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Cyclometalated group 4 complexes supported by tridentate pyridine-2-phenolate-6-(σ-aryl) ligands: Catalysts for ethylene polymerization and comparisons with fluorinated analogues

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Dedicated to Prof. Dr. Gerhard Erker for his inspiring research on the occasion of his 60th birthday.

Abstract

An adaptable synthetic methodology for the tridentate dianionic pyridine-2-phenolate-6-aryl [O,N,C] ligand framework, comprising the aromatic σ-carbanion moiety as a chelating component, has been developed. A series of non-fluorinated group 4 bis(benzyl) complexes supported by [O,N,C] auxiliaries, with halogen and alkyl groups at the 'R^1' position *ortho* to the metal-C(σ-aryl) bond, have been prepared by exploiting the cyclometalation of the ligand. All derivatives have been characterized by NMR spectroscopy, and the spectral features concerning the metal-bound diastereotopic methylene groups have been highlighted. The capabilities of these complexes as catalysts for olefin polymerization have been tested, and comparisons with the recently reported fluorine-containing Ti-[O,N,C] analogues and related Hf-[N,N,C] derivatives are discussed. The titanium catalysts, in conjunction with MAO, displayed moderate to high activities for ethylene polymerization (up to 200 g $mmol^{-1}$ h^{-1}).

Keywords: Benzyl complexes; Cyclometalation; Olefin polymerization; Post-metallocenes; σ-Aryl ligand

1. Introduction

The development of new 'post-metallocene' complexes as olefin polymerization catalysts, propelled by the pursuit of novel materials and properties, and superior control over reactivity, have proliferated [1]. The myriad of ancillary ligand combinations that can support an active catalytic species continues to expand, and in the impetus to avoid the cyclopentadienyl group, C-based anionic ligands have largely been overlooked. For group 4 complexes, the limited studies have focused on simple allyl ligands [2] plus tropidinyl [3] and heteroatom analogues [4], but in general their inertness is insufficient and modest catalytic activities are obtained. The σ-aryl moiety has been employed as a chelating unit by Hessen and coworkers [5], although only low to moderate activities in propylene polymerization was reported for Zr(IV) catalysts with tridentate dianionic bis(σ-aryl)amine ligands [6].

We previously presented the first direct observation of weak intramolecular C–H···F–C contacts in Group 4 post-metallocene catalysts bearing tridentate pyridine-2-phenolate-6-(fluorinated σ-aryl) ligands [7]. Moreover, the structural parameters of the controversial [8] C–H···F–C interaction was accurately determined for the first time by a recent neutron diffraction study [9]. The observed C–H···F–C interactions are important with regards to design implications in olefin polymerization catalysts. In particular, they substantiate the DFT-derived ortho-F···H(β) ligand–polymer contacts proposed by Fujita [10] to account for the remarkable living olefin polymerization behavior at elevated temperatures displayed by Group

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4 fluorinated phenoxyimine 'FI' catalysts [11]. Indeed, unlike conventional agostic [12] and metal···cocatalyst contacts [13,14], weak attractive non-covalent interactions between a 'non-innocent' ligand and the polymer chain may be considered as a new concept in polyolefin catalysis. In this work, a new collection of Group 4 catalysts with non-fluorinated substituents in the locality of the metal center has been designed and synthesized from the facile ortho-cyclometalation of pyridine-2-(2′-phenol)-6-(aryl) substrates. The principal aims of the present study is to probe (a) the influence of the metal ion (Ti, Zr, Hf), and (b) the impact of replacing the F or CF_3 group [9] adjacent to the metal–C(σ-aryl) bond (termed the R^1 position; see Scheme 1) with substituents displaying different steric and electronic characteristics, namely Br, Cl and methyl, upon NMR spectroscopic properties and polymerization behavior. The development of bromine-substituted ligands is interesting because this potentially allows further derivatization to novel ligands with a variety of aryl moieties at R^1 using Suzuki/Stille-type C–C coupling reactions. The systematic study of all group 4 metals was deemed appropriate since researchers at Symyx and Dow have very recently observed excellent propylene polymerization activities for related hafnium(IV) catalysts bearing tridentate cyclometalated pyridylamido ligands [15].

