Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Organometallic Chemistry 691 (2006) 2517–2527

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, structure, and bridge-terminal alkyl exchange kinetics of pyrazolate-bridged dialuminum complexes containing bridging *n*-alkyl groups

Chatu T. Sirimanne, Zhengkun Yu, Mary Jane Heeg, Charles H. Winter *

Department of Chemistry, Wayne State University, Detroit, MI 48202, United States

Received 18 January 2006; received in revised form 19 January 2006; accepted 19 January 2006
Available online 28 February 2006

Abstract

Treatment of triethylaluminum with 3,5-diphenylpyrazole in a 2:1 stoichiometry afforded the ethyl-bridged complex $Et_2Al(\mu\text{-}Ph_2pz)(\mu\text{-}Et)AlEt_2$ (79%) as a colorless crystalline solid. Treatment of tri-*n*-propylaluminum with 3,5-di-*tert*-butylpyrazole in a 2:1 stoichiometry afforded the *n*-propyl-bridged complex $(nPr)_2Al(\mu\text{-}tBu_2pz)(\mu\text{-}nPr)Al(nPr)_2$ (63%) and the dimeric complex $[(nPr)_2Al(\mu\text{-}tBu_2pz)]_2$ (3%), respectively, as colorless crystalline solids. Treatment of tri-*n*-propylaluminum (1 equiv.) or triisobutylaluminum (1 or 2 equiv.) with 3,5-di-*tert*-butylpyrazole afforded exclusively the dimeric complexes $[(nPr)_2Al(\mu\text{-}tBu_2pz)]_2$ (68%) or $[(iBu)_2Al(\mu\text{-}tBu_2pz)]_2$ (96%), respectively, as colorless crystalline solids. The solid state structures of $Et_2Al(\mu\text{-}Ph_2pz)(\mu\text{-}Et)AlEt_2$ and $(nPr)_2Al(\mu\text{-}tBu_2pz)(\mu\text{-}nPr)Al(nPr)_2$ consist of 3,5-disubstituted pyrazolato ligands with a di-*n*-alkylalumino group bonded to each nitrogen atom. An ethyl or *n*-propyl group acts as a bridge between the two aluminum atoms. The kinetics of the bridge-terminal exchange was determined for the bridging *n*-alkyl complexes by ^{13}C NMR spectroscopy, and afforded $\Delta H^\ddagger = 1.5 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -46.8 \pm 39.0$ cal/K mol, and $\Delta G^\ddagger_{(298\ K)} = 15.4 \pm 11.7$ kcal/mol for $Et_2Al(\mu\text{-}Ph_2pz)(\mu\text{-}Et)AlEt_2$ and $\Delta H^\ddagger = 1.7 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -46.6 \pm 43.4$ cal/K mol, and $\Delta G^\ddagger_{(298\ K)} = 15.6 \pm 11.7$ kcal/molpz)(μ-*n*Pr)Al(*n*Pr)$_2$. The negative values of $\Delta S^\ddagger$ imply ordered transition states relative to the ground states, and rotation along the N-AlR_3 vector without aluminum–nitrogen bond cleavage is proposed.

Keywords: Aluminum; Trimethylaluminum; Triethylaluminum; Tri-*n*-propylaluminum

---

1. Introduction

It is broadly recognized that saturated hydrocarbon groups can bridge between two aluminum centers [1,2]. In spite of the fundamental importance of such interactions, structurally characterized complexes remain small in number and nearly all contain methyl bridges [2]. A few crystallographically characterized aluminum complexes have been reported that contain bridging ethyl [3] or cyclopropyl [4] ligands. Additionally, heterobimetallic compounds have been structurally characterized in which a methyl [5] or ethyl [6] group bridges between aluminum and a transition metal, main group, or lanthanide ions. Recent advances in olefin polymerization catalysis have underscored the importance of bridging alkyl ligands in group 13 complexes. Methylalumoxane and aluminum alkyls are frequently employed as co-catalysts in alkene polymerization processes, but their exact roles are not well understood [7]. Cationic aluminum complexes are capable of polymerizing ethylene, epoxides, and lactide, and the highly electrophilic nature of the these species may promote the formation of alkyl-bridged complexes [3c,8]. Perfluoroaryl-substituted boranes and other boron-containing species act as methide/hydride abstracting agents and precatalyst activators in transition metal catalyzed single-site homogeneous olefin polymerization [9,10]. In the catalyst resting state, the boron center is often coordinated to the

---

* Corresponding author. Fax: +1 313 577 8289.
E-mail address: chw@chem.wayne.edu (C.H. Winter).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.040

metal-bound methyl group, resulting in a bridging methyl ligand. Several groups have reported the use of boron compounds containing two Lewis acidic diarylboryl groups as effective activators for single-site olefin polymerization catalysis [11].

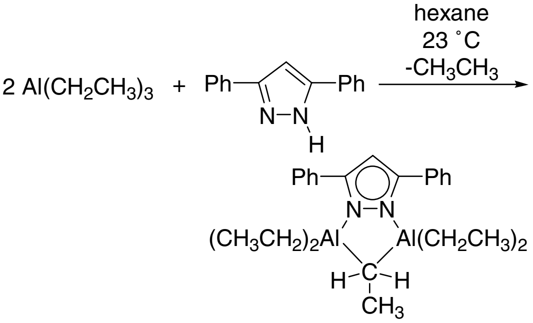
More recent research has shown that Lewis acids comprised of two closely-linked boron centers might be superior polymerization precatalyst activators [11a,12], since bidentate coordination of the abstracted alkyl group should afford a more weakly coordinating anion and higher polymerization activity. Finally, dinuclear complexes have been of considerable recent interest as Lewis acid catalysts [13]. Closely spaced metal centers may cooperatively bind Lewis bases, which could lead to new types of substrate activation compared to traditional mononuclear metal-based Lewis acids.

