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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Synthesis of Hf(IV) Complex from Cyclam (1,4,8,11-Tetraazacyclotetradecane)-Containing Amino-Amido Groups

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Accepted author version posted online: 26 Jul 2011. Published online: 14 Sep 2011.

To cite this article: Munusamy Thirumavalavan & Jiunn-Fwu Lee (2012) Synthesis of Hf(IV) Complex from Cyclam (1,4,8,11-Tetraazacyclotetradecane)-Containing Amino-Amido Groups, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:2, 223-226, DOI: <u>10.1080/00397911.2010.523337</u>

To link to this article: http://dx.doi.org/10.1080/00397911.2010.523337

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SYNTHESIS OF Hf(IV) COMPLEX FROM CYCLAM (1,4,8,11-TETRAAZACYCLOTETRADECANE)-CONTAINING AMINO-AMIDO GROUPS

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GRAPHICAL ABSTRACT



Abstract The reactivity of cyclam (1,4,8,11-tetraazacyclcotetradecane)-containing aminoamido groups with hafnium(IV) chloride was described.

Keywords Amino-amido; cyclam; Hf(IV) complex; IR; NMR

INTRODUCTION

In coordination chemistry, polyaza macrocycles, though robust ligands, rarely have been used in their deprotonated forms as amido ligands^[1–3] or as ancilliary ligands in organometallic chemistry for supporting organic functionalities. This usage can be particularly addressed to the synthesis and use of amido and polyamido ligands in early transition and transition-metal chemistry.^[4–7] Such macrocyclic polyamines have a number of basic advantages in tuning the properties of the target complex using variants such as the number and type of donor atoms, ring size, and structural variations. The macrocyclic effect should play an important role in the stabilization of any resulting organometallic fragments. In this work, we illustrate these principles with tetraaza macrocycle (1,4,8,11-tetraazacyclotetradecane, H_4L)^[8] and

Received May 19, 2010.

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Scheme 1. Synthesis of macrocyclic Hf(IV) complex.

show how in the appropriate form it can be successfully reacted with early transition metals, illustrated here by Hf(IV). We report the synthesis of Hf(IV) complex. Scheme 1 is the schematic representation of the reaction of the amido-amino form of H₄L with HfCl₄ · 2THF. Addition of 2 equivalents of nBuLi to a tetrahydorfuran (THF) solution of the amine gave the soluble dianionic Li₂H₂L. Here we illustrate its reaction with HfCl₄ · 2THF, which was best achieved in situ and led to insoluble products. The Schlenk technique (connected with vacuum line and nitrogen) was used to synthesize the appropriate complex.

EXPERIMENTAL

A solution of nBuLi (3.33 ml, 1.60 M in hexane) was added to a stirred slurry of cyclam (0.5330 g, 0.0026 mol) in THF over 30 min. The solution was stirred for 60 min, and solid HfCl₄ · 2THF (1.2359 g, 0.0026 mol) was added to the resulting brown solution. The mixture was then left stirring for 4 h to finally give a red-brown cloudy solution. The solvent was pumped off. Pyridine was added to the residue, the brown solution was extracted, and the solvent pyridine was pumped off to get a pale brown solid. The solid was recrystallized in pyridine to get shiny, pale brown microcrystals (flakes), but these shiny crystalline flakes were not suitable for x-ray analysis. Yield: = 0.8336 g (70%). The synthesized Hf(IV) complex was characterized by elemental and spectral analyses. Analytical data for C₁₀H₂₂N₄Cl₂Hf · C₄H₈O: Calculated (%): C, 32.30; H, 5.81; N, 10.77. Found (%): C, 32.59; H, 5.89; N, 10.59. Mass (FAB) m/z: 520 (M + 1). Selected IR (KBr): 3135 (s) cm⁻¹ (N-H stretching).

RESULTS AND DISCUSSION

The N-H stretching of cyclam was observed at 3268 and 3186 cm⁻¹. ¹H (300 MHz) NMR (δ ppm in C₅D₅N): 2.84–3.89 and 1.56–2.36 (complex CH₂ region). One unpredictable peak was obtained at δ = 5.70, which may be due to N-H protons. ¹³C (75 MHz) NMR (δ ppm in C₅D₅N): 22.50 (*C*<u>C</u>H₂C), 24.88 (*C*<u>C</u>H₂C), 29.63 (*N*<u>C</u>CH₂), 30.66 (*N*<u>C</u>CH₂), 45.67(*N*<u>C</u>H₂C), 46.40 (*N*<u>C</u>H₂C), 48.75 (*C*H₂<u>C</u>N), 52.72 (*C*H₂<u>C</u>N), 61.14 (*N*H<u>C</u>CH₂), and 75.04 (*N*H<u>C</u>CH₂). The ¹³C NMR spectra confirm 10 chemically inequivalent carbon resonances as C attached to CH₂, C attached to N, C attached to NH, C attached to N-CH₂ and C attached to NH-CH₂. Before recrystallization, the NMR spectrum seems to be complex, but after fractional



Scheme 2. Hafnium complex-catalyzed esterification reaction.

recrystallization,^[3] the NMR spectrum is simpler. Both elemental analysis and NMR spectral analysis led to the interesting result that the complex contained one THF molecule, either coordinated or as free lattice molecule. Although the addition of BuLi-cyclam solutions to the metal suspensions resulted in immediate dissolution, the formation of complex required reflux. Considering that in general the metathesis of metal halide bonds with lithium amides occurs readily, the higher energy barriers associated with these reactions must result from the structural features of BuLi-cyclam. To attain the structure depicted in Scheme 1, cyclam has to undergo structural transformation to bind the four nitrogen atoms to the same metal center. This complex exemplifies a direction in the use of amido-amino ligands and in particular in the form of the macrocycle. To confirm the activity, we describe here highly efficient and direct esterification of 4-phenylbutyric acid (1 mmol) and benzyl alcohol (1 mmol) catalyzed by Hf complex (1 mol%) in toluene under reflux at inert conditions for 10 h as shown in Scheme 2. The reaction led to 100% conversion of ester as product. For the uncatalyzed reaction, the observed yield was only 33%.

CONCLUSION

We believe that this complex will have improved catalytic activity and we are actively studying this.

ACKNOWLEDGMENTS

M. T. gratefully acknowledges the financial support received from FCT (Fundação Para a Ciência e a Tecnologia, Grant No. SFRH/BPD/14985/2004), Portugal, and the financial support by the National Science Council (NSC), Taiwan, China.

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