Synthesis of (Imido)niobium(V) Complexes and Some Reactions

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Design and synthesis of efficient molecular catalysts for precise olefin polymerization has been an important subject in organometallic chemistry, catalysis and polymer chemistry. Due to promising characteristics displayed in classical Ziegler-type vanadium catalysts (remarkable reactivity toward olefins),[1] study on group 5 metal complex catalysts attracts considerable attention. However, reported examples for synthesis of a series niobium complexes and their reaction chemistry have been limited. We thus herein introduce our explored results for synthesis of various (imido)niobium(V) complexes containing ketimide, phenoxide or alkoxide ligands to expand a possibility to use these complexes as catalysts for olefin polymerization.

Nb(NAr)Cl_2(O-2,6-$R_2C_6H_3$)(dme) [dme = 1,2-dimethoxyethane; Ar = 2,6-$Me_2C_6H_3$; R = ^{i}Pr (**1a**), Ph (**1b**)] could be prepared from Nb(NAr_3)Cl_3(dme) by treating with 1.0 equiv of LiOAr in Et_2O (Scheme 1). The complexes (**1a**,**b**) were identified by NMR spectra, elemental analysis, and their structures were determined by X-ray crystallography (Fig. 1). These complexes displayed catalytic activities for ethylene polymerization in the presence of MAO, however, the activities were low probably because of coordination of dme.

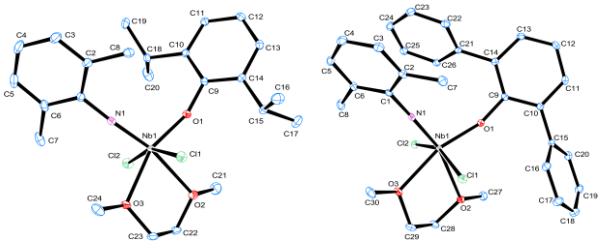
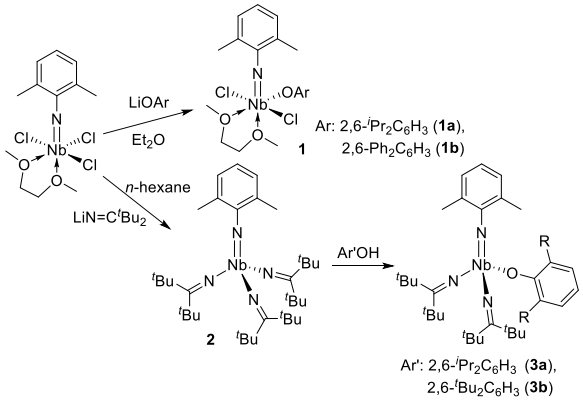


Fig. 1. ORTEP Drawings for **1a** (left), **1b** (right).

Solvent free tris(ketimide) analogue, Nb(NAr)(NC^tBu_2)$_3$ (**2**) could be thus prepared from Nb(NAr)Cl_3(dme) by addition of 3.0 equiv of LiNC^tBu_2 in toluene. Complex **2** was identified by NMR spectra, elemental analysis (**Scheme 1**).



Scheme 1. Reactions of Nb(NAr)Cl_3(dme).

Reactions of complex **2** with various phenol were investigated. Treatment of **2** with 1.0 or 2.0 equiv of 2,6-$^i Pr_2C_6H_3OH$ in *n*-hexane afforded Nb(NAr)(O-2,6-$^i Pr_2C_6H_3$)(NC^tBu_2)$_2$ (**3a**), Nb(NAr)(O-2,6-$^i Pr_2C_6H_3$)$_2$(NC^tBu_2) (**4**), respectively; structure of **3a** could be determined by X-ray crystallography (Fig. 2).

Reactions of **2** with 1.0 or 2.0 equiv of 2,6-$^t Bu_2C_6H_3OH$ in toluene at high temperature afforded Nb(NAr)(O-2,6-$^t Bu_2C_6H_3$)(NC^tBu_2)$_2$ (**3b**). However, attempts for synthesis of bis(phenoxide) complex by reaction of **2** with $^t Bu_2C_6H_3OH$ afforded only **3b** even at 100 ºC.

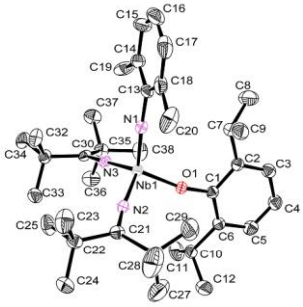


Fig. 2. ORTEP Drawing for **3a**.

Reactions of **2** with fluorinated alcohols were also explored. More details including applications as the olefin polymerization catalysts will be introduced in the symposium.

REFERENCES

[1] K. Nomura, S. Zhang, Chem. Rev., 111 (2011) 2342.