N-Heterocyclic Carbene Ligands as Alternatives to Phosphine Ligands in Homogeneous Catalysis

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The term N-heterocyclic carbene is used to describe compounds prepared by deprotonation of an imidazolium precusor. The first stable, isolable carbenes (Figure 1), were synthesized by Arduengo in 1991.[1] Less stable derivatives are generated and used *in situ*.[2] Transition metal complexes bearing N-heterocyclic carbene ligands have been known since 1968. However, the availability of free carbenes has renewed interest in utilizing these compounds as ligands, and in applying the resulting complexes in homogeneous catalysis.[3]

As ligands, N-heterocyclic carbenes display two similarities to phosphine ligands. N-heterocyclic carbene ligands demonstrate strong sigma–donating ability. In this regard, they appear to surpass the sigma–donating ability of phosphine ligands.[4] The many possible derivatives (e.g., dimethyl, diphenyl, diisopropyl) allow for variation of steric properties.[3] At present, however, there are no convenient or systematic measures of the steric properties possessed by N-heterocyclic carbene ligands. The behavior of N-heterocyclic carbene ligands differs from that of phosphine ligands in two aspects. The pi-accepting ability of N-heterocyclic carbene ligands is negligible. Also, ligand dissociation equilibria have not been observed.[5]

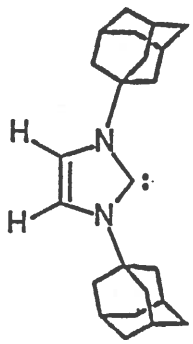

Figure 1

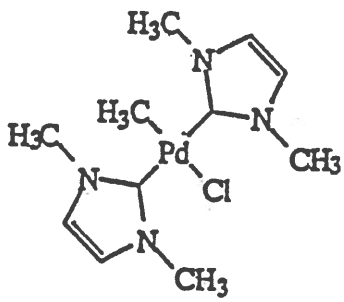

Figure 2

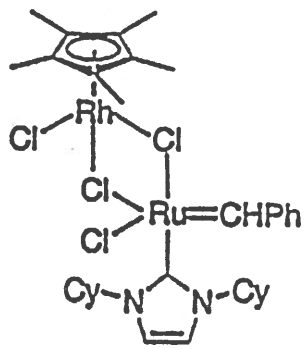

Figure 3

The utility of N-heterocyclic carbene ligands has been examined in two homogeneous catalytic applications: the Heck Coupling Reaction, and olefin metathesis, particularly, Ring Closing Metathesis (RCM).

The most commonly used Heck Coupling catalyst is a mixture of palladium(II)acetate with 2-4 equivalents of triphenylphosphine. One of the substrates must be an aryl-/vinyl-iodide or an activated (by *para* electron withdrawing groups) aryl-bromide.[6] In contrast, bis-N-heterocyclic carbene palladium(II) complexes have been shown to affect coupling with not only the labile substrates mentioned above, but also with deactivated aryl-bromides and activated aryl-chlorides.[7] The ability to successfully employ aryl-chlorides in Heck Reactions can be of considerable economic benefit due to the greater expense of both aryl-iodides and aryl-bromides. Additionally, both mono- and bis-N-heterocyclic carbene palladium(II) complexes (Figure 2), that couple activated aryl-bromides with turnover numbers in excess of 100,000 have been reported.[8,9]

A pentacoordinate ruthenium alkylidene complex, $(PCy_3)_2Cl_2Ru{=}CHPh$, developed by Grubbs in 1996, is extensively used as a Ring Closing Metathesis catalyst.[10] Recently, both mono- and bis-N-heterocyclic carbene derivatives of this parent catalyst precursor have demonstrated RCM catalytic activity.[11-13] Additional recent developments include the synthesis and reported RCM catalytic activity of bimetallic ruthenium alkylidene complexes.[14,15] These bimetallic complexes (Figure 3), bear either a single phosphine ligand or a single N-heterocyclic carbene ligand. All of these compounds show activity greater than $(PCy_3)_2Cl_2Ru{=}CHPh$.[16] Many of these new catalyst precursors demonstrate the ability to metathesize tetrasubstituted dienes, a characteristic that $(PCy_3)_2Cl_2Ru{=}CHPh$ does not possess.[13,17]

Finally, a series of thermochemical studies have examined the relative binding energies of phosphine and N-heterocyclic carbene ligands in the context of 16-electron Ru(II) complexes. The results indicate both steric and electronic properties of N-heterocyclic carbene ligands can be influenced by exocyclic substituents.[12,18,19]

With regard to both Heck Coupling and olefin metathesis, the use of N-heterocyclic carbenes as ligands in homogeneous catalysis has led to increased catalytic activity. In some cases, the active catalyst is also more stable. Overall, N-heterocyclic carbene ligands appear to be effective alternatives to phosphine ligands. As such, N-heterocyclic carbenes warrant consideration in homogeneous catalytic system design.

References

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