Low-Valent First-Row Transition Metal Complexes Featuring Vanadocene or Chromocene Bisamide ligands

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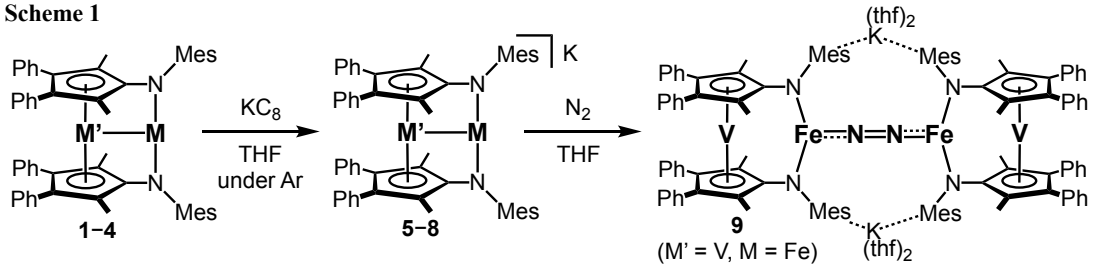
A number of dinitrogen complexes of iron have been thus far prepared while only a few research groups have reported significant N-N bond weakening of dinitrogen moiety. As a representative example, Holland group has achieved reduction of iron *β*-diketiminate complexes to provide dinitrogen complexes with N-N bond lengths of 1.215(6)-1.257(8) Å[1]. To achieve more effective activation of dinitrogen, we employed metallocene bisamide ligands, in which 1) the amide groups make the metal center electron-rich and 2) metallocene units would slightly stabilize a reduced state of the metal center through a metal-metal interaction. We report synthesis and reductions of iron and cobalt complexes derived from 1,1'-bis(arylamide)vanadocene and chromocene ligands. Reduction of the vanadium-iron complex was found to result in formation of a three-coordinate dinitrogen complex, where the N-N bond length lies in the longest category of the reported values[2].

Metallocene bisamide ligands were prepared from the reactions of M'Cl_2 (M' = V, Cr) and N-(cyclopentadienyl)amide. Treatment of the metallocene ligands with MCl_2 (M = Fe, Co) led to the formation of VFe, VCo, CrFe, and CrCo complexes **1**-**4** (Scheme 1). X-ray crystallography showed that the complexes possess short M'-M distances, indicative of bonding interactions between two metal centers. Addition of KC_8 to the complexes **1**-**4** under argon atmosphere was found to provide Fe(I) and Co(I) products **5**-**8**, respectively. Surprisingly, under 1 atm of N_2, the complex **5** was converted to the complex **9**, where two iron centers bind to the molecular dinitrogen in end-on fashion. The N-N bond distance of 1.208(5) Å is considerably elongated, compared to free N_2 (1.098 Å), comparable to the reported values for N=N double bonds.

Scheme 1



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