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Erratum

Erratum to "Synthesis of racemic chiral-at-metal complexes of the Group 4 metals by a lithium chloride catalysed ligand redistribution reaction" [Journal of Organometallic Chemistry 553 (1998) 507–509]

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The Publisher sincerely regrets that the above article was printed in the journal without chemical structures **1**–**11b**, and accepts full responsibility for this error. The corrected article is published in its entirety on the following pages.

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[1] Deceased.

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Preliminary communication

Synthesis of racemic chiral-at-metal complexes of the Group 4 metals by a lithium chloride catalysed ligand redistribution reaction☆

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Abstract

Lithium chloride catalysis permits ligand redistribution to be a synthetically useful method for preparation of racemic chiral-at-metal group 4 metallocene derivatives.

Keywords: Chiral; Group 4 metal; Metallocenes

1. Introduction

Chiral complexes of Group 4 metals, both racemic and enantiomerically enriched, have found numerous applications as catalysts for stereoregular polymerisations and catalysts and reagents for asymmetric synthesis [1–4]. The majority of these complexes are chiral due to the presence of one or more centres of chirality in one or more of the ligands. A further group of complexes are chiral due to conformational restrictions, notably the so-called ebi and ebthi metallocenes [4]. Our interest lies in a third, little studied class of chiral complexes of Group 4 metals such as **1** [5], where the metal atom is the sole centre of chirality. These complexes belong to a general class of metal complexes [6] that may be described as 'chiral-at-metal'.

Prominent among the chiral Group 4 complexes which are employed as catalysts are metallocene dichlorides and dialkyls. The chiral monochloro monoalkyl metallocenes **2–5 a–d** were thus obvious targets. We also decided to investigate the related monochloro monothiophenolato complexes **2–5 e**. Three strategies for the synthesis of racemic compounds **2–5 a–e** from the prochiral dichlorides **2–5 f** were considered.

2. Discussion

The simplest method for the preparation of racemic compounds **2–5 a–e** is nucleophilic displacement of one of the chlorides of a metallocene dichloride by X^- (using a Grignard reagent, organolithium reagent or thiophenolate) (Scheme 1(a)).[2] However, in our experience this reaction is synthetically useful only in cases where the nucleophile is very sterically demanding; otherwise contamination with the disubstituted product is inevitable. Hence, reaction of dichlorides **2f**, **4f** and **5f** with one equivalent of trimethylsilylmethyl magnesium chloride (**2f**) or its lithium analogue (**4f** and **5f**), in diethyl ether at low temperature, led smoothly to the racemic chiral products **2c**, **4c** and **5c**. That steric hindrance is significant in this reaction is indicated by the fact that in the cases of **2** and **5** the bis(trimethylsilylmethyl) product could not be prepared, even with an excess of the nucleophile.

The second procedure to be considered is the reaction of prochiral dialkyl or dithiophenolato metallocenes with one equivalent of a chloride source (Scheme 1(b)). Reactions of this type have been re-

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[2] A very useful summary of these methods can be found in Ref. [7].

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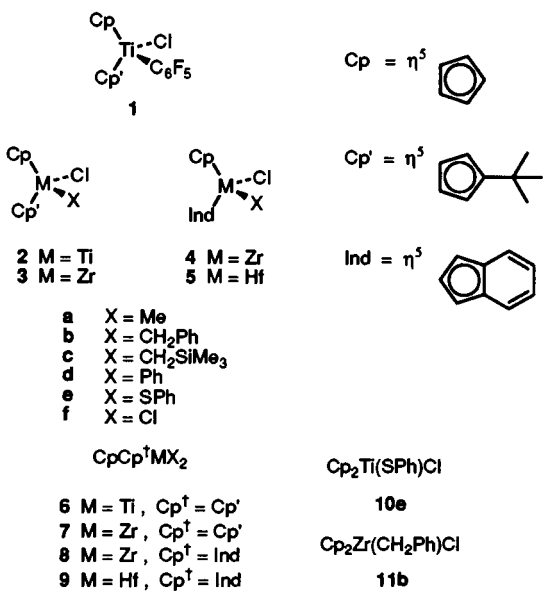
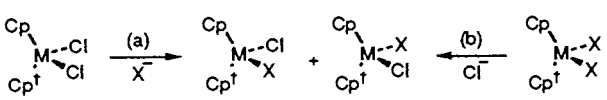
ported, but this method also leads to mixtures of mono- and di-substituted products, making work-up difficult [7].

