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Ir/Sn dual reagent catalysis for the alkylation of arenes with benzyl alcohols: Kinetic evidence for an electrophilic pathway and a guide towards electronic tuning of catalyst efficiency

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Abstract

Presented herein is a detailed account of the $[Ir(COD)(\mu\text{-}Cl)]_2/SnCl_4$ dual reagent catalyzed alkylation of arene/heteroarene with benzyl alcohols [J. Choudhury, S. Podder, S. Roy, J. Am. Chem. Soc. 127 (2005) 6162]. A high-valent heterobimetallic complex namely $[Ir^{III}(COD)(\mu\text{-}Cl)(SnCl_3)Cl]_2$ (isolated from $[Ir(COD)(\mu\text{-}Cl)]_2$ and $SnCl_4$) could also promote the alkylation. A working model on substrate binding, activation and coupling across Ir/Sn catalyst is proposed considering the hard–soft nature of the two metals (Ir and Sn) and the organic substrates (arene and alcohol). The *"tin–alcohol"* hard–hard interaction is indicated by the alkylation rate for $PhCH_2\text{-}Y$ which varied with the HSAB donor strength of Y in the order OH > OAc > OMe > OC(O)H > Cl. Hammett studies with respect to arene and alcohol indicate an electrophilic mechanism. A small secondary kinetic isotope effect ruled out a C–H activation pathway. Competitive and non-competitive rate studies (isomer distribution and k_T/k_B ratio) showed a similarity with Friedel–Crafts like kinetics. Temperature dependent kinetics showed that the reaction is characterized by a positive enthalpy of activation, and small negative entropy of activation. The stereoelectronic influence of the two metal centers on the catalyst efficiency is also studied. It is shown that the coordinated ligand at the iridium center and the Lewis acidity at the tin center control the efficiency of the Ir/Sn catalysts towards aromatic alkylation.

Keywords: Iridium; Tin; Bimetallic catalysis; Aromatic alkylation; Kinetics; Mechanism

1. Introduction

Heterobimetallic catalysis constitutes an important sub-area within the broader domain of multimetallic catalysis. The successful design of homogeneous heterobimetallic catalysts is a topic of ongoing interest [1–5]. This is due mainly to the fact that the incorporation of two metals in a single scaffold offers selective substrate binding, dual and synergistic activation, as well as enhanced reactivity [6,7]. The success of such type of catalysts depends on the properties of the two metals, and their ability to communicate electronically during substrate binding and activation. In practice, two design features exemplify such a heterobimetallic regime. The first type is an intramolecular version involving a single catalyst in which two different metals are built on a single scaffold (M–L–M′ or L–M–M′–L′). The second type is an intermolecular version involving dual partners (M–L + M′–L′), both of which participate in the transition state [6] (Fig. 1).

In the course of our continuing effort to exploit the organic reactivity of bimetallic/dual reagent systems having transition metal (Tm) and tin (Sn) as partners [8–21], we recently communicated the first example of a heterobimetallic catalyst design within "Ir–Sn" regime for the alkylation of aromatics with benzylic alcohols [8]. It may be noted that alkylative coupling of an arene and alcohol is a classical and industrially important reaction, which has been studied with traditional Lewis acid catalysts, rare-earth triflates, $H_2PtCl_6{\cdot}6H_2O$, modified clays, and Nafion-H at 10–120% loading in the temperature range of 80–120 °C [22–26]. According to our proposal the oxidative addition of tin(IV) halides across a low-valent late transition metal organometallic partner would generate a high-valent Tm–Sn bimetallic scaffold. This scaffold bears interesting features for potential application within cooperative catalysis regime. These features include (i) a high-valent and soft

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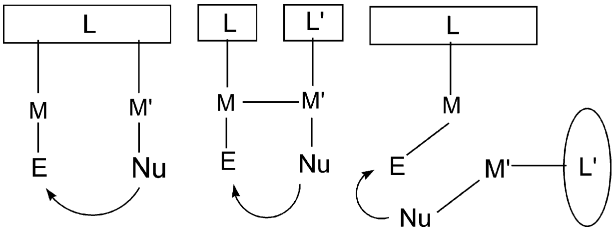

Fig. 1. Intramolecular and intermolecular heterobimetallic catalysts.

