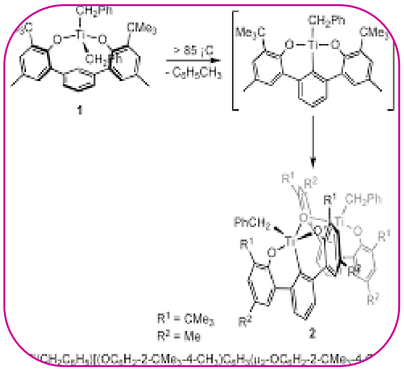
REVIEW OF RESEARCH
ISSN: 2249-894X
IMPACT FACTOR : 5.2331(UIF)
VOLUME - 7 | ISSUE - 4 | JANUARY - 2018
UGC APPROVED JOURNAL NO. 48514

STUDY THE INTRAMOLECULAR C-H ACTIVATION OF A BISPHENOLATE LIGAND TITANIUM DIBENZYL COMPLEX

Nitu Kumari[1] and Dr. Parveen Kumar[2]
[1]Research Scholar, Deptt. Of Chemistry, OPJS University, Churu, Rajasthan, India.
[2]Associate Professor, Deptt. Of Chemistry, OPJS University, Churu, Rajasthan, India.

ABSTRACT—
A titanium dibenzyl complex featuring a ligand with two phenolates linked by a benzene-1,3-diyl was found to undergo thermal decomposition to give toluene and a cyclometalated dimeric complex. The thermal decomposition followed first-order kinetics and was studied at a number of temperatures to determine the activation parameters (AH = 27.2(5) kcal/mol and AS* = -6.2(14) cal/mol-K). Deuterated isotopologs were synthesized to measure the kinetic isotope effects. The complexes with deuterium in the benzyl methylene positions decomposed slower than the protio analogs. Isotopologs of toluene with multiple deuteration positions were observed in the product mixtures. These data are consistent with competing a-abstraction and a-bond metathesis.*



KEY WORDS: titanium dibenzyl complex, cyclometalated dimeric complex etc.

INTRODUCTION :

Metal-benzyl linkages are common in the field of olefin polymerization as they can be activated by methylaluminaoxane (MAO) or stoichiometric activators (e.g. $[Ph_3C][BF_4]$). Tetrabenzyl titanium has been known to polymerize ethylene and a-olefins since 1968. More recently, metal-benzyl linkages have received attention in the field of C-H bond activation.Fundamental transformations such as C-H bond activation are usually invoked as elementary steps of higher order catalytic reactions suchas polymerization, dehydrogenation, or alkane functionalization.

group 4 dibenzyl complexes having two phenolates linked by 2,6-pyridyl, 2,5-pyrazolyl, 2,5-furanyl, 2,5-thiophenyl, or benzene-1,3-diyl groups that are active for olefin polymerization.Attempts to activate the titanium dibenzyl complex having the bisphenolate(benzene-1,3-diyl) ligand by treatment with substoichiometric amounts of reagents that remove one benzide group gave instead a cyclometalated dimeric product bridged by two phenolate oxygens where activation of the 2-C-H bond of the benzene-1,3-diyl linker resulted in cyclometalation and loss of toluene. This same product could also be obtained by simply heating the neutral dibenzyl complex. Chromium, tantalum, and molybdenum complexes having similar ligands show an analogous propensity for C-H activation; although, the resulting products remain monomeric. The mechanism(s) for thermal loss of toluene from the bisphenolate(benzene-1,3-diyl) titanium dibenzyl complex has been examined, and an interesting and unusual process involving parallel pathways has been identified.

REVIEW OF LITERATURE

Prior to the advent of transition metal co-ordination catalysts, polyethylene was manufactured via a high temperature, high-pressure, free radical polymerisation process, which typically gives highly branched products. The 1950's saw the dawn of transition metal catalysts in the form of the Ziegler-Natta, (TiCVAlCU^) and Philips silica- supported chromium heterogeneous catalyst systems. Both of these systems are active polymerisation catalysts but as with many heterogeneous systems they have a common problem, namely the difficulty in controlling polymer structure. Control is difficult due to the unknown nature and distribution of active polymerisation sites within the catalyst structure.

MATERIAL AND METHODS

Synthesis of Ti(CH2C6H5)2[(OC6H2-2-CMe3-4-CH3)2C6H3](1) and Its Conversion to Dimer 2. As described in an earlier publication, a bisphenolate(benzene-1,3-diyl) ligand featuring tert-butyl groups in the *ortho* positions and methyl groups in the *para* positions has been prepared and metalated using titanium tetrabenzyl ($TiBn_4$) *via* toluene elimination to give a ligated dibenzyl complex (1). Heating a solution of 1 in an aromatic solvent facilitates C-H bond activation to give toluene and a cyclometalated complex that readily dimerizes. The dimer was quite asymmetric showing two peaks for the *tert-butyl* groups, two peaks for the methyl groups, and two doublets for the benzyl protons in the ^{1}H NMR spectrum. This evidence alone does not prove dimeric speciation in solution because a monomeric complex featuring a C2-symmetric ligand with a single benzyl group on the same metal would exhibit identical ^{1}H NMR coupling; however, the monomeric cyclometalated complex is coordinatively unsaturated and sterically unencumbered due to the tridentate ligand thus making dimerization favorable. A single crystal X-ray structure determination of 2 reveals that each titanium is five-coordinate, bound by the two phenolates of the bisphenolate(benzene-1,3-diyl) ligand, one bridging phenolate oxygen from the ligand on the other titanium, one benzyl group positioned away from the dimer core and bent toward the linker of the ligand, and one phenyl linkage from the now metalated ligand. The reaction forming the dimer is very clean with no detectable amounts of other decomposition or side products, thus amenable to mechanistic study.