The third approach, which also starts from dialkyl and diphenolthiolato compounds, is more synthetically attractive. In principle, mixing one equivalent of the dialkyl or diphenylthiolato compound with one equivalent of its dichloro precursor can lead to the target complexes by ligand redistribution (Scheme 2). This reaction has no by-product, which should make purification of the product simpler.

Synthetically useful ligand redistribution reactions have been reported for mixtures of Cp_2TiCl_2 with Cp_2TiMe_2 and with Cp_2TiPh_2 [8]. The analogous reactions of Cp_2ZrCl_2 with Cp_2ZrMe_2 and with Cp_2ZrPh_2 proved much too slow to be preparatively important [9], although, interestingly, more rapid reactions were observed when either the difluoride or diiodide was used in place of the dichloride. Rapid ligand redistribution was noted between Cp_2ZrCl_2 and Cp_2ZrBr_2 [9,10]. Herein we describe the extent to which this method can be applied to the racemic synthesis of our chiral targets **2–5 a–e**.



The prochiral titanium dichloride **2f** was prepared as described by ourselves [11]. The prochiral zirconocene and hafnocene dichlorides **3–5 f** were prepared in a similar fashion, but adding the substituted cyclopentadienyl group second (Scheme 3). Reaction



Scheme 1.

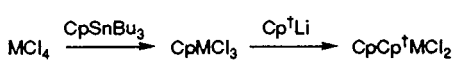
Scheme 2.

of these dichlorides with two equivalents of MeMgBr, $PhCH_2MgBr$, PhLi or PhSLi led to the disubstituted products **6–9**. The special case of $X = CH_2SiMe_3$ was mentioned above.

As expected [8], the ligand redistribution reactions of the prochiral titanium compounds proceeded smoothly to furnish the racemic chiral targets **2a, 2b** and **2e** in good yields and purity. From literature precedent [9,10], we also expected the zirconium thiophenolates to react rapidly (these reactions most closely resembling the rapid reaction of Cp_2ZrCl_2 and Cp_2ZrBr_2), but that the dialkyl substrates would react very slowly.

Our initial results were not at all consistent with these predictions. In particular, rapid reaction was observed for some dialkyl zirconocenes. However, on closer inspection, these anomalously fast reactions could be linked to the presence of lithium chloride as an impurity.[3] We thus added a small amount of lithium chloride to all the redistribution reactions which had previously been slow or non-existent and, indeed, preparatively useful reaction times (less than 1 day) were observed in all cases. To confirm the generality of this method we also examined some simple titanocene and zirconocene substrates **10e** and **11b** and one prochiral hafnocene **9e**. Rapid reactions were again found when lithium chloride was present. Our results are summarised in Table 1.

We have no satisfactory explanation for the need for lithium chloride catalysis for rapid ligand redistribution reactions of zirconocenes and hafnocenes as opposed to titanocenes. Indeed, the mechanistic role of the lithium chloride is not yet clear. A kinetic study currently underway should prove enlightening and will be the subject of a separate publication.



Scheme 3.

[3] Lithium chloride is known to be sparingly soluble in benzene; for example see Ref. [12].

Table 1
Synthesis of complexes $CpCp^{\dagger}$ MXCl[a]

M	$Cp^{\dagger}$	X	Product
Ti	Cp	SPh	**10e**
Ti	Cp′	Me	**2a**
Ti	Cp′	CH_2Ph	**2b**
Ti	Cp′	SPh	**2e**
Zr	Cp	CH_2Ph	**11b**
Zr	Cp′	SPh	**3e**
Zr	Ind	Me	**4a**
Zr	Ind	CH_2SiMe_3	**4c**
Zr	Ind	Ph	**4d**
Zr	Ind	SPh	**4e**
Hf	Ind	SPh	**5e**

[a]Test reactions were carried out by mixing 1:1 mole equivalents of $CpCp^{\dagger}MCl_2$ and $CpCp^{\dagger}MX_2$ in C_6D_6 in an NMR tube. If reaction appeared to be slow as determined by NMR a few crystals of LiCl were added. Preparative reactions were done in toluene at room temperature, with addition of LiCl as required. The products were isolated by removal of the solvent in vacuo followed by recrystallisation from an appropriate solvent.

3. Conclusions

In summary, the target chiral metallocene compounds can be prepared racemically by ligand redistribution reactions (Scheme 2). For zirconium and hafnium derivatives, the presence of lithium chloride is necessary for a synthetically useful procedure.

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