

Groups 9 and 10 Transition Metal Imido Complexes

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Literature Seminar

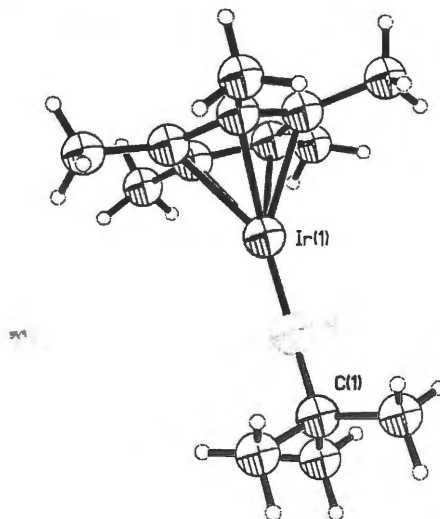
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The discovery by Sharpless and coworkers of oxyamination and diamination of alkenes mediated by Osmium (VIII) imido complexes stimulated major interest in the preparation and properties of imido complexes of the later transition metals.^{1,2} *Ab initio* calculations for transition metal imido complexes have shown that the nucleophilic character of the imido ligand and the metal nitrogen bond energies decrease up and to the right across the periodic table. Therefore late transition imido compounds may have especially interesting properties, relative to early transition-metal complexes.^{3,4} It has been demonstrated recently that transition metal imido complexes from groups 9 and 10 exhibit a wide range of reactions, i.e., carbon monoxide insertion, [2+2] cycloaddition, and pyrrole complex formation.⁵⁻⁸

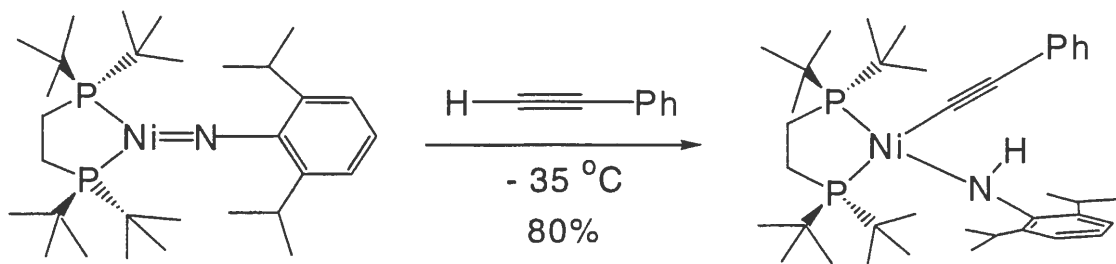
The first late transition metal imido complex was (*t*-BuN)(CpNi)₃, which is an example of a triply bridging imido complex.⁹ Triply bridging imido complexes of group 9 and 10 are numerous, but they are typically inert to reactions with small molecules. However, these types of imido complexes may have unique physical properties, such as temperature-dependent magnetic behavior.^{9,10}

Key compounds important for developing an understanding of metal-imido complexes are Cp*IrNR [R = Me₃C, SiMe₂CMe₃, 2,6-Me₂C₆H₃, 2,6-(Me₂CH)₂C₆H₃], which containing a linear imido-metal bond (Figure 1).⁷ The nitrogen atom of Cp*IrN-*t*-Bu is nucleophilic, as indicated by the reaction with excess MeI to produce [Cp*IrI₂]₂ and [Me₃N-*t*-Bu][I]. This imido compound is also capable of forming carbon-carbon bonds; for example, the addition of two equivalents of dimethylacetylenedicarboxylate to Cp*IrN-*t*-Bu results in a substituted η⁴ pyrrole ligand.⁷

Figure 1. Molecular Structure of Cp*IrN-*t*-Bu



Recently, the terminal imido-nickel complex, $(dtbpe)Ni\{N(2,6-(CHMe_2)_2C_6H_3)\}$, has been described.¹¹ The imido-nitrogen in this compound is very basic as shown by the deprotonation of phenylacetylene.



This imido compound is capable of imido group transfer reactions; for example, the addition of excess carbon monoxide to $(dtbpe)Ni\{N(2,6-(CHMe_2)_2C_6H_3)\}$ results in the isocyanate compound $OCN(2,6-(CHMe_2)_2C_6H_3)$ as well as $(dtbpe)Ni(CO)_2$.⁸

Doubly bridging imido-oxo and bis-imido complexes, $Cp^*Ir(\mu_2-O)(\mu-N-t-Bu)IrCp^*$ and $Cp^*Ir(\mu-NPh)_2IrCp^*$, have also been prepared. These compounds are capable of oxygen atom transfer or imido group transfer, respectively to a phosphine.⁵ Other doubly bridging imido complexes can undergo carbon monoxide insertion to give an isocyanate adduct; e.g., $Rh_2(\mu_2-NPh)(CO)_2(\mu_2-dppm)_2$ reacts with carbon monoxide to give $Rh_2(\mu-\eta^1:\eta^1-PhNCO)(CO)_2(\mu_2-dppm)_2$.⁶

In rare cases, both terminal and doubly bridging imido complexes exist for the same transition metal, ancillary ligands, and oxidation state has been observed. The terminal and doubly bridging bonding modes each exhibit their own unique reactivity. The terminal imido-nickel compound previous mentioned is capable of imido group transfer to carbon monoxide, yielding free isocyanate, whereas the terminal imido-iridium compound yields a stable adduct of isocyanate. This result suggests a first row transition metal may be more efficient in imido group transfer reactions. Due to the limited number of known group 9 and 10 imido complexes, further research in this area is needed to fully appreciate the prospects of using late transition metal imido complexes for synthetic or catalytic purposes.

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