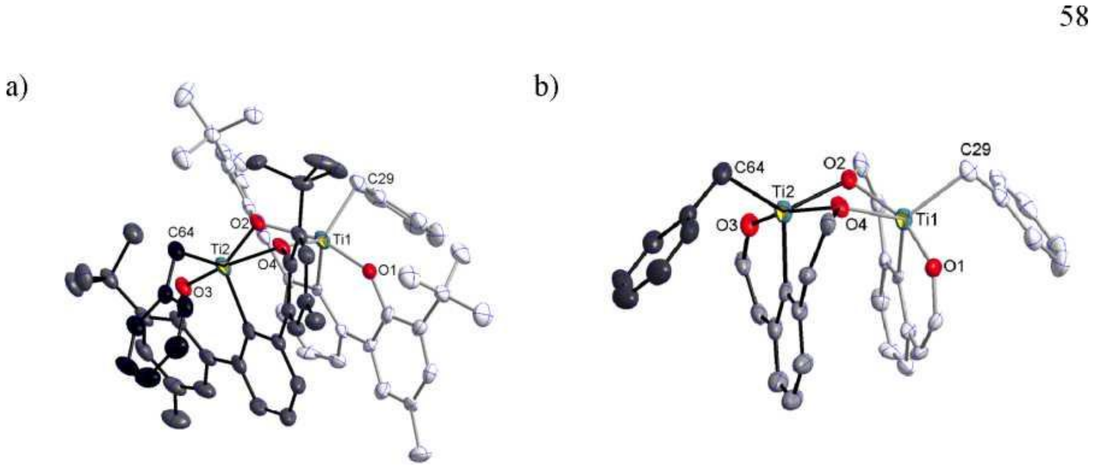
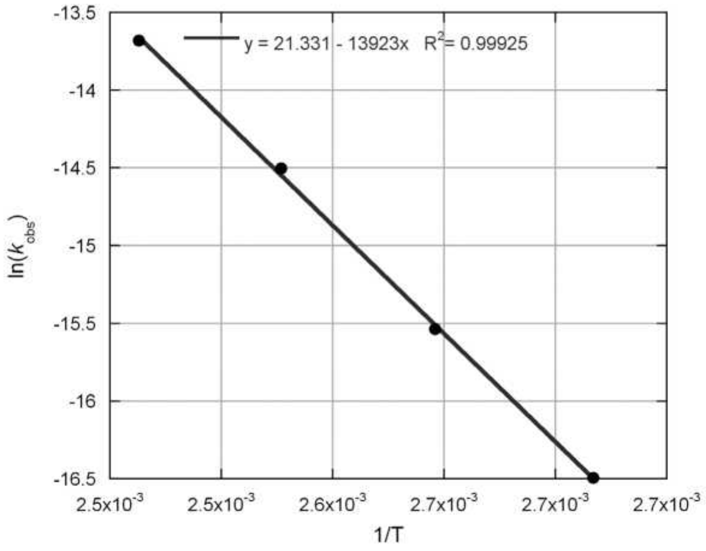


Figure 1. The solid state structure of 2. Hydrogens have been omitted for clarity: a) side view; b) skeletal view with ligand framework atoms (only) and residual benzyl ligand for each titanium. Selected bond lengths (A) and angles (°) for 2: Ti1-O2 2.038(3), Ti1-O4 2.042(3), Ti2-O2 2.049(3), Ti2-O4 2.025(2), O2-Ti1-O4 70.20(11), O2-Ti2-O4 70.34(11), Ti1-C29-C30 105.1(2), Ti2-C64-C65 106.2(2).

RESULTS AND DISCUSSION

The transformation of 1 to 2 in *o-xylene-d_{10}* was monitored over a temperature range of 30 K (368-398 K) with first order behavior observed over two half-lives for all temperatures. The rates for the temperature study are reported in Table 2 and the Eyring plot is shown in Figure 2. The activation parameters so derived (AH* = 27.2(5) kcal/mol and _AS*_ = -6.1(2) cal/mol-K) are similar to those observed for the thermal decomposition of Cp*2Ti(CH3)2 (AH* =27.6(3) kcal/mol and _AS*_=-2.9(7) cal/mol-K),$(C_5H_4CMe_2Ph)TiBn_3$ _(AH*_ = 24(2) kcal/mol and _AS*_ = -5(5) cal/mol-K),[21] and Cp*$_2$HfBn$_2$ _(AH*_ = 34(1) kcal/mol and _AS*_ = 1(3) cal/mol-K),where a-hydrogen abstraction has been proposed as the rate determining step. The other commonly proposed mechanism for transformations of early transition metal alkyls is a-bond metathesis. The reaction between Cp*$_2$ScCH$_3$ and 4-methyl styrene in hydrocarbon solvent at elevated temperature results in Cp*$_2$ScCH=CH(p-$C_6H_4CH_3$) and methane with _AH*_ = 12 kcal/mol and _AS*_ = -36 cal/mol-K via a a-bond metathesis process.

Figure 2. The Eyring plot for the formation of **2**.



REFFERENCES

1. Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* 2002, *344,* 477-493.
2. Mitani, M.; Saito, J.; Ishii, S.-I.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.-I.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *Chem. Rec.* 2004, 4, 137-158.
3. Calderazzo, F.; Englert, U.; Pampaloni, G.; Santi, R.; Sommazzi, A.; Zinna, M. *J. Chem. Soc., Dalton Trans.* 2005, 914-922.
4. NMR scale reactions were performed using 1-H_2 or 1-$TiCl_2$(THF) in bendene-d_6 to show no reaction upon mixing at room temperature, nor was there a reaction at 90°C.