

Electrophilic osmium nitrosyls: Example of inorganic functional group

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High-yield synthetic routes to osmium nitrosyls of type $[\text{OsX}(\text{NO})\text{L}_2]^{z+}$ ($\text{X} = \text{Cl}$ or Br ; $\text{L} =$ anion of quinolin-8-ol and its substituted derivatives, $z = 0$, $\text{L} = 2$ - (phenylazo)pyridine or 2-(*m*-tolylazo)-pyridine, $z = 2$) have been found out. Detailed spectroscopic, magnetic, electrochemical and other physicochemical properties show these nitrosyls to be strong electrophiles with high degree of nitrosonium ion (NO^+) character. The complexes react with a number of inorganic and organic nucleophiles affording new ligands. A special effort has been made to propose L-bound $\text{Os}^{\text{II}}-\text{NO}$ as an inorganic functional group (a new concept in inorganic chemistry) through a wide range of their reactions towards organic reagents, viz. (i) diazotization reaction with primary aromatic amines, (ii) aromatic substitution reaction via Fischer-Hepp rearrangement, (iii) reaction with alcohols/alkoxides to form alkylnitrite complexes, (iv) nitrosation reaction resulting in C-N bond formation by reaction with β -diketones, bicyclic ketones, and (v) reaction with arylhydrazones, $\text{ArCH} = \text{NNHAr}'$ to prepare arylazo oximes, $\text{ArC}(=\text{NOH})\text{N} = \text{NAr}'$. Extensive electrochemical study (using cyclic voltammetry, differential pulse voltammetry and coulometry) has been done to find out the nature of electron transfers involved in the nitrosyl precursors and the derived products. The structure-property interrelationship is determined. The new results are compared with existing reports and an attempt is made to study Os-L nitrosyls in relation to similar nitrosyls of the three congeneric elements iron, ruthenium and osmium.

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