^{3+}$ and the olefin. Complete recovery of the $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$ is obtained or reduction in the presence of an arene will give the $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-arene})]^{2+}$.

Pentaammineosmium(II) complexes have and continue to provide a diverse chemistry utilizing properties of saturated and unsaturated ligands.

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