



Review

Transformations of functional groups attached to cyclopentadienyl or related ligands in group 4 metal complexes[☆]



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[☆] Dedicated to Karel Mach for his outstanding contributions to organometallic chemistry on the occasion of his 78th birthday.

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ABSTRACT

Functional groups attached to η^5 -coordinated cyclopentadienyl or related (indenyl, fluorenyl) ligands in transition metal complexes may be subjected to various synthetic transformations giving rise to novel, often otherwise inaccessible organometallic derivatives. Alternatively, this approach may eliminate the necessity of previous elaborate ligand synthesis. A number of synthetic methods have appeared in the recent past, which are compatible even with reactive electrophilic early transition metal compounds. This review article summarizes the development of functional group chemistry performed at group 4 metallocene, half-sandwich, and related complexes.

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1. Introduction and scope of the review

Cyclopentadienyl and related η^5 -bonded ligands are undoubtedly the most frequently encountered ligands in the coordination chemistry of group 4 elements. Notably, some of the respective metallocene or half-sandwich compounds featuring these ligands act as excellent catalysts or catalyst precursors, particularly for olefin polymerization catalysis [1]. Such a successful utilization of these compounds further stimulated the research activity and throughout the years various substitution patterns of the basic ligand scaffolds were implemented in order to modify both electronic and steric properties of the resulting ligands. Moreover, a variety of functional groups was appended to η^5 -cyclopentadienyl-based moieties [2] in order, e.g., to introduce additional donors capable of bonding or coordination to the metal center. Indeed, an approach comprising the synthesis of functionalized cyclopentadiene (or its corresponding alkali metal salt) followed by the transmetalation or metathesis reaction with an appropriate group 4 metal precursor was applied in most cases. This approach, however, limits the scope of functional groups that can be introduced because of their undesired reactivity toward the alkali metal cyclopentadienyl or the strongly Lewis acidic group 4 metal precursor (such as MCl_4) [3]. On the other hand, approaches making use of a synthetic transformation involving the pendant functional group already attached to the group 4 organometallic moiety are much less frequent [4]. The reason for this deficiency is quite obvious: the functional group chemistry routinely applied in organic synthesis is often unsuitable due to reagents/reaction conditions that are incompatible with the reactive organometallic moiety. Of course, quite a contrasting case is the organometallic chemistry of late transition metals, especially that of ferrocene derivatives, which has developed into an immense diversity mainly thanks to the properties and remarkable stability of the ferrocene moiety [5]. Yet a surprising variety of reactions appeared in literature which were performed at pendant substituents of group 4 element complexes as we would like to document herein.

This article attempts to give an overview of reactions that transform pendant functional groups attached (directly or via any kind of a linker) to cyclopentadienyl and related η^5 -coordinated ligands (indenyl, etc.) in group 4 metal complexes, not necessarily retaining the original organometallic fragment completely unaffected. It is however assumed that the procedures described have some synthetic potential giving access to new and even otherwise inaccessible derivatives. The content is sorted by the type of appended functionality, which undergoes the reaction. Individual sub-chapters then comprise particular reaction types featuring

the corresponding functional groups. An alkyl group as well as an intramolecularly metal-tethered alkyl was not considered a functional group and reactions involving such species are not covered in this review [6]. On the other hand, functionalities incorporated in an *ansa*-bridge between two η^5 -ligands (thus not being truly “pendant”) that undergo any transformation fall within the scope of this article [7].

2. Alkenyl, alkynyl, and aryl groups

Unsaturated hydrocarbyl substituents are arguably the least troublesome functionalities considering their coexistence with the organometallic moiety and their easy incorporation into the ligand. A number of transformations of these groups is viable under relatively mild conditions as evident from the following survey. Unsaturated C–C bonds readily undergo, e.g., hydroelementation reactions, cycloadditions, olefin metathesis, and others. Furthermore, there are some reactions that are specific for early transition metal complexes – such as those induced by reduction of the central metal atom with subsequent oxidative additions involving the pendant groups (Section 2.1) or, notably, polymerization reactions catalyzed by the complexes that are capable of incorporating their own pendant groups into the polymer chain (Section 2.9).

2.1. Reductive–oxidative reactions involving the metal center

A redox reactivity of low valent group 4 metals with unsaturated hydrocarbons (including the pendant unsaturated groups) can be utilized for the C–C or C–M bond formation. A general mechanism of these oxidative cycloadditions leading to the formation of metallacyclic products is depicted in Scheme 1. In the first step the metal center is reduced (by removal of chloride ligands or by reductive elimination of alkane/arene from dialkyl/diaryl species) and the generated low valent species is stabilized by coordination of unsaturated substrates. Subsequently, an oxidative cyclization takes place giving rise to metallacyclopentane-/metallacyclopentene-type products.

For complexes bearing two pendant terminal alkenyl groups, doubly tethered metallacyclopentanes could thus be formed via the described oxidative coupling or in other words via a cycloaddition reaction. A reduction by magnesium in THF of the titanocenes **1a–c** (Scheme 2) bearing methylallyl, butenyl, or pentenyl functionality, respectively, gave the doubly tethered titanacyclopentanes **2a–c** [8]. Notably, a double shift to an internal position occurred prior to cyclization in the ω -pentenyl group to maintain an ideal

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