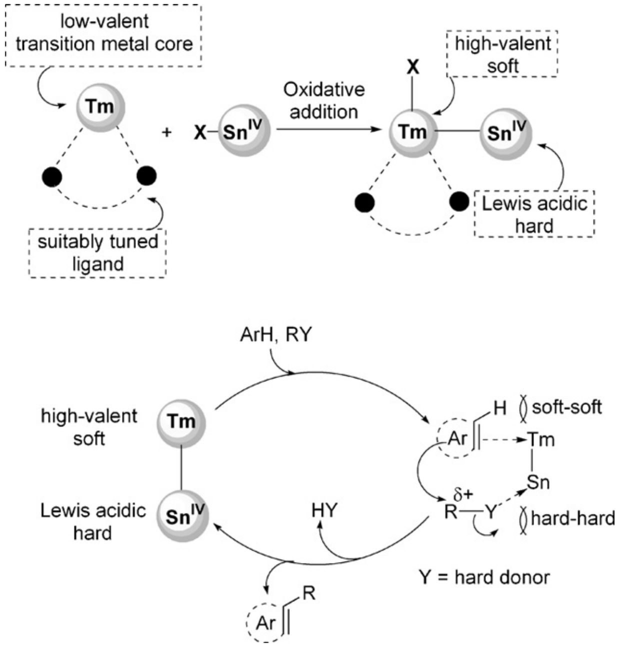

Fig. 2. Proposed model on the generation and reactivity of high-valent Tm–Sn heterobimetallic motif.

electrophilic late transition metal center (Tm) for the activation of soft nucleophiles such as a π-system, (ii) a hard Lewis acidic tin center (Sn^{IV}) for the activation of substrates having hard donor atoms and (iii) close proximity of Tm and Sn centers for proximal binding and subsequent coupling between different organic substrates (Fig. 2).

Herein we present a detailed account of our results on aromatic alkylation with benzyl alcohols via Ir/Sn catalysis. We mainly focus on kinetic evidences that entailed us to glimpse on the substrate activation modes, initial bond-breaking/bond-making steps, and the interplay of stereoelectronic influence across the two metal centers, which controls the catalyst efficiency.

2. Experimental

2.1. General method

All preparations and manipulations were performed under a dry, oxygen-free argon atmosphere using standard vacuum lines and Schlenk techniques. All solvents, used for the synthesis, were dried and distilled by standard methods and previously deoxygenated in the vacuum line. Pre-coated silica gel $60F_{254}$ (Merck) was used for thin layer chromatography and silica gel 100–200 mesh (SRL) was used for column chromatography. $IrCl_3 \cdot xH_2O$ (Arora Mathey Ltd.), 1,5-cyclooctadiene (Aldrich), 2,5-norbornadiene (Lancaster), and tin tetrachloride (Fluka) were commercially available. $SnBr_4$ [27], SnI_4 [27], $[Ir(COD)(\mu\text{-}Cl)]_2$ [28], $[Ir(NBD)_3Cl]_n$ [29], $Ir(CHD)_2Cl$ [30] and $[Ir(COD)_2(SnCl_3)]$ [31] were prepared by literature procedure. Synthetic procedure and X-ray structure of $[Ir(COD)(\mu\text{-}Cl)(SnCl_3)(Cl)]_2$ were reported in our previous communication [8].

^1H (200 MHz) and ^{13}C NMR (54.6 MHz) spectra were recorded on Bruker-AC 200 MHz spectrometer at 300 K. IR spectra were obtained using a Thermo Nicolet FTIR Spectrometer (NEXUS-870). Elemental analyses were performed on Perkin Elmer Instruments 2400 Series II CHNS/O Analyzer.

2.2. General note on GC analysis

GC analyses were on a Chemito-8610 instrument equipped with a FID using 6 ft × 1/8 in. × 2 mm SS 10% Silicone OV-1 packed column (from Chrompack), and 30 m × 0.25 mm i.d. × 0.25 μm TR-1 capillary column (from Thermo Electron, UK).

For the kinetics study, the relevant parameters were as given:

Column	6 ft × 1/8 in. × 2 mm SS 10% Silicone OV-1 packed column
Injection temperature	130 °C
Detector temperature	240 °C
Oven temperature program	80 °C–1 min–5 °C/min–100 °C–20 °C/min–160 °C–20 min
Carrier gas (N_2) flow	1.9 bar
Retention time (min)	
Diphenylmethane	11.5
Benzyltoluenes	14.4
Ditolylmethanes	18.5
4-Chlorodiphenylmethane	18.9
4-(Chlorophenyl)tolylmethanes	25.9

For the analysis of the other coupling products a common isothermal oven temperature could not be used due to the difference in volatility and nature of the compounds. Therefore, these were subjected to different temperature programming for the oven temperature whichever was found appropriate and matched with standard samples.

For example, to determine the *ortho*:*para* isomer ratio of benzyltoluenes, ditolylmethanes, and (4-chlorophenyl) tolylmethanes the following procedure was adopted:

Column	6 ft × 1/8 in. × 2 mm SS 10% Silicone OV-1 packed column
Injection temperature	130 °C
Detector temperature	240 °C
Oven temperature program	50 °C–10 min–5 °C/min–100 °C–2 °C/min–120 °C–1 °C/min–140 °C–15 min
Carrier gas flow	1.8 bar
Retention time (min)	
2-Benzyltoluene	45.77
4-Benzyltoluene	46.60