While the solution and solid state structures of trimethylaluminum have been intensively studied [2a,2b,2c,2e, 2j,14], less is known about the related structures of higher *n*-alkyl derivatives of aluminum. NMR studies have demonstrated that tri-*n*-alkylaluminum complexes exist predominantly as dimers in nonpolar organic solvents and possess structures that are similar to dimeric trimethylaluminum [15]. Solution molecular weight measurements have suggested that trialkylaluminum complexes with alkyl substitution on the α- or β-carbon atoms of the alkyl ligands are monomeric in solution [15f,16]. There have been no reports of X-ray crystal structures of dimeric tri-*n*-alkylaluminum complexes.

We have previously reported the synthesis, structure, molecular orbital calculations, and bridge-terminal methyl exchange kinetics of dialuminum pyrazolato complexes containing bridging methyl groups [2j]. In particular, molecular orbital calculations suggested that the bridging methyl group was stabilized by 6–7 kcal/mol, relative to dimeric trimethylaluminum, by extended orbital interactions involving the bridging methyl group and pyrazolato ligand-based orbitals. Such stabilization suggested that dialuminum pyrazolato complexes might stabilize other bridging alkyl ligands. Herein, we report the synthesis, structure, and bridge-terminal alkyl group exchange kinetics of dialuminum pyrazolato complexes that contain bridging ethyl or *n*-propyl groups. The strong aluminum–nitrogen bonds in these complexes stabilize them toward loss of triethylaluminum or tri-*n*-propylaluminum. We also report the synthesis and structural characterization of several dimeric dialkylaluminum complexes that contain bridging pyrazolato ligands. A portion of this work was communicated [3a].

2. Results and discussion

Treatment of 3,5-diphenylpyrazole with triethylaluminum (2 equiv.) in hexane at ambient temperature led to slow ethane evolution over 18 h and afforded μ-diphenylpyrazolato-μ-ethyl-tetraethyldialuminum (**1**, 79%) as a colorless crystalline solid (Eq. (1)). The formulation of **1** as the ethyl-bridged structure was based upon spectral and analytical data, and by X-ray crystallography. At −40 °C in toluene-d_8, resonances due to terminal ethyl groups were observed in the ^{1}H NMR spectrum at δ 1.27 (t) and −0.30 (q) while another set of ethyl resonances appeared at δ 1.00 (t) and 0.93 (q). The ratio of these two sets of peaks (δ 1.27, −0.30 and 1.00, 0.93) was 4:1, suggesting the presence of a bridging ethyl ligand. In the ^{13}C{^{1}H} NMR spectrum at −40 °C, the terminal ethyl carbons resonated at 9.79 and 1.79 ppm while sharp bridging ethyl ligand resonances were observed at δ 7.35 and 4.08 ppm. Upon warming from −40 to 20 °C in toluene-d_8, the methyl and methylene resonances of the bridging ethyl resonance gradually broadened and shifted downfield slightly. Above 20 °C, only one type of ethyl group was observed, suggesting rapid exchange of terminal and bridging ethyl sites.



1, 79%

(1)

Treatment of 3,5-di-*tert*-butylpyrazole with tri-*n*-propylaluminum (2 equiv.) in hexane at ambient temperature afforded μ-3,5-di-*tert*-butylpyrazolato-μ-*n*-propyl-tetra-*n*-propyldialuminum (**2**, 63%) and bis(μ-3,5-di-*tert*-butylpyrazolato)tetra-*n*-propyldialuminum (**3**, 3%) as colorless crystalline solids (Eq. (2)). The formulations of **2** and **3** were assigned based upon their spectral and analytical data and by X-ray crystallography, as described below. The formulation of **2** as the *n*-propyl-bridged structure was suggested initially by the^{1}H and ^{13}C{^{1}H} NMR spectra. At 23 °C in toluene-d_8, resonances due to terminal *n*-propyl groups were observed in the ^{1}H NMR spectrum at δ 1.50 (m), 1.15 (t) and 0.40 (t) while another set of *n*-propyl group resonances appeared at δ 1.77 (m), 1.17 (t), 1.05 (br s). The ratio of these two sets of resonances (δ 1.50, 1.15, 0.40 and δ 1.77, 1.17, 1.05) was 4:1, suggesting the presence of a bridging *n*-propyl ligand. In the ^{13}C{^{1}H} NMR spectrum of **2** at −70 °C in toluene-d_8, the methylene resonances (Al–*C*H$_2$) of the terminal *n*-propyl group resonated at 16.56 ppm while the methylene resonance (Al–*C*H$_2$) of the bridging *n*-propyl group was observed at 16.73 ppm. Upon warming from −70 to 20 °C in toluene-d_8, the methylene resonance (Al–*C*H$_2$) of the bridging *n*-propyl resonance gradually broadened and shifted downfield slightly. Above 20 °C, only one type of methylene resonance was observed, suggesting rapid exchange of terminal and bridging *n*-propyl sites.