

Transition Metal Nitrides:
Some Properties of a Multiply Bonded Ligand

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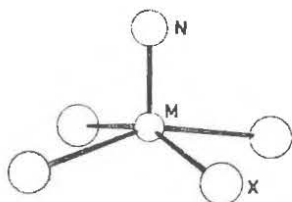
Literature Seminar

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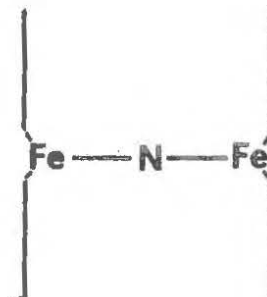
Stabilization of high oxidation states in inorganic chemistry may be achieved by use of highly anionic ligands, such as nitride (N^{3-}). Nitrides are found in many metal coordination environments, ranging from terminally bound nitrides [1] to multi-metal imides [2] and interstitial nitrogen clusters [3]. Those compounds in which nitrogen is bound to three metals or less are in a group of nitrides whose syntheses are relatively well established, but which have only recently been examined for their physical properties.

The successful synthesis of metal nitrides has centered primarily on the use of an azide derivative (such as sodium azide, a halo-azide (ClN_3), or trimethylsilylazide (Me_3SiN_3)) and a metal halide. Generally, nitride compounds are oxygen and water stable, and are isolated in high yields (60-80%). By far the most extensive characterization of nitrides has been by infrared spectroscopy ($\nu(MN)=1150-950\text{ cm}^{-1}$) and x-ray crystallography ($r(MN)=1.5-1.7\text{ \AA}$). The reactivity of nitrides is limited by the weak nucleophilicity of the nitrogen and its strong trans-labilizing effect, although ligand exchange reactions are common and provide routes to new nitride complexes [4].

Nitrides are among the strongest known π -donating ligands, second perhaps only to carbynes, and as such investigations into their bonding characteristics can yield useful information on ligand bonding effects, as well as interesting comparisons with other π -donating ligands (e.g., metal-oxo species, $M=O$) [5]. One of the more well studied compound classes, the isostructural d^0 , d^1 , and d^2 tetrahalo metal nitrides (MNX_4 , 1) [6]. Electron spin resonance (Esr) studies



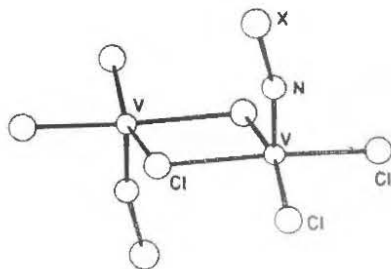
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have indicated that valence electrons occupy mainly metal- d_{xy} based molecular orbitals, and have provided atomic orbital coefficients in molecular orbital calculations [7]. Esr has also shown the greater π -bonding characteristics of nitrides over analogous oxo compounds. Similarly, preliminary investigation of bis(porphinatoiron)nitride ($[(TPP)Fe]_2N$, 2) as a member of the series $(PFe)_2X$ ($X=C, N, O$) has illustrated the effects of varying degrees of π -bonding on the molecular orbitals of bridged dimers [8].

One of the more unique classes of metal-nitrogen compounds are the halonitrenes, best illustrated by Cl_3VNCl and its derivatives. With a formal N-Cl single bond, these compounds exhibit metal nitrogen distances typical of triple



bonds, and have magnetic moments indicating a high degree of vanadium-nitrogen multiple bonding [9]. These complexes display no nitrogen nucleophilicity, and the reactions of these compounds occur almost without exception at vanadium. The halogen is not labile. Some recent work has indicated that Cl_3VNCl may prove to be a good nitride transfer reagent to later-series transition metal complexes [10].

The future of inorganic nitride chemistry may well expand along several fronts. Physical measurements on the bonding in nitrides are not yet complete, nor are studies into the trends between carbide, nitride, and oxide as strong π -donating ligands. Apparently untouched in physical analyses are the mixed valence bimetallic nitrides, for which several examples may exist. Areas also needing attention include a) expansion of the known nitrides past Group 6, 7, and 8, b) organometallic nitride examples, and c) increasing the available metal and ^{15}N NMR data on nitrides.

References

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