Oxidative Si-Si Bond Cleavage in Oligosilanes by Isocyanide-Coordinated Group 9 Metal Species

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It has been demonstrated that organosilicon compounds containing one or multiple Si-Si bonds can serve as good precursors for the formation of transition metal clusters with a twoor three-dimensional architecture ¹. In the last few years, our research group has reported that group 10 metal species bearing isocyanide ligands such as $[Pd(CN'Bu)_2]_3$ can react with oligosilanes such as cyclotetrasilane and ladder polysilanes to afford corresponding palladium clusters. In addition, suitable methods for the activation of Si–Si bonds in disilanes bearing two hypercoordinate silicon centres have been extensively studied in order to pursue more access to catalytically active organometallic complexes. There are precedents concerning the incorporation of hypercoordinate organosilicon ligands into group 10 metal species², yet a paradigm shift from group 10 to group 9 has been little discussed. In this presentation, we wish to report that oligosilanes having various backbones react with group 9 metal precursors with the general formula (RNC)₄M₂X₂ (M = Rh or Ir, X = any counter anion species) to give group 9 complexes or clusters, where silicon atoms are directly bound to the metal centres.

In our previous reports, we described that introducing isocyanide ligands to low valent metal precursors was an efficient methodology to generate a series of highly reactive metal precursors. In this study, group 9 metal precursors with the formula [(COD)MCl]₂ (COD = 1,5-cyclooctadiene, M = Rh or Ir) were selected, and isocyanide ligands were introduced onto the metal centres via ligand exchange from those precursors. In this manner, air-sensitive isocyanide-coordinated metal halide precursors were generated *in situ*, which was followed by the addition of an array of hypercoordinate silicon compounds, $R_2Si(\mu-Pz^{Me2})_2SiR_2$ ($Pz^{Me2} = 3,5$ -dimethylpyrazolyl). For instance, the reaction of [(COD)IrCl]₂ with 8 equiv. of CN'Bu was performed in toluene for 2 hours, and then 1 equiv. of $R_2Si(\mu-Pz^{Me2})_2SiR_2$ was added to the solution. Although no reaction took place at room temperature, formation of new organometallic complexes was confirmed upon heating overnight. The detailed molecular structures of these metal clusters obtained, as well as their application to catalytic transformations, will also be reported.

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