

Review

Insights into group 4 and 5 *ansa*-bis(cyclopentadienyl) complexes with a single-atom bridge

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Abstract

This review describes the different synthetic strategies employed in the preparation of group 4 and 5 *ansa*-bis(cyclopentadienyl) complexes containing a group 14 single-atom bridge. The general preparative routes can be summarized in: (i) metathesis reactions using alkali-metal *ansa*-ligand precursors; (ii) transmetalation with tin substituted cyclopentadiene compounds; (iii) reaction of the metal amide derivatives with *ansa*-bis(cyclopentadiene) compounds. Excluding fused ring systems, such as indenyl or fluorenyl, from this study, it is still nevertheless evident the wide variety of complexes that have been reported. Substituents can be varied in nature, position and/or number at the C₅ ring and/or at the single-atom *ansa*-bridge. Functional groups have also been introduced into the *ansa*-ligand framework and their reactivity in, for example, hydroboration or hydrosilylation is described in this review.

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1. Introduction

The synthesis in 1951 of the first metallocene complex, ferrocene, by Pauson and Miller [1] and the subsequent preparation, by Wilkinson, of the transition metal and lanthanide analogues [2], firmly put metallocenes at the forefront of organometallic chemistry. The discovery that early transition metallocene complexes are catalytically active in the polymerization of olefins [3] only increased even more rapidly the development in the chemistry of these compounds [4]. Catalytic activity, molecular weight, microstructure or comonomer content and distribution of the polymers produced can, in many cases, be directly related to the geometric and electronic characteristics of the metallocene catalyst. The main emphasis therefore in this research field has been concentrated towards the design and synthesis of novel complexes capable of directing the catalytic process towards polymers with specific physical properties.

The term *ansa* (Latin for bent handle attached at both ends) was applied to describe bridged metallocene complexes and it was quickly acknowledged that the use of these rigid group 4 *ansa*-bis(cyclopentadienyl) systems greatly improved catalytic activity and selectivity. It is now also well known that the inclusion of an *ansa*-bridge in the metallocene complex alters its chemical behaviour with respect to its unbridged analogue (the so called “*ansa*-effect”) [5].

Although the principal application of these complexes is that of catalyst precursors in olefin polymerization, their use as reagents in organic synthesis [6] and in the dehydrocoupling of hydrosilanes to form polysilanes [7] is also of importance.

The first group 4 *ansa*-metallocene complex, [Ti{H₂C(η⁵-C₅H₄)₂}Cl₂], was prepared by Katz and Acton in 1970 [8] and initially for the *ansa*-bis(cyclopentadienyl) systems there were only isolated reports from Köpf and co-workers [9], Brintzinger and co-workers [10], Petersen and co-workers [11] and Jutzi and Dickbreder [12]. It was not until Brintzinger and co-workers published, in 1989, the synthesis of substituted group 4 *ansa*-metallocene complexes [13] that a wider interest in this field was initiated. Group 5 *ansa*-metallocene complexes were at first ignored due to their low or zero catalytic activity in polymerization. Klouras reported,

in 1991, an *ansa*-vanadocene complex [14] and in 1996 the first *ansa*-niobocene complexes were described by Herrmann et al. and by our research group [15]. Recently, Bercaw and co-workers have used *ansa*-niobocene complexes as models to study the mechanism in olefin insertion processes [16].

The majority of the compounds reported in this survey contain a silicon *ansa*-bridge. This can be explained by the fact that the ligand precursors are readily prepared from the corresponding dichlorosilane and the cyclopentadiene reagent. The wide variety of silane compounds, which are either commercially available or easily prepared, accounts for the numerous modifications that have been made to the *ansa*-bridge. Carbon *ansa*-bridge ligands are normally prepared from fulvene precursors and the ease or difficulty in the synthesis of these reagents directly dictates the viability of the synthesis of the *ansa*-metallocene complex. Germanium *ansa*-bridge ligands are prepared in a similar manner to their silicon analogues, although far fewer complexes have been reported most probably due to the higher economic cost of the dichlorogermane precursors compared with their silane counterparts. Due to the fragile nature of the Sn–C bond, tin bridged *ansa*-complexes are unknown except for one report [17,18].

Apart from changing the group 14 bridging heteroatom, the *ansa*-bis(cyclopentadienyl) system can be varied by substitution at the C₅ ring or the bridging atom. This substitution can be designed to modify electronic and/or steric effects which may influence catalytic activity and selectivity.

For the purpose of this review, we have considered as *ansa*-metallocene complexes only those that contain the *ansa*-ligand chelating the group 4 or 5 metal centre which in turn is linked to the cyclopentadienyl moieties in an η⁵:η⁵ fashion. We have excluded from this survey fused ring systems such as indenyl and fluorenyl derivatives and double-bridged complexes. For the group 4 *ansa*-metallocene complexes, our study is concentrated on the initially formed dichloride species. The derivatization (generally alkylation) of these compounds at the ancillary ligands is not normally discussed. The number of *ansa*-metallocene complexes of the group 5 elements is greatly inferior to those reported for their group 4 counterparts and for this reason the survey will, in addition to the halide complexes, include imido and hydride derivatives.

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