2. Results and discussion

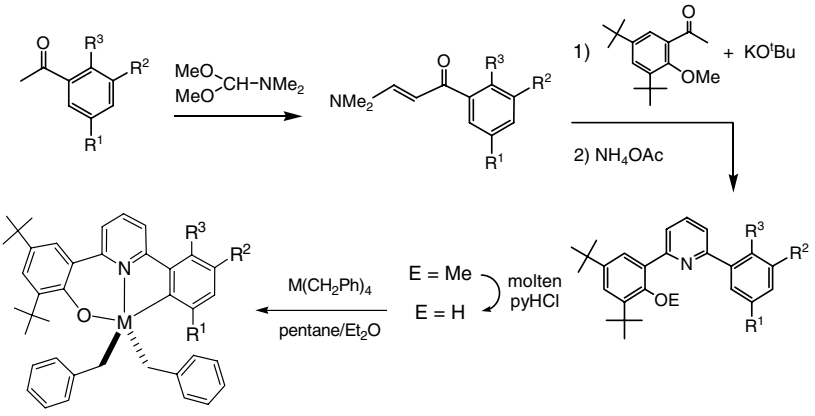
2.1. Design approach

We became attracted to the design and assembly of the tridentate non-symmetric pyridine-2-aryloxide-6-(σ-aryl) [O,N,C] framework as a suitable ligand ensemble in olefin polymerization catalysts: (1) aryloxide- and alkoxide-based chelating ligands have been one of the cornerstones of advances in post-metallocene catalyst design [16]; (2) from our recent work on a family of Zr(IV) catalysts bearing tridentate pyridine-2,6-bis(aryloxide) [O,N,O] auxiliaries, we concluded that strong binding by the central pyridyl moiety is a critical factor in achieving exceptional catalytic efficiencies [17]; (3) aromatic σ-carbanions are predominantly σ-donors with minimal π-donation (in contrast to strong π-donors such as Cp), and can engender a catalytic center with enhanced electrophilicity.

The geometry and rigidity of the [O,N,C] ligand are important features, dictating that the R^1 substituent *ortho* to the metal–C(σ-aryl) bond (Scheme 1) is in close proximity to the metal/catalytic site but is nevertheless 'tied back' to preclude interaction with the metal center. Furthermore, facile modification of the R^1 substituent has been demonstrated through the development of a versatile synthetic methodology for the ligand (see below). Lastly, as noted by Hessen [6], it is a pre-requisite that the resultant metal–C(σ-aryl) bond is more inert compared with aliphatic counterparts [e.g. metal–C(polymer chain)].

2.2. Synthesis of Group 4 complexes bearing tridentate pyridine-2-phenolate-6-(σ-aryl) ligands

The 2-(2′-phenol)-6-arylpyridine ligands were prepared by significant modification of a literature synthesis for 2,6-bis(2′-phenol)pyridine [18]. The 1-*N*,*N*-dimethylamino-3-(substituted aryl)-3-oxo-1-propenes were prepared from the reactions of *N*,*N*-dimethylformamide dimethyl acetal with acetophenones bearing functional groups at the R^1/R^2 or R^1/R^3 positions (Scheme 1). Treatment of the oxopropene substrates with 3,5-di-*tert*-butyl-2-methoxyacetophenone/potassium *tert*-butoxide followed by ammo-



R^1	R^2	R^3	Ligand (E = H)	Complex M = Ti	M = Zr	M = Hf
Br	Br	H	H_2L^{Br}	**1**	**4**	**7**
Cl	H	Cl	H_2L^{Cl}	**2**	**5**	**8**
CH_3	H	CH_3	H_2L^{Me}	**3**	**6**	**9**

Scheme 1.